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Atomic & free Radical reaction

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ATOMIC AND FREE RADICAL REACTIONS

THE KINETICS OF GAS-PHASE REACTIONS INVOLVING
ATOMS AND ORGANIC RADICALS

By

E. W. R. STEACIE

National Research Laboratories, Ottawa



American Chemical Society
Monograph Series

REINHOLD PUBLISHING CORPORATION
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GENERAL INTRODUCTION

American Chemical Society Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A.C.S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this introduction) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first monograph of the series appeared in 1921. After twenty-three years of experience certain modifications of general policy are indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. This differentiation is fast becoming nebulous. Research in private enterprise has grown apace and not a little of it is pursued on the frontiers of knowledge. Furthermore, most workers in the sciences are coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and now frankly recognize that their objectives are common, namely the search for new knowledge for the service of man. The officers of the Society

therefore have combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the series, it seemed expedient to construe rather broadly the definition of a monograph. Needs of workers had to be recognized. Consequently among the first one hundred monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the monograph character which means more complete and critical treatment of relatively restricted areas, and where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change desirable.

These monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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Preface

It is becoming more and more apparent that the "reactions" of chemical kinetics and photochemistry are frequently not simple, but rather consist of a series of elementary steps which often involve atoms and free radicals. Such elementary reactions are therefore of major importance in the elucidation of the mechanism of thermal and photochemical reactions. Unfortunately, however, information concerning elementary reactions is widely spread throughout the literature of chemical kinetics, photochemistry, pyrolysis, etc., and it is usually very difficult to assemble the existing data on any given reaction.

This book is an attempt to bring together such data, and to treat the reactions of atoms and radicals in their own right, rather than as an incidental part of the mechanism of more complex changes. As far as possible all pertinent data which bear on the rate of such reactions have been discussed. In some cases much information is available from which it is possible to arrive at definite and accurate values of the activation energies of the reactions. In other cases all that exists is a proposed mechanism which involves the reaction, but which rests on little or no direct evidence.

The discussion will be confined to elementary reactions involving organic substances. The reason for this limitation is that our knowledge of inorganic elementary processes is usually confined to their participation in relatively few reaction mechanisms, and they are thus adequately taken care of by texts on photochemistry and chemical kinetics. Organic elementary processes, on the other hand, are of a much more ubiquitous nature, and the need for a consistent treatment of them is correspondingly greater. Inasmuch as the primary purpose of the book is to elucidate the kinetics of elementary reactions rather than to discuss the structure of organic radicals, no mention is made of the stable radicals of the Gomberg type. Also, since little quantitative information is available on elementary reactions in the liquid phase, the discussion is confined almost entirely to reactions in the gaseous state.

The writer is greatly indebted to Dr. H. E. Gunning and Dr. B. de B. Darwent of the National Research Council of Canada for advice and criticism; to Prof. H. S. Taylor of Princeton University and Prof. O. K. Rice of the University of North Carolina for reading the entire manuscript and making many valuable suggestions; and above all to Prof. D. J. LeRoy, formerly of the National Research Council of Canada and now at the University of Toronto, who assisted greatly in all stages of the preparation of the manuscript.

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Chapter I

Introduction

In this chapter a few general facts in connection with reaction rates, free radicals, etc., will be discussed. No attempt will be made to enter into any detailed discussion of chemical kinetics, however, since numerous texts on the subject exist.¹

1. Order and Mechanism

According to the law of mass action, the rate of a chemical reaction is proportional to the product of the active masses (or concentrations) of the reactants. On this basis the course of the reaction can be described provided that the instantaneous concentrations of the reactants are known at all times. This has led to the custom of classifying reactions according to their order, i.e., for a first order reaction

$$\frac{-dC}{dt} = kC,$$

where C is the concentration of the reactant at time t , and k is the rate constant. Similarly for a second order reaction

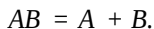
$$\frac{-dC}{dt} = K$$

where there is only one reactant, or

$$\frac{-dC_A}{dt} = \frac{-dC_B}{dt} K C_A C_B$$

for a reaction involving two different species of molecule.

It is important to recognize that the order of a reaction need have no direct relation to the stoichiometric equation for the reaction. Thus the decomposition of a molecule AB to give A and B would normally be written

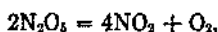


Actually, however, the reaction might equally well proceed by a process involving two molecules of AB . It should therefore be recognized that the order of a reaction is an experimental quantity which expresses the depend-

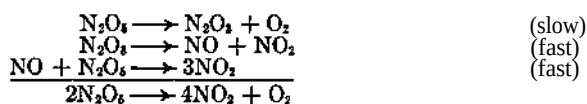
¹ See especially L. S. Kassel, *The Kinetics of Homogeneous Gas Reactions*, New York, 1932; C. N. Hinshelwood, *The Kinetics of Chemical Change*, Cambridge, 1940; H. J. Schumacher, *Chemische Gasreaktionen*, Leipzig, 1938; R. N. Pease, *Equilibrium and Kinetics of Gas Reactions*, Princeton, 1942.

ence of the reaction rate on concentration, and that the order of a reaction need not be, and very frequently is not, integral.

It is now recognized that many reactions are not simple chemical changes but actually involve a series of steps. Thus the decomposition of nitrogen pentoxide follows the stoichiometric equation



and might therefore be expected to be of the second order, whereas it is actually a classical example of a first order reaction. The explanation appears to be ² that the reaction occurs in stages:



The latter two steps are so fast that they are virtually instantaneous compared to the first stage, which thus governs the rate, and the overall reaction is therefore of the first order.

In other cases a series of reaction steps may lead to an overall order which is fractional, or zero. It is thus apparent that the reaction order will only correspond to the actual molecular mechanism, or to the stoichiometric equation, provided that the reaction is a simple one, and does not involve a series of stages.

2. Elementary Reactions

The individual stages of simple order, which together make up an observed overall reaction, are known as elementary reactions. In a more limited sense the term *elementary reaction* is used for those part reactions which involve atoms, radicals, or other substances of a transitory nature.

One of the earliest examples of a mechanism involving such reactions was furnished by the "Nernst chain" for the photochemical synthesis of hydrogen chloride, viz.



Reactions (2) and (3) involve atoms, and together constitute a chain which can occur over and over, and thus accounts for the high quantum yield of the reaction. Since the Nernst chain was proposed, numerous examples of chain reactions have been discovered, both photochemical and thermal.

There are two possible types of mechanism for such chain reactions. In *material chains*, such as the Nernst chain, the chain carriers are highly reactive substances, such as atoms or free radicals. Once such substances are formed, they react within a relatively short time interval (usually a

small fraction of a second) and the chain is thus rapidly propagated. In an *energy chain* mechanism, on the other hand, the chain carriers are energy-rich molecules, rather than distinct chemical species. Such energy chain mechanisms have been freely postulated, but it has generally been found that when more information becomes available the mechanism turns out to involve a material rather than an energy chain. On the whole, material chain mechanisms seem to be much more plausible, and energy chains are generally regarded with some suspicion, although they appear to be undoubtedly involved in certain cases.

It should be noted that the rates of the elementary reactions involved in such material chain mechanisms are independent of the manner in which the participating atoms or radicals arise. It is thus possible to carry over information about a given elementary reaction from one overall reaction to another. The determination of the rates of the more frequently postulated elementary reactions thus becomes one of the major problems of chemical kinetics.

3. Types of Elementary Reaction

Elementary reactions may belong to any of the ordinary types, *i.e.*, first, second, or third order (or unimolecular, bimolecular, and termolecular, since in the case of an elementary reaction the order and the molecularity are, by definition, the same thing). Unimolecular elementary reactions include the decomposition of stable substances to give atoms or radicals, and the decomposition of radicals to give other radicals, or stable molecules. The main factor governing such reactions will be the strength of the bonds in the decomposing molecule or radical, since the activation energy of the reaction cannot be less than the strength of the pertinent bond, and may be greater.

Bimolecular elementary reactions are of two main types. One of the most frequently occurring is a metathesis in which an atom or radical reacts with a molecule to form a molecule and a different atom or radical, *viz.*,



The case in which Y is a hydrogen atom is particularly common, *i.e.*,



The other common type of bimolecular elementary reaction is one involving the recombination of two atoms or radicals to form a stable molecule. Here certain restrictions come into play. In a bimolecular reaction in which two or more molecules are formed the products can carry off part of the excess energy due to the activation energy and the heat of the reaction by their relative motion, as they separate. In the case of an association reaction, however, this is prevented by the conservation of momentum. The molecule formed thus possesses the energy necessary for its dissocia-

tion, and it will dissociate unless it can lose this energy by collision, or by distributing it among its internal degrees of freedom. In the case of atom recombinations the possibility of the redistribution of the energy among internal degrees of freedom is lacking, and the life of the activated complex is very short. The reaction cannot therefore occur unless a stabilizing collision takes place practically simultaneously with the coming together of the atoms: in other words, the reaction occurs by a termolecular mechanism



With more complex molecules or free radicals there seems to be no doubt that the large number of internal degrees of freedom will permit readjustment of the internal energy and remove the three-body restriction. However, there seems to be no general agreement as to the degree of complexity necessary to permit such an association. Or, put in another way, it is not certain how small the "probability factor" may be in the case of the association reactions of the simpler free radicals. This point will be frequently referred to in the later discussion of specific elementary reactions.

Termolecular elementary reactions appear to be of importance only in cases where two atoms or radicals combine in the presence of a third body.

4. Surface Effects

In ordinary gas reactions there are many cases where the wall of the reaction vessel acts as a catalyst for the reaction. In reactions with a simple mechanism it is usually possible to decide whether or not the reaction is heterogeneous by direct tests in which the surface-volume ratio of the reaction system is altered. In the case of more complex reactions, however, the results of such tests are apt to be more or less ambiguous. The indirect and somewhat complex techniques which are necessary in the investigation of elementary reactions usually make it very difficult to assess the role of the surface. This is especially true in the case of radical recombination reactions.

5. The Temperature Coefficient

The variation of the rate constant of a reaction with temperature can be expressed by the Arrhenius equation

$$k = Ae^{-E/RT},$$

where k is the rate constant, E the activation energy of the reaction, and A is a constant which is usually referred to as the "frequency factor." Actually A is slightly temperature-dependent. However, with the accuracy attainable in work of the type to be discussed here the variation of A with temperature is negligible, and the Arrhenius equation may be regarded as strictly true for our purpose.

Activation energies are best obtained from the temperature coefficient of the reaction by means of the Arrhenius equation, *i.e.*, by plotting $\log k$ against $1/T$ and calculating E from the slope of the line thus obtained. It frequently happens, however, that information is available at only one temperature, and in such case for bimolecular reactions recourse is usually made to the "collision yield" of the reaction. This is arrived at as follows: the quantity $e^{-E/RT}$ represents approximately the fraction of the molecules which possess energy equal to or greater than E , *i.e.*, the fraction of the molecules which are activated. If it is assumed that reaction occurs at every collision of activated molecules, then

$$\frac{\text{number of molecules reacting per c.c. per sec.}}{\text{number of molecules colliding per c.c. per sec.}} = e^{-E/RT}$$

The quantity on the left-hand side is usually referred to as the collision yield of the reaction, and may be denoted by S . The activation energy can then be calculated from

$$S = e^{-E/RT}.$$

Actually, however, it is generally conceded that not all collisions involving activated molecules are fruitful, but only a fraction, p , *i.e.*,

$$S = p e^{-E/RT},$$

where p is called the "steric factor" of the reaction. The steric factor is usually not very small, except in association reactions, and in the absence of more detailed information it is usually arbitrarily assumed to be 0.1 or unity.

The main difficulty with the collision yield type of calculation lies in the estimation of the collision number, or the number of molecules colliding per c.c. per sec. The collision number is given by kinetic theory, and involves the squares of the molecular diameters, or the collision cross-section. Since the concept of a cross-section is a vague one, and varies with the phenomenon under investigation, it is always a matter of great uncertainty what value of the cross-section should be used in the calculation. As a result S and E are always rather uncertain when calculated in this way.

In the case of unimolecular reactions the quantity A in the Arrhenius equation does not have any such simple physical significance. In most cases, however, it is not far from 10^{13} , so that failing direct information a rough estimate of the activation energy can be made from the rate constant at a single temperature by the relation

$$k = 10^{13} e^{-E/RT} \text{ sec}^{-1}.$$

6. Units

The integrated form of the rate equation for a unimolecular reaction is

$$\log. {}^{\text{co}}J_c = kt,$$

where C_0 is the initial concentration, C is the concentration at time t , and k is the rate constant. Since the L.H.S. is a pure number, the dimensions of k are sec.^{-1} , i.e., k does not involve the concentration of the reacting substance. Actually k can be regarded for small amounts of reaction as the fraction of the reacting substance which decomposes per second. In the case of a bimolecular reaction the rate equation in its integrated form for a reaction of the type



is

$$\frac{C_0 - C}{C_0 C} = kt,$$

where the symbols have the same meaning as before. The dimensions of k are thus $(\text{concentration})^{-1} \text{sec.}^{-1}$. The value of k will thus depend on the units in which it is expressed. For example, if moles per c.c. are used, the dimensions of k will be $\text{cm.}^3 \text{mol.}^{-1} \text{sec.}^{-1}$.

7. The Theoretical Estimation of Activation Energies

Polanyi, Eyring, and their collaborators³ have done a great deal of work on the a priori estimation of reaction rates and activation energies on a quantum mechanical basis. This work has been of the greatest importance in furnishing a consistent theoretical basis for chemical kinetics. In general, however, the method is semi-empirical in its application to specific cases, and drastic approximations are necessary in order to carry through the calculations. This is especially true when polyatomic molecules or radicals are concerned,

While the results of such work are of the greatest interest, they are highly approximate, and consequently are not of much help in arriving at the "best" value of the activation energy of any specific elementary reaction. It thus appears that with the present state of our knowledge not much can be expected from theoretical estimates of activation energies, and that for the moment at least experiment is far ahead of theory.

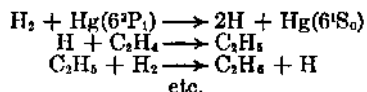
8. The Role of Atoms and Radicals in Chemical Reactions

The transitory existence of atoms and free radicals has long been established in spectroscopy. Line spectra, of course, have their origin in free atoms, and investigations on band spectra have quite definitely shown the existence of radicals such as OH, CN, CH, C_2 , etc. There is no question that the lack of the existence of free radicals under ordinary conditions is not in general due to any intrinsic lack of stability, but rather to their high reactivity which results in their rapid disappearance by reaction with themselves or with other substances which may be present.

³ For a full discussion see S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, New York, 1941.

The idea that reactions involving free atoms may be of importance in chemical mechanisms first came from photochemistry. Once the significance of the Einstein Law of Photochemical Equivalence was recognized, it became apparent that some sort of chain mechanism must be responsible for the very large quantum yields of reactions such as the photochemical synthesis of hydrogen chloride. The Nernst chain, previously referred to, was the first case in which such atomic elementary reactions were seriously suggested. It soon became evident that such atomic reactions are of major importance in photochemistry. This is especially true in cases where the initial act is the absorption of light in its continuum by a diatomic molecule, and the spectroscopic evidence for an initial split into atoms is thus clean cut.

The first suggestion that organic chain reactions involving free radicals might occur in a similar way was made by Taylor in 1925.⁴ Taylor suggested that the mercury photosensitized hydrogenation of ethylene, which has a quantum yield greater than unity, occurred by a chain mechanism involving hydrogen atoms and ethyl radicals, viz.



In subsequent years such free radical mechanisms for photochemical reactions became increasingly prevalent. Taylor also suggested that if metal alkyls were decomposed in the presence of ethylene and hydrogen, free radicals would be produced which would sensitize the reaction between ethylene and hydrogen. This was found to be the case,⁵ the sensitized polymerization of ethylene occurring at the same time.

The reactions of hydrogen atoms can also be investigated in a much more direct way by the Wood-Bonhoeffer method. It was first shown by Wood that it was possible under certain circumstances to pump hydrogen atoms out of a hydrogen discharge tube in large quantities, and to carry them for considerable distances before recombination occurred. The method was adapted to the investigation of hydrogen atom reactions by Bonhoeffer in 1924,⁶ and since that time many reactions have been investigated by this method, especially those of organic substances. It was early evident that free radicals must be involved in such processes. The same method was later extended to oxygen⁷ and halogen⁸ atoms, and an extensive series of

⁴ H. S. Taylor, *Trans. Faraday Soc.*, 21, 560 (1925).

⁵ H. S. Taylor, *Proc. Am. Phil. Soc.*, 65, 90 (1926); H. S. Taylor and W. H. Jones, *J. Am. Chem. Soc.*, 52, 1111 (1930).

⁶ K. F. Bonhoeffer, *Z. physik. Chem.*, 113, 199 (1924).

⁷ P. Harteck, *Z. Physik*, 64, 881 (1929).

⁸ W. H. Rodebush and W. C. Klingelhoefer, *J. Am. Chem. Soc.*, 55, 130 (1933); G. M. Schwab and H. Friess, *Naturwiss.*, 21, 222 (1933).

investigations on the reactions of sodium atoms with organic compounds, by a method which will be described later, was made by Polanyi and his co-workers⁹ commencing in 1930.

It was first shown by Paneth and Hofeditz¹⁰ that free methyl radicals, formed by the thermal decomposition of lead tetramethyl, could be detected by their reaction with a metallic mirror deposited on the walls of a tube through which a carrier gas together with the radicals was flowing. This work proved conclusively that methyl and ethyl radicals were capable of existence for an appreciable fraction of a second at room temperature and low pressures. Subsequent work by Rice and his co-workers¹¹ showed that free radicals could be detected in the thermal decomposition of a large number of organic compounds.

On this evidence Rice suggested that most organic compounds decompose by a free radical chain mechanism. This question is fully discussed in Chapter III, and while there is considerable doubt as to the validity of many of Rice's mechanisms, there is no question that his suggestions stimulated a great deal of interest in organic free radicals and their reactions.

9. The Arrangement of the Book

In the first half of the book (Chapters II to V) a general discussion is given of experimental methods and of the role of atoms and radicals in thermal and photochemical reactions. The last half (Chapters VI to XIV) is a systematic survey in which an attempt is made to discuss all data which have a bearing on the rates of individual elementary reactions. In some cases where a great deal of work has been done on a single problem, as, for example, the acetone photolysis, it is not possible to discuss a single one of the elementary steps involved without detailed reference to the other steps in the mechanism. In such cases, therefore, the main discussion is given in Chapter V on the mechanism of the photolysis, and only a brief summary is given in the later sections dealing with specific elementary steps such as



In other cases, where the material is less voluminous, the main discussion is given under one of the part reactions involved, and reference is made to this in the discussion of other part reactions. In all such cases full cross-references are given.

In the chapters dealing with the specific elementary reactions, systems involving carbon and hydrogen only are considered first (Chapter VI), followed in order by oxygen, nitrogen, chlorine, bromine, iodine, sodium,

• H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930), etc.

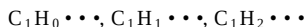
¹⁰ F. Paneth and W. Hofeditz, *Ber.*, **62B**, 1335 (1929).

¹¹ See, for example, F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

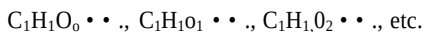
other metals, and sulphur (Chapters VII to XIV). Reactions involving deuterium are considered with those of hydrogen. In the individual chapters the order in which the reactions are presented is governed by the reactants. In a case where there is more than one reactant, the atom or simplest radical is placed to the left of the other reactant(s) and determines the order of arrangement. Atoms and inorganic free radicals come first in the order



The organic radicals then follow in an order determined as follows: all C_1 compounds are treated before C_2 compounds, etc. For a given carbon number, say C_1 , compounds with the least hydrogen are considered first, *i.e.*, in the order



Of compounds with a given number of carbon and hydrogen atoms, those with the least oxygen come first, *i.e.*,



A similar arrangement is followed successively for N, Cl, Br, I, Na, etc.

For reactions involving more than one reactant, the second reactant is ordered in a similar way, except that here no distinction is made between radicals and stable molecules.

Chapter II

Experimental Methods

1. Introduction

There are two sources of information regarding the rates and activation energies of elementary reactions. One of these is the investigation of ordinary overall reactions of stable substances leading to stable products. By considering the effect of various factors, such as temperature, pressure, concentration of the reactants, etc., on the rate of such a reaction it may be possible to establish a mechanism with a considerable degree of certainty. If such a mechanism involves a number of elementary reactions, it may also be possible to deduce their rates and activation energies. However, the indirectness of such a procedure always leaves the results somewhat open to question. Furthermore in many cases it is not possible to establish a unique mechanism, and while a certain mechanism may be favored on theoretical or other grounds, any conclusions about the part reactions will be decidedly speculative. It is therefore of great advantage to draw information about the rates of elementary reactions from another and more direct source, viz., from experiments planned for the express purpose of determining the rate of a certain elementary reaction. This chapter will be concerned with a discussion of the methods which have been devised for this purpose.

Unfortunately, on account of the short life of the atoms or radicals involved, such methods can never be entirely direct. This fact arises from a number of causes:

(a) It is impossible to prepare substances of such short life in high concentration, or in a state of purity. As a result the atoms or radicals must usually be prepared in situ, in the presence of a very large excess of other substances.

(b) On account of the short life of the active substances, their estimation and identification is difficult.

(c) The products of an elementary reaction often include other substances of short life. These substances react further, and it is often very difficult to disentangle the primary process from such secondary reactions.

(d) The methods of preparing atoms and radicals often produce several

•The material of this chapter is largely taken from E. W. R. Steacie and D. J. LeRoy, *Chem. Reviews*, 31, 227 (1942).

active species simultaneously, and numerous side reactions may therefore occur which mask the process under investigation.

It may be pointed out (*Cf.* Rice¹) that we are primarily interested in four main types of process:

- (1) The rupture of a bond in a stable molecule, leading to the formation of atoms or radicals.
- (2) Reactions between atoms or radicals and molecules.
- (3) Reactions between two atoms or radicals.
- (4) The decomposition of radicals.

The Estimation of Activation Energies of Elementary Reactions

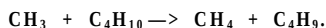
To make an unequivocal determination of the activation energy of an elementary reaction the following information is necessary:

- (a) The identity of the atoms or radicals produced by the method employed.
- (b) The concentrations of the atoms or radicals and other substances.
- (c) The amount of product produced in a definite time, and the identity of the product.
- (d) The effect of temperature on (a), (b), and (c).
- (e) The occurrence of secondary or side reactions, and their rates, temperature dependence, etc.

There is no question that up to the present no investigation of an elementary reaction has yielded direct and accurate information on all the above points. As a result information on the activation energies of elementary reactions comes from a knowledge of one or more of the above factors, together with inference from analogous cases, etc., in place of the deficient information. The results are therefore, as Kassel puts it, "tainted with contingency." However, as information accumulates, more and more confidence can be placed in the values assigned to the simpler reactions.

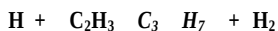
Virtually all estimates of activation energies have been made by one of the following procedures:

- (a) The rate of production of the product is measured as a function of temperature. For example, the photolysis of mercury dimethyl leads to the production of methyl radicals. In the presence of butane, methane is formed. This is assumed² to be due to the occurrence of the reaction



By measuring the rate of formation of methane as a function of temperature, we can thus arrive at the activation energy of this reaction.

- (b) The rate of disappearance of the reactant is measured as a function of temperature. Thus the reaction

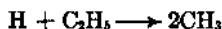


¹ F. O. Rice and K. K. Rice, *The Aliphatic Free Radiccate*, Baltimore, 1935.

² J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, 7, 390 (1939).

may be followed by determining the rate of disappearance of propane in a system containing propane and hydrogen atoms.⁸

(c) The value of the activation energy is obtained by an analysis of the mechanism of a complex change. Thus we may make an approximate estimate of the activation energy of the reaction

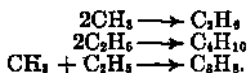


from an analysis of the mechanisms of various reactions involving ethane and hydrogen atoms.^{4,5}

(d) The activation energy is obtained from the rate of reaction at one temperature, together with suitable assumptions about the frequency factor. This method is very frequently employed.

(e) The lower or upper limit to the value of the activation energy is obtained by the appearance or non-appearance of the reaction under certain conditions. Thus hydrogen atoms do not react with methane at room temperature in a contact time of one second, so that it may be concluded that the activation energy is not less than 10 kcal.⁶ In such cases there is always the danger that the non-occurrence of the reaction might be due to a low frequency factor, rather than to a high activation energy.

(J) The relative values of the activation energies of two reactions may be inferred by assuming equal frequency factors (or by assigning different values to them on the basis of steric or other considerations) and comparing the amounts of products formed. Thus in the photolysis of methyl ethyl ketone equal amounts of methyl and ethyl are presumably formed in the primary step. Since the amounts of ethane, propane, and butane obtained as products are roughly those estimated from probability considerations,⁷ it may be concluded that there is little difference in the activation energies of the three recombination reactions



(g) The activation energies of part reactions are obtained by comparing an assumed mechanism with experiment. This method has been widely used in photochemistry and by Rice.¹

(h) The result is obtained by inference from thermal data and bond strengths.

(i) The result is obtained from a knowledge of the activation energy of the reverse reaction, and of the heat of reaction. In practice the main

⁸ E. W. R. Steacie and N. A. D. Parlee, *Can. J. Research*, B17, 371 (1939).

⁴ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 6, 179 (1938); *Can. Research*, B16, 303 (1938).

⁸ N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, 6, 203 (1937).

[•] K. H. Geib and E. W. R. Steacie, *Z. physik. Chem.*, B29, 215 (1935).

⁷ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 466 (1940).

difficulty is that we rarely know the heats of elementary reactions with any degree of accuracy.

(j) Theoretical methods. These are rarely accurate enough to be of much assistance.

2. Experimental Methods

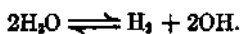
In general the two characteristic features of any experimental method are (a) the means of producing the active species, and (6) the method by which they are estimated. In the following pages we will discuss these two questions in detail separately, together with a description of the main combinations of the two which have been used in practice. Ordinary methods which are used for the investigation of reactions of stable substances will not be discussed here.

3. Thermal Methods of Producing Atoms and Radicals

(a) *The Active Species Are in Thermal Equilibrium with the Substance from Which They Are Produced*

In the case of the common diatomic molecules sufficient information exists to enable the degree of dissociation to be calculated precisely at all temperatures. Table I gives the temperatures corresponding to various amounts of dissociation when the pressure of the gas is one mm.⁸ It will be seen from the table that at room temperature the alkali metals are appreciably dissociated into atoms; at moderate temperatures iodine is as well. With most other diatomic molecules, however, very high temperatures must be reached before the atom concentration becomes appreciable.

Definite information about the dissociation of more complex molecules has been obtained experimentally in a few cases. For example, Bonhoeffer and Reichardt⁹ made a spectroscopic investigation of the dissociation of water vapor, and determined the equilibrium for the reaction



In general this method is of little use in the production of free radicals by the thermal decomposition of organic molecules. While the strengths of the bonds in organic molecules are still a matter of some controversy, the values given in Chapter III are in the main certainly correct as to order of magnitude. It is evident that these values are so high that, except possibly in the case of iodides, the equilibrium concentration of free radicals or atoms is far too small to be of importance except at temperatures so high that secondary reactions come into play and make the situation extremely complex. As a result little use can be made of the stationary

⁸ K. H. Geib, *Ergeb. exakt. Naturwiss.*, **15**, 44 (1936).

⁹ K. F. Bonhoeffer and H. Reichardt, *Z. physik. Chem.*, **A139**, 75 (1928).

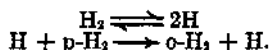
TABLE I. DISSOCIATION OF DIATOMIC MOLECULES

Substance	Heat of dissociation	Temperature in °K at which the degree of dissociation is		
		1 %	0.01 %	0.0001 %
K ₂	11.8 kcal.	270	—	—
Na ₂	17.0	390	280	—
Li ₂	26.7	590	420	330
I ₂	35.2	680	510	410
Br ₂	45.2	850	640	510
Cl ₂	56.9	1040	800	640
HI	70	1310	975	780
HBr	86.7	1590	1200	965
HCl	101.5	1830	1380	1115
H ₂	102.7	1910	1425	1140
D ₂	104.6	1920	1440	1160
S ₂	102.6	1930	1430	1140
O ₂	117.4	2000	1530	1240
P ₂	115	2200	1620	1260
NO	122.5	2100	1600	1290
CO	160 (?)	2580	1990	1620
N ₂	170	2850	2200	1800

state concentration of free radicals in equilibrium with organic molecules, and the method has been widely used only for the investigation of the following types of atomic reactions:

(i) *Reactions involving Atomic Hydrogen*

The thermal conversion of para- to ortho-hydrogen was investigated by Farkas^{10, 11} at temperatures in the range 600° to 750°. The reaction was of the 3J2 order, indicating the mechanism



Numerous other investigations strongly support this mechanism. In a similar way Farkas and Farkas¹² investigated the thermal conversion of ortho- to para-deuterium, and the exchange reactions



There seems to be no doubt that in all these cases the reaction involves the stationary concentration of hydrogen or deuterium atoms in thermal equilibrium with undissociated molecules.

The thermal reactions of deuterium with methane, ammonia, and water also appear to proceed through the agency of the equilibrium concentration

¹⁰ A. Farkas, *Z. Elektrochem.*, 36, 782 (1930).

¹¹ A. Farkas, *Z. physik. Chem.*, **B10**, 419 (1930).

¹² A. Farkas and L. Farkas, *Proc. Roy. Soc. (London)*, **A152**, 124 (1935).

of deuterium atoms.^{13,14} However, it is only with exceptionally stable substances such as ammonia, methane, and water that this method can be used to investigate the hydrogen atom reactions, since with most substances the high temperatures necessary would result in decomposition and other complications.

(ii) Alkali Metal Atoms

As we have seen, sodium, even at room temperature, is appreciably dissociated, and at 200° to 300° is mainly in the atomic state. The reactions of sodium atoms with many substances have been investigated by Polanyi and his co-workers by two rather similar methods. The so-called method of dilute flames is a modification of the ordinary flow method which is suitable for the investigation of very fast atomic reactions.

The original form of the method, that of "highly dilute flames," is as follows.^{15,18} Two reactants, A and B, are led into a tube from opposite ends. The pressures are so low that the mean free paths are greater than the diameter of the tube. Under these circumstances the gases mix solely by diffusion. As A penetrates into B it is consumed, and its pressure sinks to zero. Similarly with B as it penetrates into A. We thus have the state of affairs shown in Figure 1. The curve U represents the product $P_A P_B$

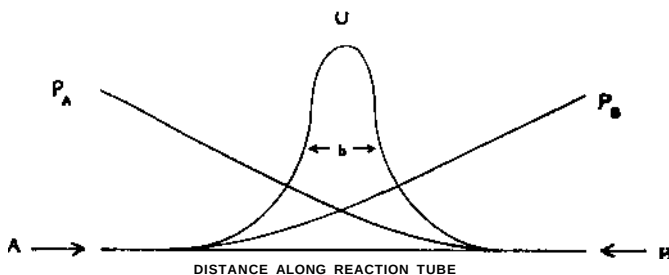


Figure 1.

and should thus be proportional to the rate of reaction if the reaction is bimolecular. The essential feature of the method is the determination of the rate of reaction from the breadth of the curve. It is obvious that a relationship should exist, since the slower the reaction the farther the reactants will penetrate into one another. The exact relation is

$$k = \frac{27}{b^2} \frac{1}{2 q U k_A k_B'}$$

¹⁸ A. Farkas, *J. Chem. Soc.*, **1936**, 26.

¹⁴ A. Farkas and H. W. Melville, *Proc. Roy. Soc. (London)*, **A167**, 625 (1936).

¹⁵ H. Beutler, S. v. Bogdandy, and M. Polanyi, *Naturwiss.*, **14**, 164 (1926).

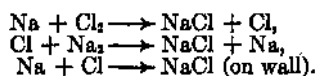
¹⁶ H. Beutler and M. Polanyi, *Naturwiss.*, **13**, 711 (1925); *Z. Physik*, **47**, 379 (1928).

¹⁷ S. v. Bogdandy and M. Polanyi, *Z. physik. Chem.*, B1, 21 (1928).

¹⁸ M. Polanyi, *Atomic Reactions*, London, 1932.

where k is the rate constant of the reaction, k_A and k_B are the diffusion resistances of the two gases, q is the cross-section of the tube, and b is the "half-breadth" of the curve U . The form of the curve is easily obtained if the product of the reaction is a solid. Thus in the reaction between sodium and chlorine, the curve can be obtained from the thickness of the sodium chloride deposit at any point. This can be obtained by direct weighing or by opacity measurements.

By a determination of the overall rate constant in this way, together with an examination of the luminescence accompanying the reaction, Polanyi and his collaborators have obtained information about the rates of many reactions involving metal atoms, and incidentally about reactions of halogen atoms, etc. Examples are:



For a review of this work see Polanyi.¹⁸

A modification of this method is that of "diffusion flames." This is suitable for reactions somewhat slower than those considered above, i.e., for those with an activation energy of a few kcal.¹⁹⁻²² This method is similar to the dilute flame method in that the rate of reaction is inferred from measurements of the distance which one component penetrates into the other before being used up. To make this distance shorter so that slower reactions can be investigated, a foreign gas at a pressure up to 10 mm. is added. This slows down diffusion and acts as a carrier for the reactants. The apparatus is illustrated in Figure 2.

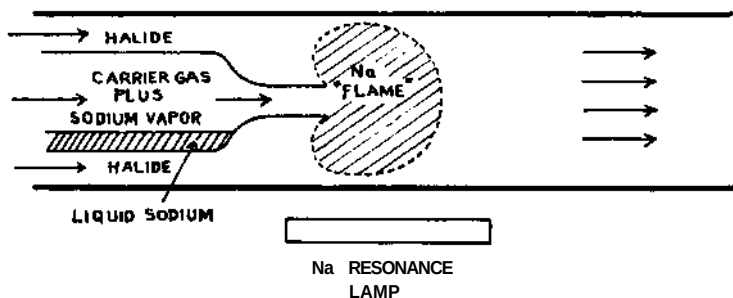


Figure 2. Diffusion flame apparatus.

One reactant, say sodium vapor, together with an inert gas as carrier enters through a jet into a chamber containing the other reactant, say

¹⁹ H. v. Hartel, *Trans. Faraday Soc.*, **30**, 187 (1934); H. v. Hartel, N. Meer, and M. Polanyi, *Z. physik. Chem.*, **B19**, 139 (1932).

²⁰ H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

²¹ W. Heller, *Trans. Faraday Soc.*, **33**, 1556 (1937).

²² N. Meer and M. Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932).

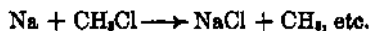
methyl chloride. The partial pressures of the reactants are of the order of 2×10^{-3} mm. for sodium, and 0.02 to 0.5 mm. for the alkyl halide. By illuminating the sodium vapor with a resonance lamp giving the D doublet, it is possible to make the sodium vapor visible. We can thus measure the size of the "flame" to a distance at which the concentration of sodium vapor is so low that it cannot be detected by this method. We can then calculate the rate constant of the reaction from the size of the flame, or zone of penetration of one reactant into the other, by means of considerations similar to those used in the case of the dilute flame method.

The conditions are adjusted so that for simplicity

- (1) The size of the flame is smaller than the tube diameter, and wall effects are thus eliminated.
- (2) The rate of flow of carrier gas in the jet is fast enough so that no appreciable back diffusion of the reactant against the sodium stream occurs.
- (3) The flow of the reactant and its amount are so arranged that its concentration is constant throughout the tube, and is not appreciably affected by the flow of carrier gas, or by reaction. (It is always present in large excess compared with sodium.)

In practice the partial pressure of the reactant is varied until a certain size of flame is produced. It is evident that the slower the reaction rate the higher will be the necessary partial pressure. Thus with methyl iodide, where reaction occurs at approximately every collision, 10^{-8} mm. is sufficient, while with methyl fluoride even with 10 mm. pressure the reaction is so slow that the whole tube is full of sodium vapor, *i.e.*, less than 1 collision in 10^6 is effective. In general, the suitable range of reactions whose rates can be measured are those in which from 1J10 to 1J100000 of the collisions between the reactants are effective.

Polanyi and his co-workers have investigated a whole series of reactions by this method, all of them involving metal atoms and halides, *e.g.*,



As a result of the absence of luminescence in the reactions it is not possible to obtain as much information about secondary reactions as is the case with the dilute flame method. It has, however, proved possible to make accurate measurements of the activation energies of numerous metal atom-halide reactions.¹⁸ (See Chapter XII.)

The method has also been used successfully but to a limited extent with potassium, magnesium, cadmium, and zinc.

A modification of the diffusion flame technique which is somewhat more accurate is the so-called "life-period" method.²⁸ In this method sodium

²³ E. Cremer, J. Curry, and M. Polanyi, *Z. physik. Chem.*, **B23**, 445 (1933); L. Frommer and M. Polanyi, *Trans. Faraday Soc.*, **SO**, 519 (1934); F. Fairbrother and E. Warhurst, *Trans. Faraday Soc.*, **31**, 987 (1935).

vapor together with an inert carrier gas is introduced into an excess of the halide and a stationary reaction zone is formed, as before. Instead of measuring the size of the flame, however, the number of sodium atoms introduced in unit time, and the number present in the flame are measured. From this the average life of a sodium atom in the reaction zone is determined. Knowing the average life of a sodium atom in the flame and the concentration of the halide, the rate constant of the reaction follows directly.

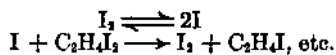
In the original form of the life period method the determination of the number of sodium atoms in the flame involved point-to-point photometry and was extremely laborious. A later modification²⁴ simplified the procedure greatly and merely involves the determination of the average sodium concentration in the flame by a single measurement of the absorption of sodium resonance radiation by the entire flame.

(iii) Iodine Atoms

Since the strength of the carbon-iodine bond is relatively low, iodine atoms are frequently formed in the thermal reactions of organic iodides. In some cases the concentration of atomic iodine appears to be that corresponding to the equilibrium



Thus, for example, the thermal decomposition of ethylene iodide is strongly catalysed by iodine, and the rate is proportional to the square root of the iodine concentration.^{25, 26, 27} There seems to be no doubt that the mechanism is



Iodine also catalyses a large number of other decomposition reactions, possibly through the intermediate formation and decomposition of an alkyl iodide. (See²⁸ for a review of catalysis by iodine.)

(b) The Active Species Are Produced by Thermal Decomposition

Atoms or radicals are produced in the thermal decomposition of many substances. There are a number of methods by which advantage is taken of this fact in practice: these differ mainly in the time during which the reactant remains in the heated zone.

(i) The Static and Flow Methods

By means of the ordinary static and flow methods the kinetics of many thermal reactions have been investigated. In a number of cases analysis

²⁴ F. Fairbrother and J. L. Tuck, *Trans. Faraday Soc.*, 32, 624 (1936); E. Warhurst, *Trans. Faraday Soc.*, 35, 674 (1939).

²⁵ L. B. Arnold and G. B. Kistiakowsky, *J. Chem. Phys.*, 1, 166 (1933).

²⁶ M. J. Polissar, *J. Am. Chem. Soc.*, 62, 956 (1930).

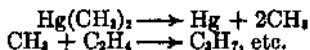
²⁷ H. J. Schumacher and E. O. Wiig, *Z. physik. Chem.*, B11, 45 (1931).

²⁸ H. J. Schumacher, *Chemische Gasreaktionen*, Leipzig, 1938.

of the kinetics of such reactions leads to the conclusion that atoms or free radicals are involved and to the setting up of a mechanism involving a number of elementary reactions. From the temperature coefficient and other factors it is then possible to draw conclusions regarding the rates of the elementary part reactions. Such conclusions, however, are always more or less speculative, and are greatly strengthened by confirmation by other, more direct, methods.

(it) Sensitized Decompositions

By means of the ordinary static and flow methods atom or radical reactions can also be investigated by mixing a substance, the sensitizer, with the reactant and heating the mixture to a temperature at which the reactant is normally stable, while the sensitizer decomposes with the formation of atoms or radicals. The first investigation of a sensitized reaction of this kind was that of Taylor and Jones²⁹ who decomposed mercury and lead alkyls in the presence of hydrogen and ethylene. They found that the main result was polymerization of the ethylene, pointing to the occurrence of the sequence



In order to apply the method in such a way as to obtain quantitative information it is essential to know the kinetics of the decomposition of the sensitizer, and especially the radicals formed in its decomposition. As a result the sensitizers which have been at all widely used are comparatively few in number. The main ones are:

Ethylene Oxide

The decomposition of ethylene oxide is discussed in detail in section (III—16), and there is no doubt that methyl radicals are involved. It has been suggested that on the average 0.3 methyl radical is produced per molecule of ethylene oxide decomposed.

Many investigations have been made using ethylene oxide as a sensitizer.³⁰⁻³⁵ The production of carbon monoxide has usually been used as an indication of the amount of decomposition of ethylene oxide, and hence of the number of methyl radicals generated in the system.

Thus Echols and Pease³³ investigated the ethylene oxide sensitized decomposition of a number of paraffins by mixing the paraffin and ethylene

²⁹ H. S. Taylor and W. H. Jones, *J. Am. Chem. Soc.*, 52, 1111 (1930).

⁸⁰ W. W. Heckert and E. Mack, *J. Am. Chem. Soc.*, 51, 2706 (1929); D. V. Siokman, *Chem. Phys.*, 4, 297 (1936).

³¹ C. J. M. Fletcher, *J. Am. Chem. Soc.*, 68, 534 (1936).

⁸² C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2135 (1936).

³³ L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, 68, 1317 (1936).

³⁴ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2129 (1936).

³⁸ E. W. R. Steacie and H. O. Folkins, *Can. J. Research*, B17, 105 (1939).

oxide at temperatures around 400°, allowing the ethylene oxide to decompose, and then analysing the products for unsaturates and carbon monoxide. On the assumption that all the unsaturates come from the paraffin and all the carbon monoxide from the ethylene oxide decomposition, the ratio C_nH_{2n}/CO is thus a measure of the chain length of the sensitized decomposition. Thus at 425° with an 8J1 mixture of n-butane and ethylene oxide they found

$$C_nH_{2n}/CO = 12.0$$

Hence if we assume 0.3 methyl is formed for each molecule of decomposing ethylene oxide, we obtain a chain length of about 40. It may be noted that irrespective of any uncertainty about the mechanism of the ethylene oxide decomposition these results definitely indicate that chains are set up, since even with the extreme, and unlikely, assumption of 2 radicals from each molecule of ethylene oxide decomposed, the chain length would still be at least 6.

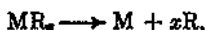
Azomethane

The azomethane decomposition also involves methyl radicals. The reaction is discussed in section (III—17).

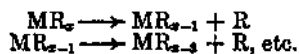
There are numerous cases of decompositions and polymerizations induced by radicals from azomethane. Examples are: butane,³⁶ acetylene,³⁶ ethylene,⁸⁶ propylene,³⁶ acetaldehyde,^{37,38} divinyl ether,⁸⁹ heptane,⁴⁰ methyl ethyl ether,⁴¹ propylamine.⁴¹

Metal Alkyls

These are by far the most important sensitizers. There seems to be little doubt that in all cases the mechanism of the decomposition is



where M is a metal and R is an alkyl radical. The above process presumably occurs in steps,



In interpreting the results of induced decompositions there are possible complications. For example, in the case of mercury diethyl, apart from the obvious secondary reactions



⁸⁶ D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, 4, 239, 608 (1936).

⁸⁷ A. O. Allen and D. V. Sickman, *J. Am. Chem. Soc.*, 56, 2031 (1934).

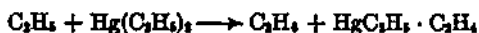
⁸⁸ D. V. Sickman and A. O. Allen, *J. Am. Chem. Soc.*, 56, 1251 (1934).

⁸⁹ H. A. Taylor, *J. Chem. Phys.*, 4, 116 (1936).

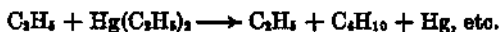
⁴⁰ R. Maess, Oel, Kohle, Erdoel, Teer, 15, 299, 321 (1939).

⁴¹ F. O. Rice, W. D. Walters, and P. M. Ruoff, *J. Chem. Phys.*, 8, 259 (1940).

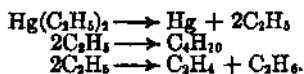
there is also the chance of



or



In general, however, there is no doubt that the main process is the simple formation of radicals, which then undergo secondary reactions. These substances have been used in the main in two distinctly different ways for the investigation of radical reactions. In the one method a static system is used and the metal alkyl is decomposed in the presence of another substance and causes its induced decomposition. In the other method a flow system is employed, the metal alkyl is decomposed, and from the products obtained it is possible to draw conclusions regarding the relative rates of recombination and disproportionation reactions, viz.



The following metal alkyls have been used as sensitizers: lead tetramethyl, lead tetraethyl,⁴²⁻⁴⁷ mercury dimethyl,⁴⁷⁻⁵³ mercury diethyl.^{47,54}

Other Substances

Various other substances have been used as sensitizers. Some examples follow: methyl ether,⁵⁵ ethyl ether,^{55,56} diacetyl,⁵⁷ propane,⁵⁸ butane,⁵⁸ ethyl vinyl ether,⁵⁹ triphenyl methyl azobenzene,^{60,61} silane,⁶² ethyl

⁴² O. Beeck and F. F. Rust, *J. Chem. Phys.*, **9**, 480 (1941).

⁴³ J. A. Leermakers, *J. Am. Chem. Soc.*, **56**, 4508 (1933).

⁴⁴ P. L. Cramer, *J. Am. Chem. Soc.*, **60**, 1406 (1938).

⁴⁵ J. A. Leermakers, *J. Am. Chem. Soc.*, **56**, 1899 (1934).

⁴⁶ J. H. Simons and M. F. Dull, *J. Am. Chem. Soc.*, **55**, 2696 (1933).

⁴⁷ H. S. Taylor and W. H. Jones, *J. Am. Chem. Soc.*, **52**, 1111 (1930).

⁴⁸ F. E. Frey, *Ind. Eng. Chem.*, **26**, 198 (1934).

⁴⁹ F. O. Rice, E. L. Rodowskas, and W. R. Lewis, *J. Am. Chem. Soc.*, **56**, 2497 (1934).

⁵⁰ F. S. Romm, *J. Gen. Chem.* (U.S.S.R.), **10**, 1784 (1940).

⁵¹ J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

⁵² H. S. Taylor and J. O. Smith, *J. Chem. Phys.*, **8**, 543 (1940).

⁵³ W. Jost and L. v. Muffling, *Z. Elektrochem.*, **47**, 766 (1941).

⁵⁴ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 396 (1940).

⁵⁵ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2129 (1936).

⁵⁶ J. S. A. Forsyth, *Trans. Faraday Soc.*, **87**, 312 (1941).

⁵⁷ F. O. Rice and W. D. Walters, *J. Am. Chem. Soc.*, **68**, 1701 (1941); C. H. Klute and W. D. Walters, *J. Am. Chem. Soc.*, **67**, 550 (1945).

⁵⁸ W. J. Hessels, D. W. van Krevelen, and H. I. Waterman, *Refiner*, **19**, 127 (1940).

⁵⁹ S. N. Wang and C. A. Winkler, *Can. J. Research*, **21B**, 97 (1943).

⁶⁰ G. V. Schulz, *Naturwiss.*, **27**, 659 (1939).

⁶¹ G. V. Schulz, *Z. Elektrochem.*, **47**, 265 (1941).

⁶² H. J. Emeleus and C. Reid, *J. Chem. Soc.*, **1939**, 1021.

iodide,^{63,64} ethyl bromide,⁶⁴ tetraphenyl succinic acid dinitrile,⁶¹ oxygen,^{66,66} products of the paraffin decompositions.⁵⁸

(iii) *The Paneth-Rice Method— Very Fast Flow*

The method by which Paneth and Hofeditz⁶⁷ first discovered the free methyl radical is, in reality, only a very fast flow method. Since the main feature of this work is not the means by which radicals are produced, but rather the means used for their detection, the method is discussed in section (II-6).

(iv) *Methods Using Heated Filaments*

The classical experiments of Langmuir were the first example of this method.^{68,70} Langmuir investigated the heat loss from metal filaments heated in vacuo, or in the presence of hydrogen, oxygen, or other gases. The apparatus used was a more or less standard type of filament lamp bulb. He showed that at very high temperatures hydrogen was dissociated into atoms on the filament, and that the atomic hydrogen thus produced reached the walls of the bulb at low pressures, where its activity was shown by the reduction of metallic oxides, and other reactions.

Considerable information on catalytic reactions has been obtained by this means, but in its ordinary form it is not of much assistance as far as homogeneous elementary reactions are concerned.

A modification of the method has been used by Storch.⁷¹ Storch wished to ascertain the initial products of the decomposition of methane, without complications due to secondary reactions. To accomplish this he decomposed methane at low pressures on a hot carbon filament in a "lamp-bulb" which was cooled in liquid nitrogen. The products thus condensed out immediately they were formed. He showed that under these circumstances the first recognizable product was ethane.

The main use of the filament method in the investigation of elementary reactions is that of Belchetz and Rideal.^{72,73} They employed two different types of apparatus. In both of these the gas streamed through at a high velocity (ca. 100 cm. per sec), and at 0.1 mm. pressure, over a heated platinum or carbon filament. In the first apparatus any radicals formed by the decomposition of the gas on the hot filament came into contact with a

⁶³ R. v. Tassel, *Natuurw. Tijdschr.*, **20**, 83 (1938).

⁶⁴ J. G. Roof and F. Daniels, *J. Am. Chem. Soc.*, **62**, 2912 (1940).

⁶⁵ S. Lenher, *J. Am. Chem. Soc.*, **53**, 3752 (1931).

⁶⁶ M. Letort, *Compt. Rend.*, **197**, 1042 (1933), **199**, 351, 1617 (1934), **200**, 312 (1935).

⁶⁷ F. Paneth and W. Hofeditz, *Ber.*, **62B**, 1335 (1929).

⁶⁸ A. E. Freeman, *J. Am. Chem. Soc.*, **35**, 927 (1913).

⁶⁹ I. Langmuir, *J. Am. Chem. Soc.*, **34**, 1310 (1912), **37**, 417 (1915).

⁷⁰ I. Langmuir and G. M. J. Mackay, *J. Am. Chem. Soc.*, **36**, 1708 (1914).

⁷¹ H. H. Storch, *J. Am. Chem. Soc.*, **54**, 4188 (1932).

⁷² L. Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934).

⁷³ L. Belchetz and E. K. Rideal, *J. Am. Chem. Soc.*, **57**, 1168, 2466 (1935).

water-cooled target 3 mm. away from the filament. Mirrors could be deposited on this target, and any products formed were caught in a liquid air trap. Since the distance between the filament and the target was so small, of the order of one mean free path, any radicals formed would reach the target without undergoing collisions. It should thus definitely be possible to detect the radicals without any danger of secondary processes intervening.

In the second apparatus the mirror was on the wall of the reaction vessel opposite the filament. It was considerably farther from the filament than in the former case, and the system thus, resembled the hot-tube type of apparatus employed by Paneth and by Rice.

With both sets of apparatus tellurium and iodine mirrors were used, and platinum and carbon filaments. Most of the work was done with carbon filaments.

We will return to this method later in connection with the detection of radicals. It may be mentioned here, however, that there is a considerable possibility that complications are introduced by the presence of the material of the filament and that the activation energies of the decomposition of substances into free radicals calculated from the results may refer to catalytic processes on the surface of carbon or platinum, rather than to the homogeneous split into radicals in the gas phase. Certainly in Langmuir's work the dissociation of hydrogen into atoms occurred in an adsorbed layer of the surface of tungsten, and not merely by the molecule acquiring energy on impact. By analogy there seems every reason to suspect that, *e.g.*, a hydrocarbon may be adsorbed on the carbon filament prior to dissociation into radicals: indeed theoretical considerations are overwhelmingly in favor of such an occurrence. Evidence that this is the case will be presented later in discussing the detection of radicals produced by the Belchetz-Rideal method.

A discussion of the production of hydrogen atoms by heated tungsten filaments has been given by Roberts and Bryce.⁷⁴

Haber and Oppenheimer⁷⁵ have used hydrogen atoms, produced by a hot filament, in a flow system to start sensitized explosions in hydrogen-oxygen mixtures at temperatures as low as 300°. (See also footnotes 76-78.)

(c) *The Active Species Are Produced by a Reaction of Higher Order than the First*

In addition to their production by thermal decomposition, radicals and atoms may arise as intermediate stages in thermal reactions of higher order.

⁷⁴ J. K. Roberts and G. Bryce, *Proc. Camb. Phil. Soc.*, 32, 648, 653 (1936); see also J. P. W. Houtman, K. Van den Berg, and P. M. Heertjes, *Rec. Trav. Chim. Pays-Bas*, 62, 672 (1943).

⁷⁵ F. Haber and F. Oppenheimer, *Z. physik. Chem.*, B16, 443 (1932).

⁷⁶ L. Farkas, P. Goldfinger, and F. Haber, *Naturwiss.*, 17, 674 (1929).

⁷⁷ F. Haber, *Naturwiss.*, 18, 917 (1930).

⁷⁸ F. Haber and H. D. v. Schweinitz, *Sitzb. preuss. Akad. Wiss.*, 499 (1928).

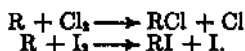
In some cases they result from the interaction of two or more relatively **stable** molecules, while in other cases one radical by reaction with a normal **molecule** may form a different radical.

(i) *Diffusion Flames*

Horn, Polanyi, and Style⁷⁹⁻⁸¹ modified the diffusion flame technique so **as** to investigate certain reactions of free radicals. A further jet was added to the apparatus, and the products of a reaction of the type



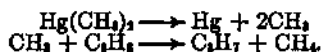
were introduced into chlorine or iodine. In this way they were able to demonstrate the occurrence of the reactions



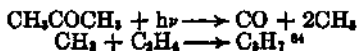
Allen and Bawn⁸² have combined the Horn, Polanyi, and Style method with the Paneth technique for the detection of radicals.

(ii) *The Indirect Production of Atoms and Radicals*

Frequently the production of an atom or radical in a system leads, by a reaction involving other substances, to the formation of other, different, atoms or radicals. Thus, for example, if mercury dimethyl is decomposed in the presence of propane,⁸³ we have



Hence this method could, in principle, be used as a source of propyl radicals. Other examples are



However, the systems thus formed are so complex that this is rarely a satisfactory way of generating atoms or radicals. Only when the complete

⁷⁹ E. Horn and M. Polanyi, *Z. physik. Chem.*, **B25**, 151 (1934).

⁸⁰ E. Horn, M. Polanyi, and D. W. G. Style, *Trans. Faraday Soc.*, **30**, 189 (1934).

⁸¹ M. Polanyi and D. W. G. Style, *Naturwiss.*, **20**, 401 (1932).

⁸² A. O. Allen and C. E. H. Bawn, *Trans. Faraday Soc.*, **34**, 463 (1938).

⁸³ J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

⁸⁴ H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937).

⁸⁵ E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

⁸⁶ F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

⁸⁷ E. W. R. Steacie and N. W. F. Phillips, *Can. J. Research*, **B16**, 303 (1938).

⁸⁸ N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, **6**, 203 (1937).

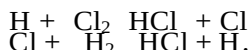
mechanism of the reaction has been accurately established can this method be used.

(iii) *Explosions, Oxidation Reactions, etc.*

There is considerable evidence that atoms and radicals play a decisive role in many explosions, oxidation reactions, etc.⁸⁹⁻⁹¹ The systems are so complex, and our knowledge of them is so slight, however, that they cannot be used in practice as reliable sources of atoms and radicals.

4. Photochemical Methods of Producing Atoms and Radicals

Since atoms or radicals are involved in most photochemical reactions, this section includes most of photochemistry. In many cases information about elementary reactions can be obtained from an analysis of the mechanism of photochemical processes. A well-known example is the photosynthesis of hydrogen chloride, in which the primary process is the dissociation of chlorine, and the investigation of which leads to detailed information about the secondary reactions



(For recent and detailed discussions see footnotes 92, 93.)

However, since it would obviously be out of place to enter into an extended discussion of photochemistry here, we will consider only those cases in which a substance is deliberately photolysed in order to provide a supply of atoms or radicals. (For modern reviews of photochemistry see footnotes 92 and 93.) Some of the main examples of this technique follow:

(a) *Photolysis*

(i) *The Halogens*

When a halogen absorbs light in the continuum the primary process involves a split into atoms, and if some other substance is present, the atoms thus produced may react with it. A wide variety of photohalogenations have been investigated in this way: the reactions are, in general, chain processes. In a large number of cases detailed investigations have been made, and the mechanism of the reactions can be inferred with considerable certainty. Activation energies of the part reactions can then be deduced by a comparison of the rate equation predicted by the mechanism with

⁸⁹ W. Jost, *Explosions- und Verbrennungs-vorgange in Gasen*, Berlin, 1939.

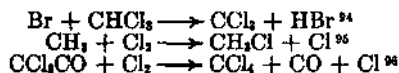
⁹⁰ B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases*, Cambridge, 1938.

⁹¹ R. G. W. Norrish, *Proc. Roy. Soc. (London)*, A150, 36 (1935).

⁹² G. K. Rollefson and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions*, New York, 1939.

⁹³ W. A. Noyes, Jr., and P. A. Leighton, *The Photochemistry of Gases*, New York, 1941.

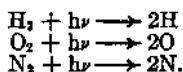
that found experimentally. In this way activation energies have been arrived at for a large number of reactions involving atomic chlorine and bromine, and for a few reactions involving atomic iodine. Some examples follow:



Reactions of this kind are discussed fully in Chapters IX to XI.

(it) *Other Atoms*

It is obviously possible in principle to obtain atoms by the reactions:



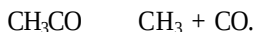
However, continuous absorption by these gases occurs only in the short ultraviolet, where experimental difficulties are too great to make this a convenient method of obtaining atoms for the investigation of elementary reactions. It has, however, been used to some extent to produce oxygen atoms.^{96a}

(iii) *Ketones*

The aliphatic ketones show a first absorption maximum in the neighbourhood of 2800Å., which is associated with the CO group. Much work has been done on the photolysis of a wide variety of ketones. (See V-6-10.) It seems to be established, for example, that in the case of acetone the primary process is mainly



At higher temperatures (above 60°) the acetyl radical decomposes



Hence at higher temperatures acetone acts as a source of methyl radicals only.

Pearson and his co-workers⁹⁷⁻¹⁰¹ have used mirror methods to detect

⁹⁴ V. Braunwarth and H. J. Schumacher, *Kolloid-Z.*, **89**, 184 (1939).

⁹⁵ W. Brenschede and H. J. Schumacher, *Z. physik. Chem.*, **A177**, 245 (1936).

⁹⁶ W. A. Alexander and H. J. Schumacher, *Z. physik. Chem.*, **B44**, 67 (1939).

^{96a} See, for example, G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **62**, 1868 (1930); G. B. Kistiakowsky and P. E. Millington, *Z. physik. Chem.*, **B13**, 155 (1931); P. Hartek and F. Oppenheimer, *Z. physik. Chem.*, **B16**, 77 (1932).

⁹⁷ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1937**, 567.

⁹⁸ T. G. Pearson, *J. Chem. Soc.*, **1934**, 1718.

⁹⁹ T. G. Pearson and H. H. Glazebrook, *J. Chem. Soc.*, **1936**, 1777.

¹⁰⁰ T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, **1935**, 1151.

¹⁰¹ T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, **1936**, 253.

and estimate free radicals in the case of acetone and numerous other ketones, and have used such photolyses as a source of free radicals.

Acetone has been used as a source of free radicals in the investigation of induced reactions by many workers.^{102,106}

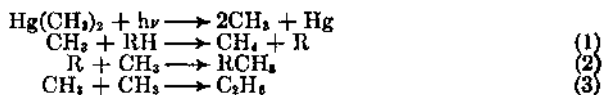
(iv) Metal Alkyls

The thermal decomposition of metal alkyls as a source of free radicals has already been discussed. The mechanism of their photolysis appears to be similar to that of their pyrolysis, yielding free alkyl radicals. (See Chapter XIII for details.)

The mercury alkyls have been much used as a source of free radicals by Taylor and his collaborators¹⁰⁷⁻¹¹⁰ who by their use have investigated a whole series of reactions of the type



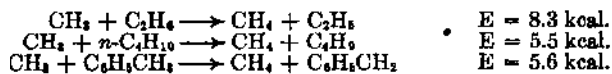
Thus Smith and Taylor^{109,110} photolysed mercury dimethyl in the presence of deuterium, ethane, neopentane, butane, isobutane, benzene, toluene, diphenyl methane, and propylene. They assume in the case of the hydrocarbons that the main steps in the mechanism are



This yields for the rate of methane production

$$\frac{d}{dt}[\text{CH}_4] = k_1[\text{RH}] \cdot \left(\frac{-2k_1[\text{RH}] + (4k_1[\text{RH}]^2 + 8k_2 I_{\text{abs}})^{\frac{1}{2}}}{2k_2} \right) = k_1[\text{RH}] \cdot A$$

At low temperatures where ethane (from reaction (3)) is the principal product, A will be approximately constant, and hence the rate of production of methane will give a true measure of k_1 . Hence by measuring the rate of formation of methane as a function of temperature the activation energy of reaction (1) can be obtained. In this way they found, for example,



¹⁰² J. A. Leermakers, *J. Am. Chem. Soc.*, **66**, 1899 (1934).

¹⁰³ H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937).

¹⁰⁴ R. Maess, *Del, Kohle, Erdoel, Teer*, **16**, 299, 321 (1939).

¹⁰⁵ E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 890.

¹⁰⁶ C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A179,169** (1941).

¹⁰⁷ J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.*, **6**, 359 (1938).

¹⁰⁸ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 396, 466 (1940).

¹⁰⁹ J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

¹¹⁰ H. S. Taylor and J. O. Smith, *J. Chem. Phys.*, **8**, 543 (1940).

(v) *Alkyl Halide*⁸

A great deal of work has been done on the absorption spectra and photolysis of the alkyl halides, especially the iodides. (See V-14.) There is some disagreement regarding the mechanism of the reactions, but the evidence is strongly in favor of a primary split into a radical and a halogen atom,*e.g.*

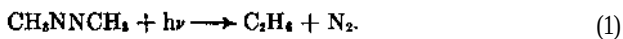


The quantum yield is low owing to the high efficiency of the reverse reaction, but may be increased by the addition to the system of any substance capable of fixing the iodine formed.¹¹¹

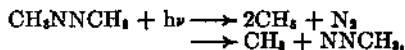
The photolysis of alkyl iodides has been used as a source of free radicals by Jungers and Yeddanapalli¹¹² (methyl, ethyl, n-propyl, and iso-propyl iodides), Tassel¹¹³ (ethyl iodide), and Joris and Jungers^m (ethyl iodide).

(vi) *Azomethane*

A number of investigations of the photolysis of azomethane have been made. (See V-12.) Early work seemed to suggest a simple mechanism leading directly to the final products,



However, it now appears to be established that the primary step is a split into free radicals



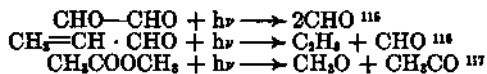
or

and that reaction (1) does not occur to any appreciable extent.

The photolysis of azomethane has been used as a source of free radicals by Maess⁴⁰ and by Blacet and Taurog.¹¹⁴

Other Radicals

Numerous other radicals have been produced by photolysis, although in many cases the evidence is not entirely definite as to their identity. A number of cases are discussed in detail in Chapter V. Other examples are



¹¹¹ G. G. Joris and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 47, 135 (1938).

¹¹² J. C. Jungers and L. M. Yeddanapalli, *Trans. Faraday Soc.*, 36, 483 (1940).

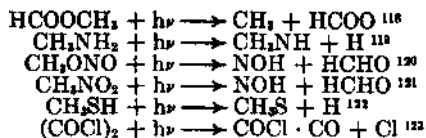
¹¹³ R. v. Tassel, *Natuurw. Tijdschr.*, 20, 83 (1938).

¹¹⁴ F. E. Blacet and A. Taurog, *J. Am. Chem. Soc.*, 61, 3024 (1939).

¹¹⁵ F. E. Blacet and R. W. Moulton, *J. Am. Chem. Soc.*, 63, 808 (1941).

¹¹⁶ F. E. Blacet, G. H. Fielding, and J. G. Roof, *J. Am. Chem. Soc.*, 59, 2375 (1937).

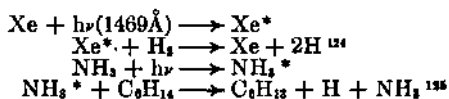
¹¹⁷ W. L. Roth and G. K. Rolleson, *J. Am. Chem. Soc.*, 64, 490 (1942).



(b) Photosensitization

In order that a photochemical reaction may occur it is necessary in the first place that the magnitude of the quantum of the incident light be large enough, and secondly that the light be absorbed. In many cases substances have dissociation energies corresponding to wave lengths in a convenient region of the spectrum, but are transparent down to the Schumann region where photochemical experiments are difficult to carry out. Thus hydrogen has a dissociation energy of 102.7 kcal., corresponding to a quantum of wave length of 2776Å, but the continuum in its absorption spectrum does not begin till 849Å.

If we add to hydrogen a substance which will absorb somewhere below 2776Å and can transfer this energy to the hydrogen, we can produce a *photosensitized* dissociation of hydrogen. This method is of wide applicability and has been much used. A variety of sensitizers have been used for many reactions, e.g.,



From an experimental point of view, however, the main sensitizers are metal atoms, since with them it is possible to use very intense and convenient sources of resonance radiation. Of these, mercury has been most used. In experiments of this sort mercury vapor is mixed with the reactant gas, and the mixture is illuminated with the mercury resonance line at 2537Å. (A little work has also been done with the lower resonance line, 1849Å.^{126,127}) This is absorbed by the mercury vapor in the system, normal 6^1S_0 mercury atoms being raised to the 6^3P_1 level. This lies 4.8 volts,

¹¹⁸ J. K. Royal and G. K. Rollefson, *J. Am. Chem. Soc.*, **63**, 1521 (1941).

¹¹⁹ O. C. Wetmore and H. A. Taylor, *J. Chem. Phys.*, **12**, 61 (1944).

¹²⁰ H. W. Thompson and C. H. Purkis, *Trans. Faraday Soc.*, **32**, 674 (1936), **32**, 1466 (1936); H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, **33**, 1546 (1937).

¹²¹ E. Hirschlaff and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 1580.

¹²² N. P. Skerrett and H. W. Thompson, *Trans. Faraday Soc.*, **37**, 81 (1941).

¹²³ K. B. Krauskopf and G. K. Rollefson, *J. Am. Chem. Soc.*, **68**, 443 (1936).

¹²⁴ H. R. Calvert, *Z. Physik.*, **78**, 479 (1932).

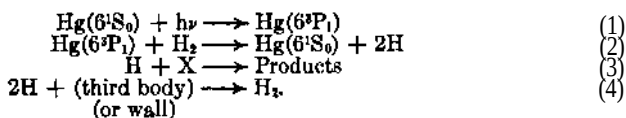
¹²⁵ L. Farkas, *Z. physik. Chem.*, **B23**, 89 (1933).

¹²⁶ J. E. Cline and G. S. Forbes, *J. Am. Chem. Soc.*, **61**, 716 (1939).

¹²⁷ G. S. Forbes and J. E. Cline, *J. Am. Chem. Soc.*, **63**, 1713 (1941).

or 112 kcal., above the ground state. Such excited mercury atoms may then transfer their energy by collision to other molecules. If such transfer occurs efficiently, a wide variety of reactions is possible since 112 kcal. is greater than the activation energy of almost all chemical reactions. (See, *e.g.*, footnotes 128-131).

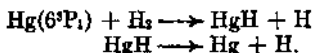
The mercury photosensitization method is especially important since Taylor and his co-workers have shown that it allows the investigation of reactions involving hydrogen atoms. In the presence of hydrogen and a reacting substance, X, we have



Under these circumstances a stationary concentration of hydrogen atoms exists, and, knowing the rates of reactions (1), (2), and (4), the rate constant of reaction (3) can be calculated. (See, for example, footnotes 136-140.) This is an extremely useful method, although the results are not always easy to interpret, since in many cases the reactant also "quenches" the resonance radiation to an appreciable extent, and decomposition reactions, etc., are thus superimposed on the hydrogen atom reaction.

Many hydrogenation reactions have been investigated by this method, *e.g.*, the reactions with methane, ethane, propane, and butane. These are discussed in some detail in Chapter VI.

* From recent work there is some doubt as to whether reaction (2) proceeds as written, or goes by (footnotes 132-135)



followed by

However, this would not affect the general conclusions to be drawn from mercury photosensitization experiments.

¹²⁸ G. Cario and J. Franck, *Z. Physik*, 11, 161 (1922).

¹²⁹ H. S. Taylor and J. R. Bates, *Proc. Nat. Acad. Sci.* (Washington), 12, 714 (1926).

¹³⁰ H. S. Taylor and D. G. Hill, *J. Am. Chem. Soc.*, 51, 2922 (1929), *Z. physik. Chem.*, **B2**, 449 (1929).

¹³¹ H. S. Taylor and A. L. Marshall, *J. Phys. Chem.*, 29, 1140 (1925).

¹³² H. Beutler and E. Rabinowitsch, *Z. physik. Chem.*, **B8**, 403 (1930).

¹³³ E. Gaviola and R. W. Wood, *Phil. Mag.*, 6, 1191 (1928).

¹³⁴ L. O. Olsen, *J. Chem. Phys.*, 6, 307 (1938).

¹³⁵ F. F. Rieke, *J. Chem. Phys.*, 4, 513 (1936).

¹³⁶ I. Amdur, *Phys. Rev.*, 43, 208 (1933); *J. Am. Chem. Soc.*, 67, 856 (1935), 60, 2347 (1938).

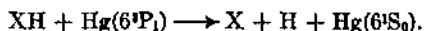
¹³⁷ I. Amdur and A. L. Robinson, *J. Am. Chem. Soc.*, 55, 1395 (1933).

¹³⁸ L. Farkas and H. Sachsse, *Z. physik. Chem.*, **B27**, 111 (1935).

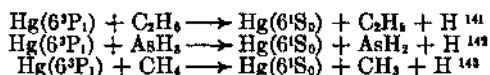
¹³⁹ H. M. Smallwood, *J. Am. Chem. Soc.*, 56, 1542 (1934).

¹⁴⁰ W. Steiner, *Trans. Faraday Soc.*, 31, 623, 962 (1935).

By mercury photosensitization it is also possible to produce atoms and radicals by decomposition reactions, especially by reactions of the type



This has been much used, although it is generally difficult to make a sufficiently detailed interpretation of the mechanism to enable reliable estimates to be made of the activation energies of the individual elementary reactions. Examples are:

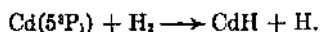


The method can obviously be used equally well for deuterium atoms. (See footnotes 143-146.)

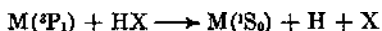
By using other metals as sensitizers it is possible to vary the energy input to the reacting molecule. Thus with mercury, cadmium, and zinc, the following excitation energies are involved.

$\text{Hg}(6^1\text{P}_1)$	(1849Å)	153.9 kcal
$\text{Hg}(6^1\text{P}_1)$	(2537Å)	112.2
$\text{Cd}(5^1\text{P}_1)$	(2288Å)	124.4
$\text{Cd}(5^1\text{P}_1)$	(3261Å)	87.3
$\text{Zn}(4^1\text{P}_1)$	(2139Å)	133.4
$\text{Zn}(4^1\text{P}_1)$	(3076Å)	92.5

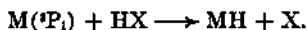
In the case of cadmium (and probably zinc), however, there is one important difference. Olsen's work¹⁴⁷ makes it probable that with mercury-hydrogen mixtures the primary step is a direct split into two hydrogen atoms, rather than an intermediate formation of mercury hydride. However, in the case of cadmium-hydrogen mixtures illuminated with the resonance line at 3261Å Bender¹⁴⁸ and Olsen have obtained strong resonance excitation of CdH bands. This indicates that CdH is formed in the normal state, and suggests that the primary step is



It is, therefore, not at all certain a priori whether with reactions involving a C-H bond split in a hydrocarbon or other organic molecule we have in a given case



or



¹⁴¹ E. W. R. Steacie and N. W. F. Phillips, *Can. J. Research*, **B16**, 303 (1938).

¹⁴² N. L. Simmons and A. O. Beckmann, *J. Am. Chem. Soc.*, **68**, 454 (1936).

¹⁴³ K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Chem. Phys.*, **5**, 212 (1939).

¹⁴⁴ A. Farkas and H. W. Melville, *Proc. Roy. Soc. (London)*, **A167**, 625 (1936).

¹⁴⁵ E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research*, **B16**, 314 (1938).

¹⁴⁶ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, **4**, 461 (1936).

¹⁴⁷ L. O. Olsen, *J. Chem. Phys.*, **6**, 307 (1938).

¹⁴⁸ P. Bender, *Phys. Rev.*, **36**, 1535 (1930).

If the latter mechanism holds, the bond split will be less endothermic by an amount equal to the heat of formation of the **hydride**. Hence bonds may be broken which are "stronger" than the excitation energy of the metal atom by 8.5 kcal. in the case of mercury, 15.5 with cadmium, and 23.1 with zinc. There is no doubt that some cadmium photosensitized reactions proceed in this way, since CdH bands have been detected in the cadmium photosensitized reactions of propane.¹⁴⁹

A number of investigations of cadmium and zinc photosensitized reactions have recently been made.¹⁶⁰ These include the reaction of Cd(⁵Pi) atoms with ethane,¹⁵¹ propane,¹⁵² and ethylene,^{153*} ¹⁵⁴ of Cd(⁴Ti) atoms with ethylene,¹⁶⁶ and of Zn(⁴P₁) and Zn(⁴P₁) atoms with ethylene.¹⁶⁶

An investigation of sodium photosensitization, using the D-doublet, was also made by Jungers and Taylor.¹⁵⁷ They found that ethylene quenched the radiation but was not chemically affected. The reason is, apparently, that the energy associated with this line (48 kcal.) is too small to cause decomposition or polymerization of ethylene.

5. Electrical Methods of Producing Atoms and Radicals

(a) *The Active Species Are Produced by an Electrical Discharge*

(i) *The Reactant Is Itself in the Discharge*

(For comprehensive recent reviews of the theory and chemical action of electrical discharges see footnotes 158, 159.)

There are two fundamentally different types of electrical discharge, the silent or non-disruptive discharge, and the disruptive discharge.

The silent discharge includes a number of types, such as the ozonizer, semi-corona, corona, glow, and electrodeless discharge. These have been used in numerous investigations with a variety of substances. There is no doubt that in many cases atoms and radicals are formed by the decomposition of organic or inorganic compounds. However, the situation is usually too complex to permit any accurate conclusions as to the rates of elementary reactions. On the other hand, the results are frequently of value as confirmatory evidence for postulated mechanisms.

The disruptive discharges, the arc and the spark, are much more violent

¹⁴⁹ E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, 12, 34 (1944).

¹⁵⁰ E. W. R. Steacie, *Annals N. Y. Acad. Sci.*, 41, 187 (1941).

¹⁵¹ E. W. R. Steacie and R. Potvin, *J. Chem. Phys.*, 7, 782 (1939).

¹⁵² E. W. R. Steacie, D. J. LeRoy, and R. Potvin, *J. Chem. Phys.*, 9, 306 (1941).

¹⁵³ J. R. Bates and H. S. Taylor, *J. Am. Chem. Soc.*, 50, 771 (1928).

¹⁵⁴ E. W. R. Steacie and R. Potvin, *Can. J. Research*, **B18**, 47 (1940).

¹⁵⁵ E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, 10, 22 (1942).

¹⁵⁶ H. Habeeb, D. J. LeRoy, and E. W. R. Steacie, *J. Chem. Phys.*, 10, 261 (1942).

¹⁵⁷ J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, 4, 94 (1936).

¹⁵⁸ G. Glockler and S. C. Lind, *The Electrochemistry of Gases and Other Dielectrics*, New York, 1939.

¹⁵⁹ C. L. Thomas, G. Egloff, and J. C. Morrell, *Chem. Revs.*, 28, 1 (1941).

in nature. There is no doubt that the main effects of these discharges are thermal, and correspond to localized heating of the gas to 1500° or higher. In general the results produced are so drastic that almost every possible atom or radical is produced by the discharge, and it is impossible to obtain much information about specific chemical reactions from work of this kind.

(ii) *The Products from a Discharge Are Mixed with Another Substance. Hydrogen Atoms*

As mentioned above, atoms and radicals are produced in electrical discharges in gases. It was first shown by Wood¹⁶⁰ that hydrogen atoms could be pumped out of a glow discharge in hydrogen and carried for considerable distances before they recombined. He found that for the success of the experiment it was essential that the walls of the tube be "poisoned" to slow down the recombination of the atoms, and that this could be done by a trace of water.

Following on preliminary experiments by Taylor and Marshall,¹⁶¹ Bonhoeffer¹⁶² modified Wood's apparatus and made extensive investigations of the chemical properties of atomic hydrogen. A typical apparatus for this kind of investigation is shown in Figure 3. Hydrogen flows through a discharge tube carrying about 300 milliamps. at several thousand volts. By the use of a fast pump and wide connecting tubing the rate of flow through the apparatus is very high, about 3 meters per sec, and hence atoms are drawn out of the tube into the reaction vessel before much recombination has occurred. The other reactant is added through a jet leading into the reaction vessel. As in Wood's work, it is essential that the walls of the vessel be thoroughly poisoned to prevent catalytic recombination of the atoms. This can be done with water vapor as used by Wood (for a modification see Trenner, Morikawa, and Taylor¹⁶³), syrupy phosphoric acid,¹⁶⁴ fused solid phosphoric acid,¹⁶⁵ or potassium chloride.¹⁶⁶ With efficient poisoning 20 to 50 per cent of hydrogen atoms may readily be obtained in the reaction vessel. The methods by which the hydrogen-atom concentration may be measured are described in a later section.

The pressures used are usually in the range 0.2 to 0.5 mm. With the pumping speeds employed this is generally equivalent to a contact time of 0.5 to 1 sec. Under these conditions the rates of reactions involving

¹⁶⁰ R. W. Wood, *Proc. Roy. Soc. (London)*, **A97**, 455 (1920), **A102**, 1 (1922); *Phil Mag.*, **42**, 729 (1921), **44**, 538 (1922).

¹⁶¹ H. S. Taylor and A. L. Marshall, *Nature*, **112**, 937 (1923).

¹⁶² K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 119, 492 (1924), **116**, 391 (1925); *Z. Elektrochem.*, **31**, 521 (1925); *Ergeb. exakt. Naturwiss.*, **6**, 201 (1927).

¹⁶³ N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, **5**, 203 (1937).

¹⁶⁴ H. v. Wartenberg and G. Schultze, *Z. physik. Chem.*, **B2**, 1 (1929).

¹⁶⁵ H. G. Poole, *Proc. Roy. Soc. (London)*, **A163**, 404 (1937).

¹⁶⁶ K. H. Geib and E. W. R. Steacie, *Z. physik. Chem.*, **B29**, 215 (1935).

hydrogen atoms can be measured at room temperature provided the activation energies are in the range 5 to 12 kcal.

The method has been used by a number of investigators at temperatures up to 180°, and by Steacie up to 500°. ¹⁶⁷ At such high temperatures wall

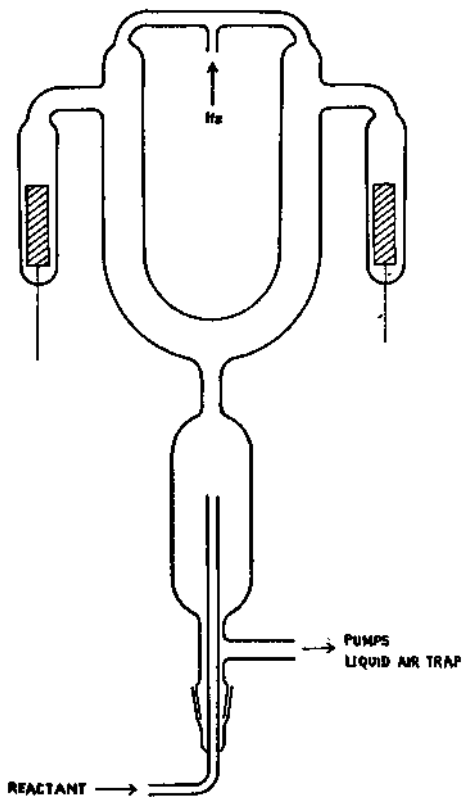


Figure 3. Discharge tube method of investigating the reactions of atomic hydrogen.

poisoning becomes difficult, and only relatively low hydrogen atom concentrations can be obtained (ca. 1 per cent). Reactions at liquid air temperature have been investigated by Geib and Harteck. ¹⁶⁸

The method has been modified by Harteck and Roeder. ^{169,170} By adding an inert gas such as neon as a carrier, it was possible to operate the discharge at pressures up to 20 mm. The issuing mixture of hydrogen molecules, hydrogen atoms, and neon could then be bubbled through liquids

¹⁶⁷ E. W. R. Steacie, *Can. J. Research*, **B15**, 264 (1937).

¹⁶⁸ K. H. Geib and P. Harteck, *Ber.*, **65B**, 1550 (1932), **66B**, 1815 (1933).

¹⁶⁹ P. Harteck and E. Roeder, *Z. Elektrochem.*, 42, 536 (1936); *Z. physik. Chem.*, **A181**, 195 (1938).

¹⁷⁰ P. Harteck and K. Stewart, *Z. physik. Chem.*, **A181**, 183 (1938).

and the reactions of atomic hydrogen with dissolved substances investigated. (See, however, Klemenc¹⁷¹ for a criticism of this work.)

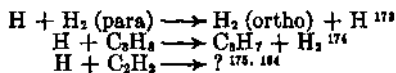
In only a few investigations by the Wood-Bonhoeffer method have activation energies been determined from the temperature coefficient of the reaction in the ordinary way. The reason for this is that atom concentration measurements are not very accurate, and since the reactions investigated have low temperature coefficients, those temperature coefficients cannot be accurately determined. In most cases, therefore, the investigations have been carried out at room temperature only. The results are then expressed in the form of a collision yield, calculated as the fraction of the number of collisions of a hydrogen atom with the reactant which are effective in causing reaction. The activation energy of the reaction is then usually estimated from the relation

$$s = pe^{-E/RT},$$

where s is the collision yield, and p is a steric factor, which is usually assumed to be equal to 0.1. This assumption is arbitrary, but is probably not far wrong in most cases, and the activation energies estimated in this way are thus usually reliable. The error in E produced by a change in p is in any case relatively small. Thus a change of a factor of 10 in p alters the calculated value of E by $4.6T$ cal., or at room temperature by 1.38 kcal. This is usually within the experimental error. If, however, a reaction should happen to have a very small steric factor, say 10^{-5} , the activation energy estimated from the collision yield on the assumption that $p = 0.1$ would be considerably in error.

Surface effects probably constitute the main source of error in this method. It is practically impossible to estimate what fraction of the observed reaction may occur catalytically on the walls of the reaction vessel.^{144, 166}

A very large number of hydrogen atom reactions have been investigated in this way. (For a review see Geib.¹⁷²) Examples are:



The method has been applied to deuterium atom reactions by a number of workers,^{163, 166, 176} the results are reviewed by Geib.¹⁷⁷

¹⁷¹ A. Klemenc, *Z. physik. Chem.*, **A179**, 393 (1937).

¹⁷² K. H. Geib, *Ergeb. exakt. Naturwss.*, 16, 44 (1936).

¹⁷³ K. H. Geib and P. Harteck, *Z. physik. Chem. Bodenstein-Festband*, 849 (1931).

¹⁷⁴ E. W. R. Steacie and N. A. D. Parlee, *Trans. Faraday Soc.*, 35, 854 (1939); *Can. Research*, **B17**, 371 (1939).

¹⁷⁵ K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **A139**, 64 (1928).

¹⁷⁶ P. Gross and H. Steiner, *J. Chem. Phys.*, 4, 165 (1936).

¹⁷⁷ K. H. Geib, *Z. Elektrochem.*, 44, 81 (1938).

It is obvious that it would be possible to produce hydrogen atoms at higher pressures by means of a streaming method with an arc or spark discharge. However, under such circumstances the rate of flow would necessarily be relatively slow, and the higher pressure would aid recombination of the atoms, and thus only minute quantities of atoms could be withdrawn from the tube. A very large number of claims of "active" modifications of hydrogen produced in this way have been made, but the results in all cases appear to be due to traces of impurity in the hydrogen.

Oxygen Atoms

Wood's method has also been applied to oxygen by a number of investigators.^{178,182} The main knowledge of oxygen atom reactions comes from the work of Hardeck and Kopsch^{183,184} and Geib,¹⁷² who used apparatus identical with that described above for hydrogen atoms. One complicating factor in dealing with oxygen atom reactions is the formation of ozone by



At low pressures and at temperatures from room temperature upward, however, this is relatively unimportant and the only "active" modification of oxygen present is atomic oxygen. Low temperature investigations of oxygen atom reactions have been made by Geib and Hardeck¹⁸⁵ and by Schenk and Jablonowski.¹⁸⁶ Nalbandyan¹⁸⁷ has produced oxygen atoms from a discharge and by sudden compression has obtained appreciable atom concentrations at relatively high pressures.

The Hydroxyl Radical

The presence of the hydroxyl radical can be demonstrated spectrographically in emission in the gas flowing from a Wood's tube with moist hydrogen,¹⁸⁸ moist oxygen, or water vapor.¹⁸⁹ Oldenberg¹⁹⁰ has succeeded

¹⁷⁸ Z. Bay and W. Steiner, *Z. physik. Chem.*, **B2**, 146 (1929), B3, 149 (1929).

¹⁷⁹ F. R. Bichowsky and L. C. Copeland, *Nature*, **120**, 729 (1927).

¹⁸⁰ L. C. Copeland, *Phys. Rev.*, **36**, 1221 (1930).

¹⁸¹ W. H. Rodebush and S. M. Troxel, *J. Am. Chem. Soc.*, **52**, 3467 (1930).

¹⁸² E. Wrede, *Z. Physik*, **64**, 53 (1929).

¹⁸³ P. Hardeck, *Z. Physik*, **54**, 881 (1929); *Trans. Faraday Soc.*, **30**, 134 (1934).

¹⁸⁴ P. Hardeck and U. Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

¹⁸⁵ K. H. Geib and P. Hardeck, *Ber.*, **66B**, 1815 (1933); *Trans. Faraday Soc.*, **30**, 131 (1934).

¹⁸⁶ P. W. Schenk and H. Jablonowski, *Z. Elektrochem.*, **45**, 650 (1939); *Z. anorg. Chem.*, **244**, 397 (1940).

¹⁸⁷ A. Nalbandyan, *Phys. Z. Sowjetunion*, **4**, 747 (1933); *Acta Physiocochemica (U.R.S.S.)*, **1**, 305 (1934).

¹⁸⁸ K. F. Bonhoeffer, *Z. physik. Chem.*, **116**, 391 (1925).

¹⁸⁹ G. I. Lavin and F. B. Stewart, *Nature*, **123**, 607 (1929).

¹⁹⁰ O. Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935).

in photographing the hydroxyl bands in absorption under similar conditions. However, the situation produced is highly complex, since we may have present also H, O, H_2O_2 , HO_2 , etc. As a result it is difficult to interpret the results obtained.^{184, 190-195}

Nitrogen Atoms

These can also be obtained by Wood's method.^{182, 183, 187}

Chlorine Atoms

Rodebush and Klingelhoeffer¹⁹⁶ produced atomic chlorine by means of a high-frequency discharge. A flow system with a fast pump was used, and the atoms could be pumped out of the tube for some distance. In this way concentrations of atomic chlorine up to about 20 per cent, as measured with a Wrede gauge, were obtained.

Schwab and Friess^{197, 198} have prepared atomic chlorine in concentrations up to 40 per cent by Wood's method. The atom concentration was measured calorimetrically. The main difficulty is to prevent too rapid recombination of the atoms on the material of the electrodes. They found that water-cooled iron electrodes gave the best results. On account of the very rapid recombination of the atoms on the walls of the apparatus (1 collision in about 20 is effective) the results obtained are much more difficult to interpret than is the case with hydrogen atoms.

Bromine Atoms

Schwab¹⁹⁹ investigated atomic bromine by Wood's method. It was found by calorimetric means that practically every collision of a bromine atom with the wall led to recombination, irrespective of the wall material. As a result it was not possible to investigate reactions of atomic bromine with other substances.

Free Radicals

Rice and Whalley²⁰⁰ used Wood's method with a variety of organic compounds, viz., $n\text{-C}_4\text{H}_{10}$, $n\text{-C}_5\text{H}_{12}$, C_2H_4 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CH_3CHO , CH_3COOH , and CH_3COCH_3 . The products were passed over metallic

¹⁹¹ A. A. Frost and O. Oldenberg, *J. Chem. Phys.*, **4**, 642, 781 (1936).

¹⁹² O. Oldenberg, *J. Chem. Phys.*, **2**, 713 (1934); *J. Phys. Chem.*, **41**, 293 (1937).

¹⁹³ E. M. Stoddart, *Phil. Mag.*, **18**, 409 (1934).

¹⁹⁴ H. C. Urey and G. I. Lavin, *J. Am. Chem. Soc.*, **51**, 3286 (1939).

¹⁹⁵ E. J. B. Willey, *Trans. Faraday Soc.*, **30**, 230 (1934).

¹⁹⁶ W. H. Rodebush and W. C. Klingelhoefer, *J. Am. Chem. Soc.*, **55**, 130 (1933).

¹⁹⁷ G. M. Schwab, *Z. physik. Chem.*, **A178**, 123 (1936).

¹⁹⁸ G. M. Schwab and H. Friess, *Naturwiss.*, **21**, 222 (1933); *Z. Elektrochem.*, **89**, 586 (1933).

¹⁹⁹ G. M. Schwab, *Z. physik. Chem.*, **B27**, 452 (1935).

²⁰⁰ F. O. Rice and F. R. Whalley, *J. Am. Chem. Soc.*, **56**, 1311 (1934).

mirrors in an attempt to identify the radicals produced, and it was found that the fragments removed antimony and lead mirrors, but not zinc or cadmium. Hydrogen atoms were undoubtedly present, but the evidence points to radicals as well, although these were not definitely identified. The work would well merit extension.

(b) *The Active Species Are Produced by Collision with Ions*

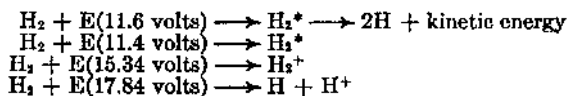
The ions may be produced by radioactive sources,²⁰¹ or by fast electrons.²⁰² Many reactions occur under these influences, "and the results obtained are of definite interest by comparison with photochemical and thermal reactions of the same substances. However, as yet, no information leading directly to the rates of elementary processes has been obtained in this way.

(c) *The Active Species Are Produced by Collisions with Slow Electrons (of Controlled Speed)*

It is obvious that if an electron with an energy of, say, 7 or 8 volts collides with a molecule and transfers its energy to it reaction can occur. In principle it should be possible to investigate many interesting reactions by using electrons of controlled speed.²⁰² Actually, however, it is found that energy transfers of this sort are not effective by mere "collision," but only occur by raising the molecule to an excited state which may then dissociate. Thus with hydrogen the possible process



does not occur. Hydrogen, however, can be dissociated or excited by such processes as



Such methods open up interesting possibilities in the investigation of the reactions of excited atoms and molecules. However, as yet no detailed information on ordinary elementary processes has been obtained from such work.

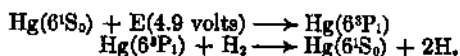
An interesting modification of the method is the investigation of mercury sensitized processes by Glockler and Thomas.²⁰³ It was found that dissociation of hydrogen did not occur in the presence of mercury vapor and

²⁰¹S. C. Lind, *The Chemical Effects of Alpha Particles and Electrons*, New York, 1928.

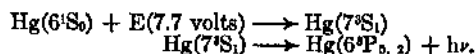
²⁰²G. Glockler and S. C. Lind, *The Electrochemistry of Gases and Other Dielectrics*, New York, 1939.

²⁰³G. Glockler and L. B. Thomas, *J. Am. Chem. Soc.*, 67, 2352 (1935).

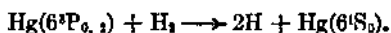
electrons of 4.9 volts energy, although it might have been expected by the mechanism



However, the hydrogen pressure used was very low (ca. 10^{-2} mm.), and almost all excited mercury atoms would radiate rather than be quenched by hydrogen. With electrons of 7.7 volts energy dissociation of hydrogen did occur, presumably by the formation of metastable atoms by



The metastable mercury atoms thus formed would then be quenched by hydrogen to an appreciable extent on account of their relatively long life, i.e.,



6. The Detection and Estimation of Atoms and Radicals by Their Chemical Properties

(a) By the Removal of Mirrors

It was first shown by Paneth and Hofeditz²⁰⁴ that free methyl radicals could be detected by their reaction with a metallic mirror deposited on the walls of a tube through which a carrier gas together with the radicals was flowing.

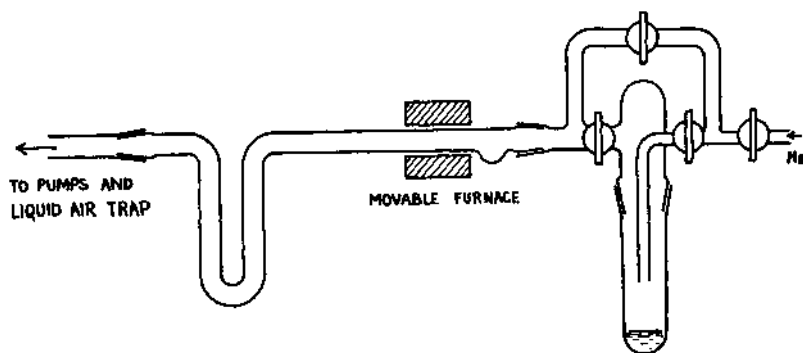


Figure 4. Paneth apparatus for the detection of free radicals.

The apparatus is shown in Figure 4. A stream of hydrogen which had been specially purified was passed at a low pressure, of the order of 1 to 2 mm., through a cooled vessel in which it was saturated with lead tetramethyl vapor, and was then led through a hard-glass tube. One end of this tube

²⁰⁴F. Paneth and W. Hofeditz, *Ber.*, **62B**, 1335 (1929).

was heated with a Bunsen burner, or better an electric furnace²⁰⁵ and in this the flowing lead tetramethyl was decomposed. The decomposition proceeded presumably by the reaction



and a "mirror" of lead was deposited on the walls of the tube. If now the tube was heated "up-stream" from the lead mirror, it was found that the first mirror gradually disappeared, even if the distance was as great as 30 cm., although the rate of removal was slower the greater the distance. This is strong evidence that the methyl radicals produced in the decomposition are removing the lead mirror by the reaction



The success or failure of the method depends entirely on the speed of the pumping system, since it is essential to carry the methyl radicals along the tube for considerable distances before they disappear by



or other reactions. In Paneth and Hofeditz' work a fast diffusion pump was employed, which with a pressure of 1-2 mm. in the apparatus produced linear speeds through the tube as high as 16 meters per sec. At such speeds no diffusion against the flow occurs, and free lead was never deposited ahead of the heated zone.

Tests were made to prove that the phenomenon of mirror removal was not due to thermal effects produced by the stream of hot hydrogen. In the first place a flame very close to a lead mirror caused no effect when a stream of pure hydrogen (without lead tetramethyl) was used, other than a very slow creeping forward of the edge of the mirror. Secondly, water cooling of the tubing between the heated zone and the mirror did not prevent the removal of the mirror. (Direct cooling of the mirror itself by water often inhibited mirror removal owing to the deposition on the mirror of traces of high-boiling substances.)

Tests showed that some lead tetramethyl passed the burner without decomposition, and in later work an electrically heated spiral of wire was wound round the tube just past the flame. Under these circumstances complete decomposition occurred.

Antimony and zinc mirrors were also used successfully.

Experiments were made by Paneth and Hofeditz to determine the life-time of the free methyl radical. Antimony mirrors were deposited on the walls of the tube under controlled conditions, so that the same amount of metal was deposited in each case. (The experimental methods of obtaining such standard mirrors are not given in any further detail by Paneth and Hofeditz.) The mirrors in successive experiments were placed at different

²⁰⁵ F. Paneth and W. Lautsch, *Ber.*, 64B, 2702 (1931).

distances from the heated zone, and the time required for the removal of the mirrors was measured. In this way it was possible to follow the decrease in the concentration of methyl radicals as the distance from the heated zone was increased. In these experiments a streaming velocity of 14 meters per second was used, and the lead tetramethyl concentration in the stream corresponded to its vapor pressure at -70° . The total pressure was approximately 2 mm. The results are given in Table II.

TABLE II

Distance, l , from heated zone to mirror, cm.	Time, z , taken to travel this distance, sec.	Time, d , re- quired to remove the mirror, sec.	Activity, A , $A = \frac{1}{1000d}$	$\log A$
4	2.9×10^{-3}	4	250.0	2.40
8	5.7	11	90.0	1.96
13	9.3	20	50.0	1.70
18	12.9	25	40.0	1.60
22	15.7	45	22.2	1.35
28	20.0	70	14.3	1.16
33	23.6	100	10.0	1.00
37	26.4	150	6.7	0.82

On plotting $\log A$ against the distance, l , or the time, z , we obtain a straight line. In other words, the concentration of radicals, or activity, falls off with time according to a first order law. This is illustrated by the data in Table III, in which the later values only are used, since the values with the mirror very close to the heated zone are not so reliable. In the table t is the time taken by the radicals in travelling from $l = 13$ cm. to $l = 1$, A is the activity at $l = 13$ cm., and A_2 is that at $l = 1$.

TABLE III

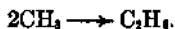
Data illustrating the first order loss of activity

l , cm.	z , sec.	t , sec.	A	$\log wA_1/At$	$\frac{k}{1t} = \frac{1}{\ln_e A_1/A_2}$
13	9.3×10^{-3}	0	50.0	—	—
22	15.7	6.4×10^{-8}	24.2	0.35	127
28	20.0	10.7	14.3	0.54	117
33	23.6	14.3	10.0	0.70	113
37	26.4	17.1	6.7	0.88	118

Whence we obtain

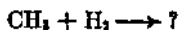
$$\text{half life} = 1/k_{\text{unimolecular}} = 5.8 \times 10^{-8} \text{ sec.}$$

The unimolecular nature of the "decay" is surprising, since it might be expected that the radicals would disappear by the reaction



The obvious possible explanations are

(a) The reaction



i.e., the methyl radicals disappear by reaction with hydrogen. This is in large excess, and hence the loss of radicals will follow a first order law.

(6) The radicals disappear by a first order wall reaction. The obvious method of deciding between these is to use other carrier gases.

In a further paper Paneth and Lautsch²⁰⁶ investigated the lives of the methyl and ethyl radicals when hydrogen and helium-neon mixtures were used as carrier gases. The lives found were not very different in the two cases and they, therefore, concluded that

- (a) radicals do not disappear in hydrogen to an appreciable extent by the reaction



- (6) At the pressures concerned three-body collisions are rare, and the recombination process



cannot be important

- (c) hence radicals disappear mainly at the wall. However, calculations show that by no means all collisions with the wall are effective in producing recombination (actually, only about 1 collision in 1000 is effective).

By using a "guard mirror" before the regular mirror and increasing its width in successive experiments, they found the maximum width of mirror necessary to remove all the radicals. These results indicate²⁰⁷ that every collision of a radical with the mirror results in the formation of metallo-organic compounds.

They also found that if a portion of the tube were cooled to -180° all radicals were removed. Hence even with glass the accommodation coefficient is approximately unity at very low temperatures. At higher temperatures the life increases, presumably because the accommodation coefficient decreases, up to about 500° . At still higher temperatures the life decreases again. In helium at 500° the life of the methyl radical can be raised to 0.1 sec.²⁰⁸

Paneth and Lautsch also showed that iron and platinum had no catalytic effect on the recombination. (See also Paneth.²⁰⁹) Since iron removes atomic hydrogen, this proves that the effects found by Paneth and his co-workers with mirrors are not due to hydrogen atoms, as claimed by Schultze and Miiller.²¹⁰ They also found²⁰⁵ that lead, arsenic, antimony, zinc, and cadmium mirrors were effective.

²⁰⁶ F. Paneth and W. Lautsch, *Ber.*, **64B**, 2708 (1931).

²⁰⁷ F. Paneth and K. F. Herzfeld, *Z. Elektrochem.*, **37**, 577 (1931).

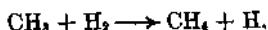
²⁰⁸ F. Paneth, W. Hofeditz, and A. Wunsch, *J. Chem. Soc.*, **1936**, 372.

²⁰⁹ F. Paneth, *Z. physik. Chem.*, **B7**, 155 (1930).

²¹⁰ G. Schultze and E. Muller, *Z. physik. Chem.*, **B6**, 267 (1930).

Precautions in the control of flow rates, etc., are described by Paneth, Hofeditz, and Wunsch.²⁰⁸

Later work²⁰⁸ seems to indicate that the wall effect was overestimated by Paneth and Lautseh, and that even at room temperature a fair amount of methyl disappears by the reaction



One further significant fact emerges from the work of Paneth, Hofeditz, and Wunsch. Lead tetramethyl was decomposed in the apparatus in the usual way. This deposited a lead mirror, which we may distinguish as mirror I. The alkyl radicals formed in the decomposition of the lead tetramethyl which resulted at the time of formation of mirror I reacted with a second mirror and formed lead tetramethyl again. This was decomposed again, and a new mirror, II, was formed. The amount of lead in mirror I was then compared with that in mirror II. The result found was that at low lead tetramethyl concentrations up to 82 per cent of the lead at I was found at II. Hence the yield of free methyl radicals on decomposing lead tetramethyl by the Paneth technique is almost 100 per cent.

Rice, Johnston, and Evering^{211,212} greatly simplified the experimental arrangement by substituting condensable gases for hydrogen or helium as carriers. Using water vapor, carbon dioxide, or organic solvents as carriers, it is possible to freeze the carrier out with liquid air. Under these circumstances high-speed pumps are unnecessary. The simplified apparatus is shown in Figure 5.

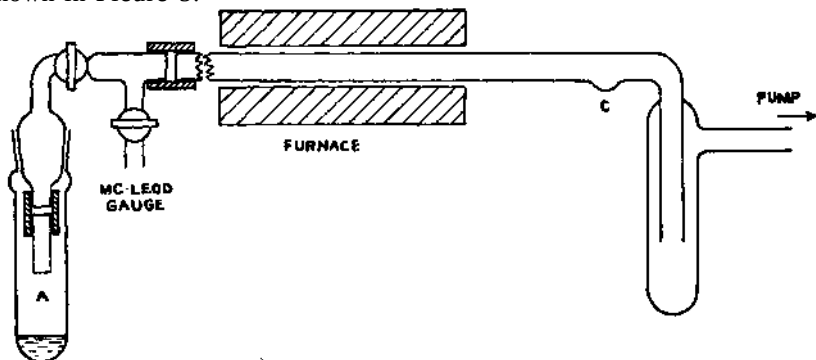


Figure 5. Rice apparatus for the detection of free radicals.

"A 1% solution of lead tetramethyl in acetone or heptane is put into tube A. The stopcock 1 is opened and the apparatus is evacuated. This automatically removes all oxygen from the apparatus and after one or two minutes the stopcock is again closed. The furnace is then heated to 500-600° and a metallic mirror is formed by heating a piece of metal which has previously been introduced into the quartz tube at C. The mirror is cooled with water, the stopcock 1 is opened, and the current of gas containing the free methyl groups is allowed to pass over the mirror."

²¹¹ F. O. Rice, W. R. Johnston, and B. L. Evering, *J. Am. Chem. Soc.*, 54, 3529 (1932).

²¹² F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

"Numerous classes of organic compounds, such as hydrocarbons, ketones, ethers, etc., can be decomposed into free radicals in the apparatus shown in Figure 5. The vapor of the material itself is used as transport gas for the free radicals; the only modification in method, from that used when an organometallic compound is decomposed, is that the furnace must be heated to a higher temperature, usually in the range 750-950°. When using this apparatus for the decomposition of nonmetallic compounds, the flask A containing the compound is evacuated for a few minutes so as to remove all air from the apparatus. The temperature of the flask and the size of the capillary are so adjusted that the vapor pressure at the inlet end of the quartz tube B is in the range 0.5 to 2 mm. A good oil pump, capable of producing a vacuum of 0.05 mm., is sufficient, although an auxiliary mercury vapor pump is desirable on account of the higher speed of evacuation."

Rice and his collaborators have shown²¹² that a wide variety of metals may be used as mirrors, viz., lithium, sodium, potassium, calcium, zinc, cadmium, mercury, lanthanum, thallium, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium. Negative results were obtained with magnesium, copper, silver, gold, and cerium.

In connection with the Paneth-Rice method, it should be noted that it is merely the standard flow method, except that the speed of flow is unusually high. The distinctive features of the work are the methods of detection of the radicals. As we will see, the main difficulties associated with the application of the method to the determination of the activation energies of elementary reactions arise in connection with the methods of detection, which are a matter of very great experimental difficulty.

Mirrors may also be formed, and more conveniently, by introducing a small pellet of metal into a small depression in the tube, and heating the tube at this point with a current of gas flowing through it. Some of the metal is thus volatilized and deposited "down-stream" as a mirror on the colder parts of the apparatus.

Paneth and Hofeditz found that the mirrors often lost their activity if the tube was cooled by running water, owing to the deposition on the mirror of traces of high-boiling substances which prevented the access of radicals to the mirror. It is also essential that all air be excluded from the apparatus, since a trace of oxygen will deactivate the mirror, presumably by forming an oxide layer on the surface.

In using "standard mirrors" Paneth and Lautsch²⁰⁶ encountered considerable difficulty in obtaining reproducible results. It was not possible to reproduce each time the surface condition of the mirrors, even though they contained the same quantity of metal. The difficulty was less, but still considerable, in new glass or quartz tubes. In consequence they reported their results as only provisional in a quantitative sense.

Paneth and Hahnfeld²¹³ found that results with tellurium were much more reproducible, since tellurium mirrors are not inactivated by traces of oxygen as are mirrors of other metals. They determined the activity not by the time for the removal of a mirror, but by its loss in weight. Details of their procedure were not given.

²¹³ F. Paneth and K. Hahnfeld, unpublished, quoted from footnote 242.

The use of tellurium mirrors was extensively investigated by Rice and Glasebrook.²¹⁴ They also pointed out²¹⁵ that in some cases mirrors are definitely specific in action. Thus methylene removes tellurium, antimony, selenium, and arsenic, but does not attack zinc, cadmium, bismuth, thallium, or lead, all of which are readily removed by alkyl radicals. The effect was shown by experiments in which the removal of mirrors was investigated, using the products of the decomposition of ether and of ether-diazomethane mixtures. The pyrolysis of ether yields methyl radicals, while that of diazomethane gives methylene. It was found that there was very little difference in the rate of removal of zinc mirrors on substituting an ether-diazomethane mixture for pure ether. However, antimony and tellurium mirrors were removed much more rapidly with the ether-diazomethane mixture. The results are illustrated by Figures 6 and 7 (reproduced from Rice and Rice).²¹²

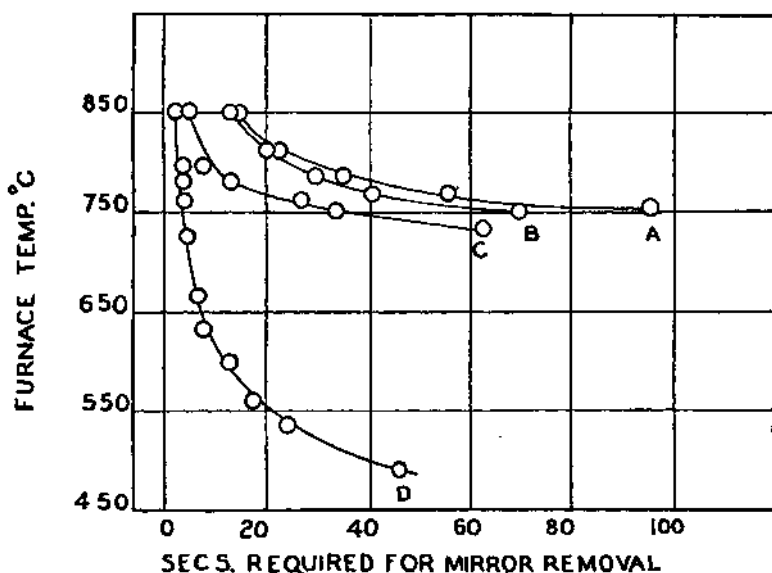


Figure 6. The removal of zinc and antimony mirrors by methyl and methylene radicals.

A, Pure ether with a zinc mirror. B, Ether-diazomethane mixture with a zinc mirror. C, Pure ether with an antimony mirror. D, Ether-diazomethane mixture with an antimony mirror.

Rice and his collaborators²¹² also investigated the effect of the temperature of the mirror on its activity. They found that the activity of lead mirrors diminished rapidly at higher temperatures. Thus a mirror which

²¹⁴ F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, 56, 2472 (1934).

²¹⁵ F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, 55, 4329 (1933), 56, 2381 (1934).

was removed in about 20 seconds at room temperature required over 200 seconds at 325° under the same conditions of radical concentration, etc. In agreement with Paneth and Hofeditz they found that lead mirrors were

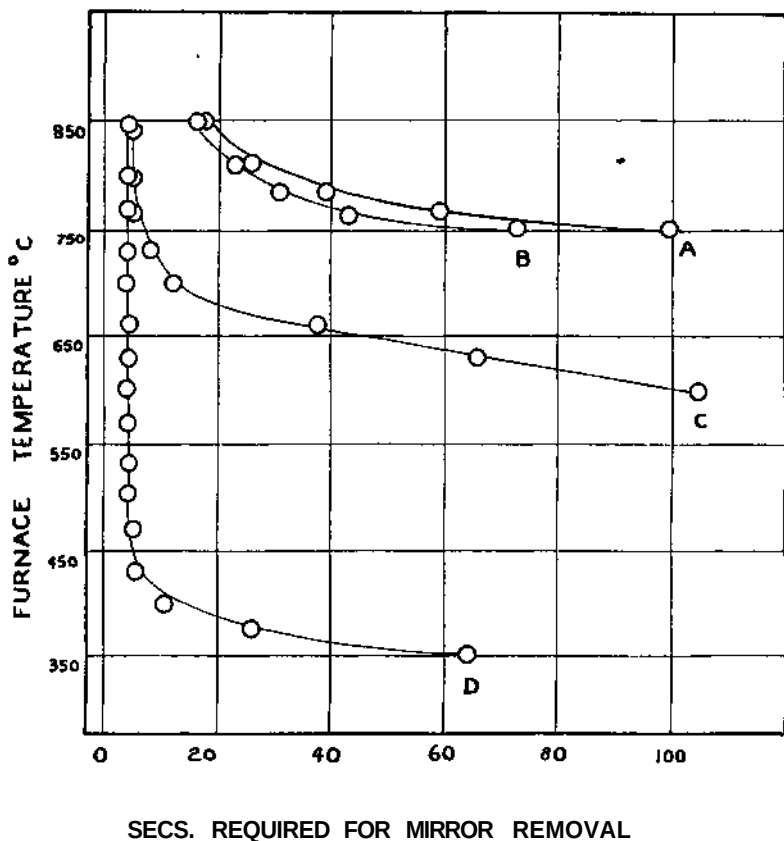


Figure 7. The removal of zinc and tellurium mirrors by methyl and methylene radicals. A, Pure ether with a zinc mirror. B, Ether-diazomethane mixture with a zinc mirror. C, Pure ether with a tellurium mirror. D, Ether-diazomethane mixture with a tellurium mirror.

frequently inactivated by cooling to 0°, presumably owing to the deposition of traces of gummy materials on the mirror. In the case of antimony mirrors the activity remained approximately constant up to high temperatures.

Rice and Johnston²¹⁶ used the standard mirror technique to investigate the activation energy of the decomposition of organic substances into free radicals. The organic compound was passed through a furnace under con-

²¹⁶ F. O. Rice and W. R. Johnston, *J. Am. Chem. Soc.*, 66, 214 (1934).

ditions such that only a small fraction of it decomposed. A standard mirror was placed at a definite distance from the end of the furnace and its time of removal was noted. The furnace temperature was then varied and the time of removal of similar mirrors was determined as a function of the furnace temperature. Since the removal time of the mirror is a measure of the radical concentration, and since this concentration is for small fractional decompositions a measure of the rate constant of the decomposition, it is thus possible to determine the temperature coefficient of the split into free radicals, and the activation energy.

Glazebrook and Pearson^{217,218} found that mirrors including those of tellurium were deactivated by traces of oxygen. They also found that the activity diminished on standing, owing perhaps to the gradual evolution of oxygen from the walls of the apparatus, or to crystallization of the metal. In depositing standard mirrors Pearson used a smoked glass tube as a comparison standard and measured the opacity.^{219,220}

Prileshajeva and Terenin²²¹ modified the Paneth technique by determining the rate of disappearance of the mirror by measuring its opacity photometrically. They found an induction period in the mirror removal, probably owing to the necessity of removing adsorbed gas before the mirror itself could be attacked.

In order to make the Paneth test more sensitive, Leighton and Mortensen²²² used lead containing Ra D, E, and F (from old emanation tubes). A beta-ray electroscope was placed above the "mirror," which was so thin as to be invisible, and the disappearance of the mirror was followed by the loss of beta-ray activity. A liquid air trap was placed in the line following the reaction tube, and its contents were also examined for beta-activity. They thus succeeded in detecting methyl radicals from the photolysis of lead tetramethyl. It was observed that only radium D (a lead isotope) was carried over, while radium E (a bismuth isotope) was not.

The radioactive indicator method was also employed with modifications by Burton, Ricci, and Davis.²²³ They used a radium D mirror, and put the gases passing the mirror through a cracking furnace at 400 to 500°. This decomposed the lead tetramethyl formed by the attack of methyl radicals on the mirror. The lead resulting from the decomposition of the lead tetramethyl carried over was then examined for radioactivity by cutting out the section of the tube where it deposited, dissolving the lead in hot nitric acid, and evaporating the solution to dryness. The lead nitrate

²¹⁷ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1937**, 567.

²¹⁸ T. G. Pearson, *Annual Repts. Chem. Soc.*, **34**, 264 (1937).

²¹⁹ T. G. Pearson, *J. Chem. Soc.*, **1934**, 1718.

²²⁰ T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, **1936**, 1151.

²²¹ N. Prileshajeva and A. Terenin, *Trans. Faraday Soc.*, **31**, 1483 (1935).

²²² P. A. Leighton and R. A. Mortensen, *J. Am. Chem. Soc.*, **68**, 488 (1936).

²²³ M. Burton, J. E. Ricci, and T. W. Davis, *J. Am. Chem. Soc.*, **62**, 265 (1940).

formed was then examined with a Lind electroscope. They announce that further work is in progress using radioactive antimony.

Pearson, Robinson, and Stoddart²²⁴ have shown that the Paneth technique may be used to detect hydrogen atoms. They found that atomic hydrogen removed arsenic, antimony, selenium, tellurium, germanium, and tin mirrors, but did not affect lead or bismuth, except for a slow movement down the tube with bismuth due to distillation. This effect did not occur with lead. Burton²²⁵ has improved the method and has used it to detect hydrogen atoms in photolyses. A heavy lead "guard mirror" was deposited first, followed by a very light antimony mirror. The guard mirror served to remove alkyl radicals, and thus allowed only hydrogen atoms to pass. These removed the antimony mirror. The method has been used by Burton and his collaborators in a number of cases.^{226,227}

A large number of rather varied substances have been tried as detectors for free radicals by the mirror technique, viz.,

With Positive Results

Pb,^{228, 229} **Sb,**^{228, 229} **Zn,**^{228, 229} **Bi,**^{228, 229} **S,**²²⁸ **Te,**^{229, 230} **Li,**²²⁹ **Na,**^{229, 231} **K,**²²⁹ **Ca,**²²⁹ **Sn,**²²⁹ **Cd,**²²⁹ **Hg,**²²⁹ **La,**²²⁹ **Th,**²²⁹ **As,**²²⁹ **Se,**²²⁹ **I,**^{232, 233} **Cl.**²³¹

With Negative Results

Oxides (most oxides must be ineffective since mirrors are inactivated by traces of oxygen), Benzoic acid,²³⁰ **Mg,**²²⁹ **Cu,**²²⁹ **Ag,**²²⁹ **Au,**²²⁹ **Ce,**²²⁹ **HgCl,**²²⁹ **HgBr,**²²⁹ **PbCl₂,**²²⁹ **PbI₂,**²²⁹ **SnI₃,**²²⁹ Indigo,²²⁹ Eosin.²²⁹

Kohanenko²³⁴ has used screens of zinc sulphide instead of mirrors as detectors. These glow when atoms or radicals recombine on them.

(6) By the Estimation of the Products Resulting from Mirror Removal

Paneth and Hofeditz²²⁸ identified the methyl radical in their original experiments by passing the gas over zinc mirrors and characterizing the zinc dimethyl formed by its melting point, boiling point, and spontaneous combustion in air with the formation of zinc oxide. They also roughly identified the antimony alkyls formed when antimony mirrors were used. Paneth and Lautsch²⁰⁵ identified the ethyl radical similarly. They also partially

²²⁴ T. G. Pearson, P. L. Robinson, and E. M. Stoddart, *Proc. Roy. Soc (London)*, **A142**, 275 (1933).

²²⁵ M. Burton, *J. Am. Chem. Soc.*, **58**, 692, 1645 (1936).

²²⁶ H. Henkin and M. Burton, *J. Am. Chem. Soc.*, **60**, 831 (1938).

²²⁷ L. May, H. A. Taylor, and M. Burton, *J. Am. Chem. Soc.*, **63**, 249 (1941).

²²⁸ F. Paneth and W. Hofeditz, *Ber.*, **62B**, 1335 (1929).

²²⁹ F. O. Rice, W. R. Johnston, B. L. Evering, and A. L. Glasebrook, quoted from F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

²³⁰ F. Paneth and W. Lautsch, *Ber.*, **64B**, 2708 (1931).

²³¹ J. H. Simons and M. F. Dull, *J. Am. Chem. Soc.*, **66**, 2696 (1933).

²³² L. Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934).

²³³ L. Belchetz and E. K. Rideal, *J. Am. Chem. Soc.*, **67**, 1168, 2466 (1935).

²³⁴ P. N. Kohanenko, *Acta Physicochimica (U.R.S.S.)*, **9**, 93 (1938).

oxidized the zinc ethyl to $C_2H_5OOZnC_2H_5$, hydrolysed this, and identified the resulting ethyl alcohol by the iodoform test.

Sodium has also been used for identification purposes.²³¹ The free radicals (methyl or ethyl) were allowed to come in contact with metallic sodium, forming a sodium alkyl. The mixture of sodium and sodium alkyl was treated with alcohol, and methane was evolved in the case of methyl, or ethane in the case of ethyl.

Simons and Dull also used carbon tetraiodide as a detector. Methyl radicals formed methyl iodide, which was allowed to react with quinoline, and the resulting quinoline methiodide was identified.

The products formed when free alkyl radicals react with a variety of metal mirrors have been summarized by Rice²³⁵ and by Pearson,²³⁶ and are given below. The information comes from a variety of sources.^{232, 233, 235-245}

<i>Pb</i>	<i>PbMe₄</i>	<i>PbEt₄</i>				
<i>As</i>	<i>AsMe₃</i>	<i>AsEt₃</i>	<i>(AsMe₂)₂</i>	<i>(AsEt₂)₂</i>	<i>(AsMe)₄</i>	<i>(AsEt)₄</i>
<i>Sb</i>	<i>SbMe₃</i>	<i>SbEt₃</i>	<i>(SbMe₂)₂</i>	<i>(SbEt₂)₂</i> *		
<i>Bi</i>	<i>BiMe₃</i>	<i>BiEt₃</i>	<i>(BiMe₂)₂</i>			
<i>Se</i>	<i>SeMe₂</i>	<i>Se(C₂H₅CH₂)₂</i>	<i>(SeCH₂)₂</i>			
<i>Te</i>	<i>TeMe₂</i>	<i>TeEt₂</i>	<i>(TeMe)₂</i> *	<i>(TeCH₂)₂</i> *		
<i>Zn</i>	<i>ZnMe₂</i>	<i>ZnEt₂</i>				
<i>Hg</i>	<i>HgMe₃</i>	<i>HgEt₂</i>	<i>HgPr₂</i>	<i>(HgMe)₂</i>	<i>Hg(C₂H₅)₂</i>	<i>Hg(C₄H₉CH₂)₂</i>
<i>Be</i>	<i>BeMe₂</i>	<i>BeEt₂</i>				
<i>I</i>	<i>MeI</i>	<i>C₂H₅I</i>	<i>CH₂I₂</i>			

The main difficulty in all this work is the very small amount of product which must be identified. In identifying the radicals from hydrocarbon decompositions Rice, Johnston, and Evering²⁴⁵ developed a technique which has been widely used. The organo-metallic compounds formed by the interaction of radicals with metallic mirrors were caught in a liquid air trap. It is very difficult to identify the compounds thus obtained, since they are mixed with a very large excess of other substances. The following procedure was therefore adopted. The radicals from the heated zone were brought into contact with a water-cooled surface on which mercury was continually condensing. In this way mercury alkyls were formed, and these were condensed in a liquid air trap. The trap contained a few cc. of a saturated alcoholic solution of mercuric bromide. By this method alkyl

* Products formed only with warm mirrors.

²³⁶ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

²³⁶ T. G. Pearson, *Annual Repts. Chem. Soc.*, 34, 264 (1937).

²³⁷ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1937**, 567.

²³⁸ F. Paneth, *Trans. Faraday Soc.*, 30, 179 (1934).

²³⁹ F. Paneth and H. Lohleit, *J. Chem. Soc.*, **1936**, 366.

²⁴⁰ T. G. Pearson and H. H. Glazebrook, *J. Chem. Soc.*, **1936**, 1777.

²⁴¹ T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, **1936**, 1151, **1936**, 253.

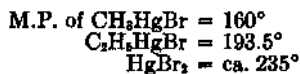
²⁴² F. O. Rice, *Chem. Reviews*, 17, 53 (1935).

²⁴³ F. O. Rice and B. L. Evering, *J. Am. Chem. Soc.*, **66**, 2105 (1934).

²⁴⁴ F. O. Rice and A. L. Glazebrook, *J. Am. Chem. Soc.*, **66**, 2381 (1934).

²⁴⁵ F. O. Rice, W. R. Johnston, and B. L. Evering, *J. Am. Chem. Soc.*, 64, 3529 (1932).

mercuric bromides were obtained in quantities up to about one gram. After freeing the material from excess mercury, etc., the residue was sublimed in a vacuum below 50° for an hour or two, and was thus separated from the less volatile excess of mercuric bromide. The alkyl mercuric bromides were then separated by fractional sublimation. Thus from the radicals from decomposing butane the following alkyl mercuric bromides were obtained.



Fraction	Time of sublimation, hrs.	Temperature of sublimation, °	Yield, gr.	M.P.,
1	1.0	40	0.217	157
2	1.0	50	0.161	160.5
3	1.5	50	0.110	172
4	1.5	50	0.048	181.5
5	1.0	60	trace	

They were unable to obtain any indications of propyl mercuric bromides. The above mixture appears definitely to consist of methyl and ethyl mercuric bromides (but see later). By comparing the melting points of the fractions with those of known mixtures of methyl and ethyl mercuric bromides, they estimated that the ratio of methyl to ethyl radicals produced from butane was 7J3. Similar results were obtained with radicals from the pyrolysis of propane. They referred to a forthcoming publication by Rice and Whalley in which X-ray determinations confirm the presence of methyl and ethyl mercuric bromides. The results of this,²⁴⁶ however, seem rather equivocal. Hein and Mesèe^{246a} have used mercury, arsenic, and lead vapors in a similar way, and have thus detected the phenyl and benzyl radicals in the decomposition of benzene and toluene respectively.

Rice and Evering²⁴³ repeated this work and ran into considerable difficulty. They concluded that at least 95 per cent of the alkyl mercuric bromides was methyl mercuric bromide, and that ethyl mercuric bromide was absent. The higher melting substance in previous work was presumably a small amount of mercuric bromide. In addition, they found that a trace of some unstable mercury alkyl is formed, probably $\text{CH}_3\text{HgHgCH}_3$. This is presumably the source of HgBr , a small amount of which was also detected. No indications of any methylene compounds were obtained. Direct tests for the presence of ethyl groups were also made by a method developed by Willstatter and Utzinger²⁴⁷ and these also were negative. Apparently then, only methyl radicals are detectable in the decomposition of propane and butane. An improved technique for the identification of

²⁴⁶ F. O. Rice and F. R. Whalley, *J. Am. Chem. Soc.*, **66**, 1311 (1934).

^{246a} F. Hein and H. J. Mesèe, *Ber.*, **76B**, 430 (1943).

²⁴⁷ R. Willstatter and M. Utzinger, *Ann.*, **382**, 129 (1911).

alkyl mercuric halides has since been devised by Rice and Rodowskas.²⁴⁸ In this the mixture of alkyl mercuric bromides and excess mercuric bromide is steam distilled. This effects a complete separation of the alkyl mercuric bromides from the mercuric bromide, which is non-volatile under these conditions.

The fact that ethyl radicals are not detected in the decomposition means merely that higher radicals are unstable at high temperatures, and does not mean that the method is unsuitable for their detection. As a matter of fact both ethyl and propyl radicals from photolyses have been identified by this technique by Pearson and his co-workers.²⁴¹ However, the above description will emphasize the difficulties encountered in work of this kind.

The products obtained from tellurium mirrors have also been widely employed for identification purposes, and have been the subject of much controversy. In particular there has been much argument as to the existence of the methylene radical in hydrocarbon decompositions as deduced from evidence with tellurium and iodine mirrors. Since the question is of fundamental importance in connection with free radical mechanisms, it will be reviewed in some detail, especially from the point of view of the occurrence or non-occurrence of the methylene radical in the pyrolysis of the paraffin hydrocarbons.

Rice and Glasebrook²⁴⁹ investigated the free radicals produced from decomposing butane by means of tellurium mirrors, and found that the only detectable product was dimethyl ditelluride, $\text{CH}_3 \text{TeTeCH}_3$. This is a deep red liquid with a low vapor pressure at room temperature, which is stable in air and melts at -19.5° . This substance was recovered in almost theoretical yield in their experiments, and its composition was confirmed by combustion. Similar results were obtained with radicals from acetone, in which case there is no doubt that methyl radicals are formed. This appears to confirm the idea that only methyl radicals are produced, ethyl and propyl presumably being decomposed at the high temperatures used. They obtained no evidence of the presence of methylene.

Rice and Dooley²⁵⁰ investigated the production of radicals when methane was decomposed at 1200° . They obtained only pure dimethyl ditelluride, with no sign of telluroformaldehyde, $(\text{TeCE}_2)_x$, which would be expected if methylene radicals were present. This points definitely to the presence of methyl and the absence of methylene. (It is, of course, possible that the methyl radicals might be produced from methylene in secondary reactions.)

The methylene radical from decomposing diazomethane was identified by Rice and Glasebrook^{244, 250} using tellurium mirrors. The product was a dark red solid of such low volatility that it condensed on the walls of the

²⁴⁸ F. O. Rice and E. L. Rodowskas, *J. Am. Chem. Soc.*, 67, 350 (1935).

²⁴⁹ F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, 66, 2472 (1934).

²⁵⁰ F. O. Rice and M. D. Dooley, *J. Am. Chem. Soc.*, 66, 2747 (1934).

tube just beyond the mirror. Analysis showed it to have the empirical formula ClfcTe , *i.e.*, telluroformaldehyde, probably in a highly polymerized state. The substance is insoluble in ordinary solvents, and decomposes at temperatures above 100° . It appears to be totally different from dimethyl ditelluride, and thus the use of tellurium offers a method of distinguishing between methyl and methylene.

The work of Belchetz and Rideal is in sharp contrast to that of Rice and his co-workers. Belchetz^m in a preliminary communication reported that by passing methane rapidly at a pressure of 0.1 mm. over a platinum filament at temperatures from 877° to 1027° , tellurium mirrors situated one mean free path away were attacked. The products were collected in a liquid air trap. Similar experiments were made using iodine mirrors. As a result of this work he concluded that methylene was the only primary product of the methane decomposition. Rice and Dooley were unable to obtain any mirror removal at such temperatures even with platinum foil in their heated quartz tube. There seems to be little doubt that Belchetz' results were in error, since the temperatures used were impossibly low for a rapid flow system unless there was a highly efficient catalytic effect due to the platinum. Also, as far as the identification of the products was concerned, Belchetz and Rideal were unable to confirm any of the results of the first paper. We may, therefore, disregard the results in the first paper and consider only Belchetz' later work.

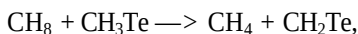
Belchetz and Rideal²³³ employed two different types of apparatus. In both of these the gas streamed through at a high velocity and at 0.1 mm. pressure. In the first the radicals formed on the hot filament were caught on a water-cooled target 3 mm. away. Mirrors could be deposited on this target, and any products formed were caught in a liquid air trap. In the second apparatus the mirror was on the wall of the reaction vessel opposite the filament. It was considerably farther from the filament, and the system thus resembled the hot-tube type of apparatus employed by Paneth and by Rice. Tellurium and iodine mirrors were used, and carbon and platinum filaments. Methane was first investigated. With tellurium mirrors and platinum filaments no volatile tellurium compounds were obtained. With platinum filaments and an iodine mirror methylene iodide was formed.

Most of the work was done with carbon filaments. With iodine mirrors the identification of methylene iodide was claimed. This identification was attempted by two methods. In the first the substance was dissolved in chloroform, shaken with mercury to remove excess iodine, filtered, the chloroform evaporated off, and the product oxidized to formaldehyde and tested by the Schryver-Rimini test. For a minute quantity of material of dubious purity, such a complicated set of operations is hardly above suspicion. Attempts were also made to form mercury addition compounds HgCH_2I_2 , etc., and to identify them, but these were unsuccessful. No

methyl iodide was found, the search for it being made merely by means of its volatility. When, however, the filament was moved 1 cm. from the mirror, the yield of methylene iodide became negligibly small, and an unidentified liquid which might have been methyl iodide made its appearance in traces in the trap. (This seems a very abrupt change on merely increasing the distance by a factor 3, especially since the radicals are not in a heated zone.)

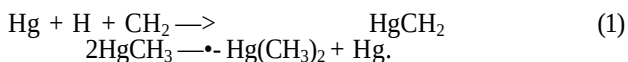
Experiments with tellurium mirrors were also made. With the second apparatus dimethyl ditelluride and dimethyl telluride were obtained. With the first apparatus the products were found to accumulate on the mirror, where they were exposed to further reaction. If the mirror were kept at 100°, the products formed distilled off and were collected in the liquid air trap. Under these conditions a trace of methyl tellurides was obtained, together with large quantities of a yellow solid which was assumed to be the telluroformaldehyde of Rice and Glasebrook. Belchetz and Rideal conclude, "These experiments indicate that methyl radicals are very readily produced in the flow experiments, but are essentially secondary products. Apart from the readiness with which methylene takes up atomic hydrogen, telluroformaldehyde is liable to be reduced by atomic or even possibly by hot molecular hydrogen."

The whole question is controversial, and other work of Belchetz and Rideal also disagrees with Rice's findings. Thus with propane, using tellurium mirrors and carbon filaments, they found small amounts of dimethyl ditelluride and of telluroformaldehyde with warm tellurium mirrors, but only methyl tellurides with cold tellurium mirrors. They suggest that this is due to reduction of telluroformaldehyde by hydrogen when it remains in contact with a cold mirror, while with the warm mirror it evaporates off quickly and thus is not reduced. (There is also the possibility that with warm mirrors we might have the reverse of this,



or some such process.)

With mercury mirrors they obtained large amounts of mercury alkyls, which with mercuric bromide gave CH_3HgBr . No ethyl mercuric bromide was found, in agreement with the work of Rice and Evering. They attribute the formation of methyl mercuric bromide to the sequence



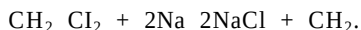
Reaction (1) seems exceedingly unlikely when the low pressure and very short reaction time are taken into consideration. Also, throughout all this work Belchetz and Rideal refer to the atomic hydrogen present, but on the basis of their mechanism where does it come from? After all, there is no

hydrogen in the reactant, and in one mean free path it cannot very well be formed by secondary processes.

Belchetz and Rideal conclude that, "In view of the experience of Rice and Glasebrook with the decomposition of diazomethane in the presence of butane or ether at temperatures above 650°, when only methyl and no methylene radicals could be detected, it is not unlikely that all the methyl radicals formed in hot-tube decompositions of the hydrocarbons are in reality only secondary products of methylene."

It will be seen from the above that there are great difficulties in the unequivocal identification of free radicals in some cases, and that considerable caution is necessary in the interpretation of the results. However, there seems to be no question that the methylene radical has been detected in certain cases.

Paneth and Lautsch²⁵¹ made numerous unsuccessful attempts to identify free methylene. These included the thermal decomposition of ketene and diazomethane, an electrical discharge in diazomethane, and the reaction between dichlor-methane and sodium²⁵²



All these attempts failed, but the failure was probably due to the detectors which they chose, benzoic acid and carbon, neither of which would be expected to react very readily with methylene.

Rice and Glasebrook²⁶³ investigated the decomposition of diazomethane by their usual technique. Diazomethane with ether or butane as a carrier was passed through a tube at 550° or less, and then over mirrors. It was found that tellurium, selenium, arsenic, and antimony mirrors were readily removed, whereas zinc, cadmium, thallium, lead, and bismuth were not affected. In the case of tellurium mirrors the product was found to be a polymer of telluroformaldehyde, $(\text{TeCH}_2)_n$. This was a non-volatile red solid which condensed on the walls just beyond the mirror. At temperatures higher than 600° it was found that no telluroformaldehyde was produced, but only dimethyl ditelluride, CHaTeTeCHs , i.e., the methylene radicals were replaced by methyls. This work appears to give a very distinct test for methylene. They give combustion data to confirm the constitution of telluroformaldehyde, viz.,

calc. for CH_2Te	C = 8.40	H = 1.41
found	8.28	1.33.

It should be noted, however, that on account of the high weight of the tellurium atom, virtually any organic tellurium compound would give a

²⁸¹ F. Paneth and W. Lautsch, *J. Chem. Soc.*, **1935**, 380.

²⁵² H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

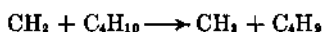
²⁵³ F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, **55**, 4329 (1933), **56**, 2381 (1934).

similar carbon analysis. The hydrogen analysis, though rather rough, is significant since $\text{Te}_2(\text{CH}_3)_2$ would give $\text{H} = 2.01$. Actually the calculated carbon value is in error, since TeCH_2 really corresponds to $\text{C} = 8.47$. The agreement is thus not quite as good, although a small amount of occluded tellurium would account for the difference.

They also found that at low temperatures no radicals were produced which would react with mercury to form mercury alkyls, but that at high furnace temperatures mercury dimethyl was formed.

They point out that telluroformaldehyde is so involatile that the compound found by Belchetz and Rideal cannot be it. Belchetz and Rideal suggest that in their work it came over as the monomer and polymerized in the trap. This, however, offers no explanation of the distinct difference between the compound found in the two investigations.

Rice and Glasebrook conclude that the disappearance of methylene and appearance of methyl radicals at higher temperatures is satisfactorily explained provided the reaction



or the corresponding reaction with ether has an activation energy of about $15 + 5$ kcal.

In a review Rice²⁴² refers to further unpublished work in collaboration with Bongiorno which casts doubt on the work of Rice and Glasebrook described above. They found that, "Cold diazomethane vapor appears to react with the tellurium vapor over a hot tellurium mirror to form telluroformaldehyde. When experiments were performed under conditions such that this error was avoided, only methyl groups came out of the furnace. Thus even with pure diazomethane in pure nitrogen, methyl groups were obtained and carbon was deposited in the furnace." Hence, it appears from this that Rice and Glasebrook's detection of the methylene radical was fallacious. However, the work of Bongiorno has never been published, which suggests that it was not confirmed by later work.

A rather thorough investigation of this question was later made by Pearson, Purcell, and Saigh.²⁵⁴ They investigated both the thermal and the photochemical decomposition of ketene, using the mirror removal technique. It was found that ketene irradiated with a hot or cold mercury arc had no effect on a cold tellurium mirror. However, if the mirror were heated to $70-80^\circ$, it was readily removed. Blank experiments showed that this was not due either to evaporation or to an attack by ketene itself on the mirror. They suggest, as had others, that the necessity for heating the mirror is to prevent the formation on it of a layer of polymer.

They were unable to obtain the red telluroformaldehyde of Rice in a simple way. However, if the tube downstream from the mirror were cooled*

²⁵⁴ T. G. Pearson, R. H. Purcell, and G. S. Saigh,

to -80° , the compound described by Rice was obtained (although they call it a deep orange while Rice described it as red). It was found that the cooling was necessary only for seeding purposes, since if the tube were cooled for only a short time the material continued to form where the cold spot had been.

They also obtained a gray substance which they took to be another modification of telluroformaldehyde. This in solution with iodine formed a substance whose identity was fairly definitely proved to be methylene iodide. They also obtained evidence of the presence of an addition compound of the approximate constitution $\text{TeCH}_2 \cdot 12.5\text{CH}_2\text{CO}$. They conclude that, "It is evident, therefore, that telluroformaldehyde is first generated as a gas, which undergoes the familiar aldehydic condensations to a white form and a red form, the latter in view of its solubility being the higher polymer." They obtained no evidence of the presence of methyl radicals.

In a similar way selenium mirrors, even when cold, were readily removed with the formation of selenoformaldehyde.

The products from the thermal and photodecomposition of diazomethane in the presence of tellurium mirrors were also investigated, and appeared to be telluroformaldehyde as before.

They conclude that since one form of telluroformaldehyde is volatile, Rice's criticism of Belchetz and RideaPs results on the ground that it could not have escaped into the liquid air trap cannot be upheld.

In a more recent brief note²⁶⁶ Rice describes some further work. "We have attempted to obtain methylene from methane and other hydrocarbons by passage over heated filaments in an apparatus similar to that used by Belchetz and Rideal. Under their conditions for detecting methylene (Fig. 1 (of their paper)), we succeeded in removing tellurium mirrors, but were unable to obtain enough tellurium compound to identify: we found that even after runs of several days, the amount of tellurium removed could not be weighed on an ordinary analytical balance. (Rice does not say whether the tellurium mirrors were heated or not.)

"On the other hand, by using much longer wires (Fig. 2 (of their paper)) and larger mirrors, our results agreed with those reported by Belchetz and Rideal, and were similar to those obtained by passing methane through a quartz furnace; dimethyl ditelluride was obtained and identified by its melting point at -19.5° ."

The whole question of the existence and identification of methylene has been reviewed by Barrow, Pearson, and Purcell²⁶⁶ at some length. They conclude: "It seems to us that the fairest conclusion that can be drawn is

²⁵⁵F. O. Rice, *J. Am. Chem. Soc.*, **61**, 213 (1939).

²⁵⁶R. F. Barrow, T. G. Pearson, and R. H. Purcell, *Trans. Faraday Soc.*, **36**, 880 (1939),

that methylene as well as methyl may be one of the primary products in the dissociation of methane. Methylene radicals so formed may then undergo a rapid reaction with either methane, hydrogen, or another methylene radical, resulting in the production of methyl radicals. This cautious conclusion is dictated by our knowledge of the difficulties inherent in the unambiguous identification of products from experiments with filaments at low pressures, by the absence of quantitative data concerning the extent to which the dissociation of the hydrocarbons proceeds via a mechanism involving free radicals, and the equivocal nature of the evidence which may be adduced from kinetic experiments."

This seems a fair summing up of the situation as far as the detection of radicals is concerned. However, Barrow, Pearson, and Purcell overlook some of the kinetic evidence which is by no means "equivocal." In work with ethane, propane, and butane Belchetz and Rideal obtained in all cases an activation energy of ca. 94 kcal., and concluded that in every case the primary process was a direct molecular split, and did not involve free radicals. This activation energy is much above the activation energies of the overall thermal decompositions (60 to 70 kcal.). Now if free radical chains exist in these reactions, as postulated by Rice, there is every reason why the primary free radical split should have an activation energy 10 to 20 kcal. higher than that of the overall reactions. If, however, as Belchetz and Rideal suggest, radicals are not involved, and the primary process is a direct molecular split into the final products, then there is no reason for the discrepancies in the activation energies. It therefore seems certain that in all of Belchetz and Rideal's work the carbon filament was a complicating factor as they themselves realized. Further, the fact that the activation energies are the same, within the experimental error, for methane, ethane, propane, and butane suggests that the primary step is a direct reaction of some sort with the carbon filament. In any case, it appears clear that while Belchetz and Rideal's work may have a bearing on the question of the detection of the methylene radical, it has no bearing whatsoever on the homogeneous decomposition of hydrocarbons in the gas phase.

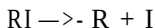
Barrow, Pearson, and Purcell also review the evidence for ethylidene in the dissociation of ethane, in the light of the work of Rice and Dooley²⁶⁰ who detected methyl radicals, and of Belchetz and Rideal who claimed ethylene and hydrogen as the primary products, possibly with ethylidene as an intermediate. In addition there is evidence from work on the decomposition of diazoethane. Rice and Glasebrook²⁵⁷ decomposed diazoethane at 650°, and found no evidence of ethylidene, but rather of ethylene. Barrow, Pearson, and Purcell report that at lower temperatures, 400-450°, radicals were obtained which combined with selenium and tellurium to yield compounds with properties resembling those of seleno- and telluro-

²⁶⁷ F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, 56, 2472 (1934).

acetaldehyde. At 600°, however, they obtained no mirror removal. It appears likely, therefore, that the ethylidene radical has been detected.

Feldman, Ricci, and Burton²⁶⁸ have modified the Paneth technique to make it more quantitative. A long heavy lead mirror is used, and the lead alkyls formed by reaction of radicals with the mirror are collected, and the lead is determined by a micro-method. This has the advantage of overcoming uncertainties due to the diminution in size of the mirror as it is removed, etc. It is thus possible to make a more definite estimate of the actual number of radicals passing through the apparatus in a given time.

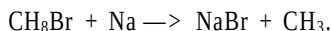
Butler and Polanyi^{258a} have used a method somewhat similar to the Paneth method to investigate the decomposition of organic iodides. The iodide at low pressures with a carrier gas was flowed at a very high rate through a heated tube, and the extent of the reaction



was inferred by determining the iodine formed. The success of the method depends on the flow rate being sufficiently high, and the dilution by the carrier sufficiently great to make the back reaction negligible. (For results obtained by this method see 111-20.)

(c) By Reactions in the Gas Phase

Free radicals have been detected by gas-phase reactions with the halogens in a number of cases. Thus Horn, Polanyi, and Style²⁵⁹ formed methyl radicals by the reaction



The methyl radicals were then identified by introducing them into chlorine or iodine and identifying the methyl chloride or iodide formed. Similar experiments have been carried out with ethyl and phenyl radicals.²⁶⁰

Gorin has used iodine to "fix" radicals and hydrogen atoms in a number of cases.²⁶¹ In photolytic experiments iodine was mixed with the reactant. Any hydrogen atoms formed were "fixed" as HI, and alkyl radicals as CH₃I, C₂H₅I, etc. In this way it was possible to determine the atoms or radicals formed in the primary reaction. Examples of this technique are discussed in some detail in Chapter V.

In a number of cases free radicals have been detected by the effects caused by their removal by gas-phase reactions. Nitric oxide has been the most widely used reagent for this purpose. Hinshelwood and his co-

²⁶⁸ M. H. Feldman, J. E. Ricci, and M. Burton, *J. Chem. Phys.*, **10**, 618 (1942).

²⁶⁰ E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943).

²⁶⁰ E. Horn, M. Polanyi, and D. W. G. Style, *Trans. Faraday Soc.*, **30**, 189 (1934).

²⁶⁰ E. Horn and M. Polanyi, *Z. physik. Chem.*, **B25**, 151 (1934).

²⁶¹ E. Gorin, *Acta Physicochimica* (U.R.S.S.), **8**, 513 (1938), **9**, 681 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

workers,²⁶²⁻²⁶⁸ have found that a number of reactions which are suspected to proceed by free radical chain mechanisms are inhibited by the addition of small amounts of nitric oxide. The function of the nitric oxide is presumably to remove the radicals, and thus prevent the further propagation of chains involving them. The nitric oxide probably forms an addition compound (See later)



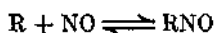
On the assumption that small amounts of nitric oxide completely stop chain propagation, it is possible to calculate the chain length in the uninhibited reaction by the relation

$$\text{Chain length} = \frac{\text{Rate in absence of NO.}}{\text{Rate in presence of NO.}}$$

In the course of the reaction the nitric oxide is gradually consumed, but only very slowly. Thus 2 mm. of nitric oxide can cut to about 1/3 the rate of decomposition of 400 mm. of ethyl ether, and yet last out the decomposition. The chain lengths found by this method in some typical cases are

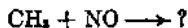
CH ₄	4.7 at 850° and 100 mm.
C ₂ H ₆	17.8 at 600° and 100 mm.
C ₄ H ₁₀	1.9 at 530° and 100 mm.

Echols and Pease²⁶⁹ have investigated the inhibition of the butane decomposition by this method. Their results indicate that the inhibitory effect is only transient, but that this is not due to the removal of nitric oxide by reaction. Thus with 200 mm. of butane and 20 mm. of nitric oxide at 520° the initial rate of reaction is almost zero. At 20 per cent decomposition, however, the rate is back to normal, and only 10 per cent of the nitric oxide has reacted. They suggest that there is an equilibrium



which is only slowly established.

Forsyth²⁷⁰ has investigated the effect of added nitric oxide on the concentration of methyl radicals by the Paneth technique, using tellurium mirrors. He obtains a value of 6.5 kcal. for the activation energy of the reaction



²⁶² L. A. K. Staveley, *Proc. Roy. Soc. (London)*, **A162**, 557 (1937).

²⁶³ L. A. K. Staveley and C. N. Hinshelwood, *Nature*, **137**, 29 (1936); *J. Chem. Soc.*, **1936**, 812, 818.

²⁶⁴ L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A164**, 335 (1936), **A169**, 192 (1937).

²⁶⁵ L. A. K. Staveley and C. N. Hinshelwood, *Trans. Faraday Soc.*, **35**, 845 (1939).

²⁶⁶ C. N. Hinshelwood, *Z. Elektrochem.*, **42**, 445 (1936).

²⁶⁷ J. E. Hobbs, *Proc. Roy. Soc. (London)*, **A167**, 456 (1938).

²⁶⁸ J. E. Hobbs and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A167**, 439, 447 (1938).

²⁶⁹ L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, **60**, 1701 (1938), **61**, 1024 (1939).

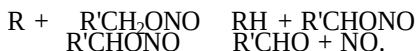
²⁷⁰ J. S. A. Forsyth, *Trans. Faraday Soc.*, **37**, 312 (1941).

There are some experiments which seem to indicate²⁷¹ that the maximum inhibition attained in the presence of nitric oxide does not correspond to complete suppression of chains, and hence that the chain lengths calculated by this method are too low. However, there appears to be no doubt that inhibition by nitric oxide is usually a reliable criterion for the presence of free radicals in a system containing a decomposing organic substance. The results obtained by this method are discussed further and in more detail in Chapter III.

The nitric oxide inhibition method has also been used to detect radicals in the photolysis of mercury dimethyl,^{272,273} azomethane,²⁷⁴ aldehydes,²⁷⁵ and ketones,²⁷⁶ and in the mercury photosensitized decompositions of ethylene²⁷⁷ and acetylene.²⁷⁸

Taylor and Bender²⁷⁹ have recently investigated the pyrolysis of formal-doxime. They conclude that all the facts of nitric oxide inhibition where methyl radicals are involved can be explained on the assumption that a CH_3NO complex is initially formed, which isomerizes into formaldoxime. The formaldoxime then decomposes and yields cyanides, ammonia, etc., which have been found by various workers in NO inhibited reactions. Other radicals presumably behave similarly, and H-atoms probably form HNO .^{279a}

Methyl and ethyl nitrites have also been used to inhibit reactions in a similar way.²⁸⁰ In this case we have nitric oxide produced in situ by the decomposition of the nitrites.^{281,282} Radicals are probably also removed by



Rice and Polly have also shown²⁸⁰ that a number of organic decompositions are inhibited by propylene. Inhibition of hydrocarbon decompositions also occurs in the presence²⁸³ of isobutene, 2,2,4-tri-Me-pentene, butadiene, cyclohexene, and isoprene. Apparently the main requisite for inhibition in

²⁷¹ E. W. R. Steacie and H. O. Folkins, *Can. J. Research*, **B17**, 105 (1939); see also C. H. Klute and W. D. Walters, *J. Am. Chem. Soc.*, **67**, 550 (1945).

²⁷² J. W. Linnett and H. W. Thompson, *Trans. Faraday Soc.*, **33**, 501 (1937).

²⁷³ H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, **33**, 874 (1937).

²⁷⁴ T. W. Davis, F. P. Jahn, and M. Burton, *J. Am. Chem. Soc.*, **60**, 10 (1938).

²⁷⁵ J. W. Mitchell and C. N. Hinshelwood, *Proc Roy. Soc. (London)*, **A169**, 32 (1937).

²⁷⁶ H. W. Anderson and G. K. Rollefson, *J. Am. Chem. Soc.*, **63**, 816 (1941).

²⁷⁷ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, **10**, 676 (1942).

²⁷⁸ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, **12**, 117 (1944).

²⁷⁹ H. A. Taylor and H. Bender, *J. Chem. Phys.*, **9**, 761 (1941).

^{279a} H. A. Taylor and C. Tanford, *J. Chem. Phys.*, **12**, 47 (1944).

²⁸⁰ F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

²⁸¹ F. O. Rice and E. L. Rodowskas, *J. Am. Chem. Soc.*, **57**, 350 (1935).

²⁸² E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.*, **2**, 345 (1934); *Proc Roy. Soc (London)*, **A146**, 388 (1934).

²⁸³ M. P. Eshevskaya, *J. Gen. Chem. (U.S.S.R.)*, **9**, 2162 (1939); *Refiner*, **19**, 264 (1940).

these cases is unsaturation, so that addition compounds may be formed with free radicals. It is well known that reactions of this type occur readily.

Smith and Hinshelwood²⁸⁴ have compared the inhibition of the propionaldehyde and diethyl ether decompositions by nitric oxide and by propylene. It was found that the limiting values to which the rates were reduced were the same, although much more propylene is required to produce a given degree of inhibition. This strengthens the conclusion that both inhibitors are really giving complete inhibition of the chain processes, rather than inhibiting to a stationary state where the inhibitor starts and stops chains with equal efficiency.

Oxygen has also been used as a detector for radicals and atoms. Locker and Patat added oxygen to formaldehyde in an investigation of its photolysis in order to detect free hydrogen atoms by reaction to form water.^{286,286} Bates and Spence²⁸⁷ used oxygen similarly in the photolysis of alkyl halides. However, the possible reactions in these cases are too complicated for the method to yield reliable results.

(d) *The Detection of Hydrogen Atoms by Reaction with Solids*

Hydrogen atoms have been detected by their reducing action on solids such as copper oxides, dyes, etc., by a number of workers. (See, e.g., footnotes 288-290.) The method, however, is not suited to quantitative application. For a very full list of compounds which are reduced by atomic hydrogen see Glockler and Lind.²⁹¹

7. The Detection and Estimation of Atoms and Radicals by Spinisomerism, Isotopic Labelling, etc.

(a) *The Para-Ortho Hydrogen Conversion*

(i) *The Determination of the Hydrogen Atom Concentration*

The equilibrium ratio of ortho- to para-hydrogen at temperatures from room temperature upwards is 3J1. At low temperatures, in the neighbourhood of that of liquid hydrogen, the equilibrium corresponds to almost pure para-hydrogen, and by using charcoal as a catalyst for the conversion at low temperatures para-hydrogen can thus be prepared. Para-hydrogen is stable at temperatures below ca. 500° for long periods, but the conversion

²⁸⁴ J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 237 (1942).

²⁸⁵ T. Locker and F. Patat, *Z. physik. Chem.*, **B27**, 431 (1934).

²⁸⁶ F. Patat, *Z. physik. Chem.*, **B26**, 208 (1934).

²⁸⁷ J. R. Bates and R. Spence, *Trans. Faraday Soc.*, **27**, 468 (1931); *J. Am. Chem. Soc.*, **63**, 1689 (1931).

²⁸⁸ K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 119, 492 (1924), **116**, 391 (1925).

²⁸⁹ G. Cario and J. Franck, *Z. Physik*, **11**, 161 (1922).

²⁹⁰ H. C. Urey and G. I. Lavin, *J. Am. Chem. Soc.*, **61**, 3286 (1929).

²⁹¹ G. Glockler and S. C. Lind, *The Electrochemistry of Gases and Other Dielectrics*, New York, 1939.

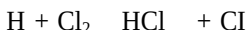
to ortho-hydrogen at room temperature and up can be catalysed by hydrogen atoms by the reaction



The kinetics of this reaction have been investigated by Geib and Harteck²⁹² using hydrogen atoms produced electrically, and by Farkas²⁹³ with thermally produced atoms. The activation energy of the reaction is 6.7 kcal., with a steric factor of about 1J17 at room temperature, and of 1J7.5 at temperatures around 700°.

It is thus possible to calculate the hydrogen atom concentration in a system which contains para-hydrogen by measuring the rate of the conversion. Thus, for example, Farkas and Sachsse²⁹⁴ have determined the H-atom concentration in a system containing hydrogen and mercury, illuminated by the mercury resonance line, 2537Å. Para-hydrogen was used in place of the ordinary equilibrium mixture, and samples of hydrogen were withdrawn from time to time and their para-ortho ratio determined by measuring the thermal conductivity of the gas.²⁹⁵

In simple systems the method is precise and yields unequivocal results.²⁹² In more complex systems, however, difficulties are encountered in its application. In the first place the method cannot be used in a simple direct way unless the reaction by which the atoms normally disappear is considerably slower than the para-ortho conversion. Thus the reaction



occurs roughly 10⁴ times as fast as the para-ortho conversion catalysed by H-atoms at room temperature, and hence it is only possible to determine the stationary hydrogen atom concentration in the photochemical synthesis of hydrogen chloride by a special technique.²⁹⁶

A further difficulty is the fact that the para-ortho conversion is catalysed by all paramagnetic substances, such as oxygen, nitric oxide, and substances containing an odd number of electrons, *i.e.*, by all free radicals. Hence in complex systems it is always difficult to ascertain if the conversion observed is due to hydrogen atoms or to other atoms or radicals.

In the case of deuterium the situation is reversed and the high temperature equilibrium corresponds to a para-ortho ratio of 2J1, and nearly pure ortho-deuterium can be prepared at low temperatures. Obviously the same technique can be applied with deuterium, and the rate of conversion of ortho- to para-deuterium can be used as a measure of the D-atom concentration.^{295, 297, 298}

²⁹² K. H. Geib and P. Harteck, *Z. physik. Chem. Bodenstein-Festband*, 849 (1931).

²⁹³ A. Farkas, *Z. physik. Chem.*, **B10**, 419 (1930).

²⁹⁴ L. Farkas and H. Sachsse, *Z. physik. Chem.*, **B27**, 111 (1935).

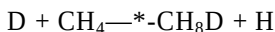
²⁹⁵ A. Farkas, *Orthohydrogen, Parahydrogen, and Heavy Hydrogen*, Cambridge, 1935.

²⁹⁶ A. Sommer, *Dissertation*, Berlin, 1934.

²⁹⁷ A. Farkas and L. Farkas, *Proc. Roy. Soc. (London)*, **A162**, 124 (1935).

²⁹⁸ A. Farkas, L. Farkas, and P. Harteck, *Proc. Roy. Soc. (London)*, **A144**, 481 (1934).

In the investigation of exchange reactions involving atomic deuterium, it is sometimes possible to interpret the kinetics of reactions by using ortho-deuterium and another substance, and making simultaneous measurements of the rates of conversion and exchange. For example, Farkas and Melville²⁹⁹ produced deuterium atoms by photosensitization in ortho-deuterium-methane mixtures, and made simultaneous measurements of the rates of the reactions



and

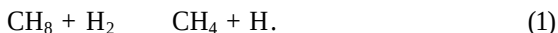


(it) *The Determination of Radical Concentrations*

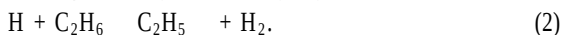
West³⁰⁰ has made use of the fact that free radicals are paramagnetic, and should thus catalyse the para-ortho-hydrogen conversion, to estimate radical concentrations. For example, methyl iodide was photolysed in the presence of para-hydrogen, and it was found that the transitory products of the photolysis catalysed the conversion. However, since atoms and other radicals also catalyse it, this cannot be regarded as a definite detection of the methyl radical by this means.³⁰¹ West obtained similar results with acetone.

Rosenbaum and Hogness³⁰² found that the conversion was catalysed by the products from decomposing hydrogen iodide. The rate was too fast to be accounted for by catalysis by hydrogen atoms, and hence the reaction must have been catalysed by iodine atoms as well.

Patat and Sachsse³⁰³⁻³⁰⁵ have used an ingenious indirect method to measure radical concentrations and to test free radical mechanisms by means of the para-ortho-hydrogen conversion. For example, they measured the rate of the para-ortho-hydrogen conversion in the presence of decomposing ethane, and were thus able to detect hydrogen atoms produced by the decomposition of ethane, or by the reaction



They assume that the direct catalysis of the conversion by methyl radicals is negligible compared with the effect due to H-atoms. If we accept the Rice-Herzfeld mechanism for the ethane decomposition,³⁰⁶ the hydrogen atoms produced by (1) are being destroyed mainly by the reaction



²⁹⁹ A. Farkas and H. W. Melville, *Proc. Roy. Soc. (London)*, **A167**, 625 (1936).

³⁰⁰ W. West, *J. Am. Chem. Soc.*, **67**, 1931 (1935).

³⁰¹ W. West, *Annals N. Y. Acad. Sci.*, **41**, 238 (1941).

³⁰² E. J. Rosenbaum and T. R. Hogness, *J. Chem. Phys.*, **2**, 267 (1934).

³⁰³ F. Patat, *Z. physik. Chem.*, **B32**, 274, 294 (1936).

³⁰⁴ F. Patat and H. Sachsse, *Z. Elektrochem.*, **41**, 493 (1935); *Nach. Ges. Wiss. Gottingen*, **III**, **1**, 41 (1935).

³⁰⁵ H. Sachsse, *Z. physik. Chem.*, **B31**, 79, 87 (1935).

³⁰⁶ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **66**, 284 (1934).

Hence the stationary concentration of hydrogen atoms is defined by the two processes, and we get approximately

$$\frac{[\text{CH}_3]}{[\text{H}]} = \frac{k_2[\text{C}_2\text{H}_6]}{k_1[\text{H}_2]}$$

Having evaluated the hydrogen atom concentration, we can compare it with that calculated from the Rice-Herzfeld mechanism. At 590° the experimentally found value is 10^{-11} mole per liter. The value predicted by the mechanism is about 1000 times larger, viz., $10^{-8.2}$. This, therefore, appears to rule out the mechanism.

However, it is difficult to obtain unequivocal results by this method since (a) the calculations depend strongly on the rate assumed for reaction (1), and are thus open to some question, and (6) the method can only yield results as to the truth or falsity of the Rice-Herzfeld mechanism in its detailed form, and depends completely on the activation energies assumed in this mechanism, especially for reaction (2). (See footnote 307.)

The method has been applied in a large number of cases by Patat and Sachsse, but it appears that its successful application demands a more detailed knowledge of the kinetics of the part reactions than is yet available in most of the cases to which it has been applied.

(6) Exchange Reactions

Just as the para-ortho-hydrogen conversion can be used as a measure of the stationary hydrogen or deuterium atom concentration in a system, so can the exchange reactions



The kinetics of these reactions have been investigated by Farkas and Farkas.²⁹⁷ From their data the H- or D-atom concentration in a system can thus be inferred from the rate of exchange. The extent to which the exchange has occurred can, like the para-ortho conversion, be inferred from thermal conductivity measurements.

An example of the use of this method is the investigation by Trenner, Morikawa, and Taylor³⁰⁸ of exchange reactions of the paraffins by the Wood-Bonhoeffer method. In this work the hydrogen atom concentration in the system was determined by running hydrogen through the discharge, mixing the resulting $\text{H} + \text{H}_2$ with deuterium, and determining the extent to which the reaction



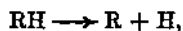
³⁰⁷ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 6,275 (1937), 6,179 (1938); *Can. J. Research*, B16, 303 (1938).

³⁰⁸ N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, 5, 203 (1937).

had occurred. The atom concentration was then calculated from Farkas and Farkas¹ results for this reaction, viz.,

$$E = 6.55 \text{ kcal.}, k_{110} = 4.9 \times 10^4 \text{ liter mole}^{-1} \text{ sec.}^{-1}, p = 0.1.$$

In many cases isotopic exchange reactions can be used to cast light on certain elementary processes. Usually this is done by rather detailed considerations of mechanism. One especially simple phenomenon which can be investigated in this way is the following. Suppose that in a photolysis the primary step appears to be



and that the quantum yield is low. It is desired to determine whether this is due to the back reaction proceeding efficiently, or to other causes. If we mix deuterium with the reactant, then due to the reaction



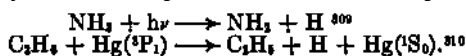
there will also be D-atoms in the system. Hence if the back reaction proceeds readily, in addition to



the reaction



will also occur. Hence by analysing the "unreacted" reactant for deuterium it is possible to determine if the reverse of the primary step is the cause of the low quantum yield. Examples of the use of this procedure are



There are many other cases in which "tracer" experiments can thus shed light on primary processes. Not only deuterium, but also other isotopes, stable and radioactive, have been used. A number of reviews of this type of work exist.^{311,314}

8. The Detection and Estimation of Atoms and Radicals by Means of Their Physical Properties

(a) Diffusion

A fairly direct and reasonably accurate method of estimating the concentration of hydrogen atoms in a gas containing only H_2 and H has been devised by Wrede³¹⁵ and Harteck.³¹⁶ This can only be used at low pres-

³⁰⁹ H. S. Taylor and J. C. Jungers, *J. Chem. Phys.*, **2**, 452 (1934).

³¹⁰ E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research*, **B16**, 314 (1938).

³¹¹ K. H. Geib, *Z. Elektrochem.*, **44**, 81 (1938).

³¹² K. H. Geib, *Z. angew. Chem.*, **51**, 622 (1938).

³¹³ O. Reitz, *Z. Elektrochem.*, **46**, 100 (1939).

³¹⁴ C. Rosenblum and J. F. Flagg, *J. Franklin Inst.*, **228**, 471, 623 (1938).

³¹⁵ E. Wrede, *Z. Instrumentenkunde*, **48**, 201 (1928); *Z. Physik*, **64**, 53 (1929).

³¹⁶ P. Harteck, *Z. physik. Chem.*, **A139**, 98 (1928).

Sures and for concentrations of atoms which are high enough to be of the same order of magnitude as that of the molecules. Hence in practice it is only of use with the discharge-tube method of producing hydrogen atoms.

In this method the stream of gas containing hydrogen atoms and molecules is led past a slit or capillary whose width is smaller than the mean free path of the gas. For hydrogen at 1 mm. pressure this necessitates an opening with a width of about 1/20 mm. Under these circumstances atoms or molecules pass through the capillary only by diffusion. On the outside of the capillary we then have both atoms and molecules. Inside the capillary, however, owing to recombination on the glass surface, or on platinum or some other metal which may be placed there, there are only molecules. As a result, in the steady state the pressure will be lower on the inside than on the outside, since atoms diffuse faster than molecules in the ratio $\sqrt{2}$, but one molecule passing through the capillary transports twice the mass of hydrogen taken through by an atom. Hence, for 100 per cent atoms outside, we have

$$\frac{\text{Pressure outside}}{\text{Pressure inside}} = 2/\sqrt{2} = 1.41.$$

Similarly, for a volume per cent, n , of atoms

$$n = \frac{100(P_1 - P_2)}{P_1(1 - 0.5\sqrt{2})},$$

where P_1 is the pressure on the outside, and P_2 that on the inside.

The pressure measurements are usually made with a Pirani gauge, since McLeod gauges have so large a volume that a very long time is required for pressure equilibrium to be established on account of the smallness of the capillary. The use of as small a gauge as possible is important, since pressure fluctuations inevitably occur in a flowing system. To speed up pressure equilibrium Chadwell and Titani³¹⁷ used a sintered glass disc instead of a single orifice.

The fact that foreign gases must be absent is a distinct handicap, since in investigating atomic reactions measurements of the atom concentration must therefore be made in blank runs when other reactants are not present. The ideal case for the use of the method is in the investigation of the para-ortho-hydrogen conversion, since in this case the above limitation does not exist.

While the method has occasionally been used for oxygen or nitrogen atoms, it is not very satisfactory since the mean free path at the same pressure is much smaller in these cases, and finer capillaries must therefore be used. As a result the establishment of equilibrium is extremely slow. In spite of these drawbacks it has been used successfully for chlorine by Rodebush and Klingelhofer.³¹⁸

³¹⁷ H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, 65, 1363 (1933).

³¹⁸ W. H. Rodebush and W. C. Klingelhofer, *J. Am. Chem. Soc.*, 66, 130 (1933).

Poole³¹⁹ has criticized all determinations with Wrede gauges on the grounds that it is doubtful if some mass-flow through the orifice has not occurred.

The method is inapplicable to free radicals, since systems containing them are always too complex.

(b) *Calorimetry*

Calorimetric methods of detecting and estimating hydrogen atoms have been frequently employed. The method is obviously attractive in principle, since the recombination of hydrogen atoms may be very easily brought about on catalyst surfaces, and the reaction is exothermic to the extent of approximately 103 kcal. per mole.

Calorimetric detection was first employed by Bonhoeffer³²⁰ who coated thermometer bulbs with various substances and found that considerable temperature rises occurred. This method has also been used by Taylor and Lavin.³²¹ Thermocouples have been used in a similar way.³²²

The use of glowing wires as a test for hydrogen atoms has been reported by Wood and a number of later workers. (See *e.g.*, footnote 323.) In this method the heat of recombination on a metal wire acting as a catalyst is sufficient to bring the wire to incandescence and thus afford a visual indication of the presence of atoms. One difficulty with this method is that the wire frequently becomes "poisoned." In one modification of the method³²⁴ the wire is maintained at a just visible red heat (at which temperature poisoning does not occur) by the passage of a current. In the presence of atoms recombination heats the wire, and less current is necessary to maintain it at the same temperature. The decreased wattage is then a direct measure of the heat received from recombining atoms. The method is rough, but convenient.

More accurate calorimetric methods have been used by a number of workers.³²⁶⁻³²⁹ In all of these a catalyst mass is placed in the reaction tube at the place where the atom concentration is to be measured, and the heat received by the catalyst is measured by noting the temperature rise and applying cooling corrections, etc. The main difficulty is to correct for the

³¹⁹ H. G. Poole, *Proc. Roy. Soc. (London)*, **A163**, 404 (1937).

³²⁰ K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 119, 492 (1924).

³²¹ H. S. Taylor and G. I. Lavin, *J. Am. Chem. Soc.*, **52**, 1910 (1930).

³²² E. Pietach and F. Seufferling, *Z. Elektrochem.*, **37**, 655 (1931).

³²³ H. C. Urey and G. I. Lavin, *J. Am. Chem. Soc.*, **61**, 3286 (1929).

³²⁴ E. W. R. Steacie, unpublished work.

³²⁵ I. Amdur and A. L. Robinson, *J. Am. Chem. Soc.*, **56**, 1395 (1933).

³²⁶ F. R. Bichowsky and L. C. Copeland, *J. Am. Chem. Soc.*, **50**, 1315 (1928).

³²⁷ J. K. Dixon, *J. Am. Chem. Soc.*, **54**, 4262 (1932).

³²⁸ H. M. Smallwood, *J. Am. Chem. Soc.*, **51**, 1985 (1929).

³²⁹ H. v. Wartenberg and G. Schultze, *Z. physik. Chem.*, **B2**, 1 (1929).

loss by gaseous conduction, which is quite high and amounts to as **much as 50 per** cent of the observed temperature rise.

Objections to calorimetric methods have been raised on the **grounds that** the introduction of an efficient catalyst which causes complete removal of atoms sets up a diffusion of atoms towards the catalyst and thus alters the normal atom concentration throughout the reaction tube.^{319,825, 329-331} However, it appears that with proper care in experimental arrangements this is not serious.

Poole³¹⁹ has recently described a continuous-flow calorimeter which seems to meet the objections which have been raised to the method, and which greatly cuts down conduction losses.

Schwab and Friess³³² have used the heating of a copper-constantan thermocouple as a method of determining the relative concentration of chlorine atoms. For absolute measurements they used a calorimeter consisting of a thin metal plate in which a thermocouple was imbedded. This was heated by atom recombination, and was calibrated by heating electrically in blank experiments.

Schwab³³³ has also used the heating of a thermocouple to measure the relative concentration of bromine atoms produced by the discharge-tube method.

There are indications that heating of a wire by recombination may have successfully indicated the presence of hydroxyl radicals.³²³

(c) Thermal Conductivity

Senftleben and Germer³³⁴ detected chlorine atoms in chlorine illuminated with light in the region of the continuum by means of the increased thermal conductivity of the gas. Senftleben and Riechemeier³³⁵ in a similar way have measured the stationary H-atom concentration in mercury-hydrogen mixtures illuminated with X2537.

(d) Pressure Change

In a few cases the increase in pressure on dissociation of a molecule into atoms (or the decrease on their recombination) has been used as a qualitative or quantitative indication of the presence of atoms. Thus by a special technique Smallwood³³⁶ was able to compress very quickly a mixture of

³³⁰ W. Steiner, *Trans. Faraday Soc.*, 31, 623 (1935).

³³¹ W. Steiner and F. W. Wicke, *Z. physik. Chem. Bodenstein-Festband*, 817 (1931).

³³² G. M. Schwab and H. Friess, *Z. Elektrochem.*, 39, 586 (1933).

³³³ G. M. Schwab, *Z. physik. Chem.*, **B27**, 452 (1935).

³³⁴ H. Senftleben and E. Germer, *Ann. Physik*, 2, 847 (1939).

³³⁵ H. Senftleben and O. Riechemeier, *Physikal. Zeits.*, 30, 745 (1929).

³³⁶ H. M. Smallwood, *J. Am. Chem. Soc.*, 66, 1542 (1934).

hydrogen molecules and atoms from a discharge, and to follow the recombination process by measuring the pressure with a diaphragm gauge with photographic recording.

In the case of chlorine and bromine, the well-known Budde effect³³⁷ indicates the production of atoms by the rise in pressure obtained when photochemically produced chlorine atoms recombine and give out heat.

(e) Mass Spectrograph

Early attempts to use the mass spectrograph as an analytical tool³³⁸ were complicated by the electron dissociation of the parent molecule, but Eltenton³³⁹ has recently taken advantage of the fact that the ionization potentials of free radicals are lower than the appearance potentials of the same ions produced by electron dissociation. In contrast with the results of Belchetz and Rideal he found methyl radicals but no methylene radicals in the decomposition of methane on carbon filaments. He was also able to detect methyl and ethyl radicals in the thermal decomposition of ethane; methylene from diazomethane, and allyl radicals in the reaction of methyl radicals with propylene.

9. The Detection and Estimation of Atoms and Radicals by Optical Methods

(a) Emission Spectra

"Emission spectra cannot serve as a quantitative measure of the concentration of free radicals since, for the appearance of an emission spectrum, not only the occurrence of free radicals but also their excitation is necessary."³⁴⁰ The same remarks obviously apply to atoms as well. Even from a qualitative point of view emission spectra cannot in general be used as an indication of the presence of atoms or radicals, except in a few special cases (see below) or where high energies are involved (as in discharges, flames, or in the photochemistry of the Schumann region) so that any radicals formed are in excited states and thus emit radiation.

In discharges, etc., a large number of radicals have been detected, such as C₂, CH, CN, NH, OH, PH, and ions of various sorts. (For reviews of this subject see footnotes 340-343.) In flames and explosions C₂, CH, OH, NH,

³³⁷ E. Budde, *J. prakt. Chem.*, 7, 376 (1873).

³³⁸ A. R. Olson and C. H. Meyers, *J. Am. Chem. Soc.*, 49, 3131 (1927).

³³⁹ G. C. Eltenton, *J. Chem. Phys.*, 10, 403 (1942).

³⁴⁰ G. Herzberg, *Molecular Spectra and Molecular Structure*, New York, 1939.

³⁴¹ F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances*, New York, 1936.

³⁴² G. Glockler and S. C. Lind, *The Electrochemistry of Gases and Other Dielectrics*, New York, 1939.

³⁴³ L. Sponer, *Molekalspektren*, Berlin, 1935.

and probably CHO and other radicals have been observed.³⁴⁴⁻³⁵³ In the Schumann region a considerable number of atoms and radicals have been detected in emission during photolyses. (See, for example, footnotes 354-356.) Spectroscopic examinations of atomic oxygen flames have also been made.^{351,352}

Resonance emission has been used in a number of cases to detect and measure the concentration of atoms and of unstable molecules. Thus Hartel and Polanyi³⁶⁷ followed the changes in the concentration of sodium atoms in reaction mixtures by illuminating with sodium-resonance radiation (the D-line) and measuring the intensity of the resonance radiation emitted.

In a qualitative way the presence of HgH in mercury-hydrogen mixtures illuminated with X2537³⁵³ and of CdH and ZnH in the corresponding experiments with cadmium and zinc^{359,360} have been established by the resonance emission of HgH, CdH, and ZnH bands. Resonance emission of CdH bands has also been detected in cadmium-propane mixtures illuminated with X3261.³⁶¹ It should be noted that the successful detection of atoms or radicals by the resonance emission of lines or bands originating on the ground state depends on the atoms or radicals being in the ground state rather than in excited states.

Bay and Steiner³⁶² have used emission spectra to measure atom concentrations in a Wood's tube. A pair of subsidiary electrodes were placed in the reaction tube, and a weak high-frequency discharge was passed between them. By observing this spectrographically and determining the ratio of the intensities of certain atomic lines to molecular bands, it was possible to use the method as a relative measure of the atom concentration. Or, by running calibration experiments against a Wrede gauge the spectroscopic

³⁴⁴ K. F. Bonhoeffer, *Z. Elektrochem.*, **42**, 449 (1936).

³⁴⁶ E. Hulthen and S. Nakamura, *Nature*, **119**, 235 (1927).

³⁴⁶ W. Jost, *Explosions- und Verbrennungs-Vorgänge in Gasen*, Berlin, 1939.

³⁴⁷ B. Lewis and G. von Elbe, *Combustion, Flames, and Explosions of Gases*, Cambridge, 1933.

³⁴⁸ N. V. Tokarev, *J. Phys. Chem. (U.S.S.R.)*, **14**, 642 (1940).

³⁴⁹ W. M. Vaidya, *Proc. Roy. Soc. (London)*, **A178**, 356 (1941).

³⁵⁰ A. G. Gaydon, *Proc. Roy. Soc. (London)*, **A179**, 439 (1942).

³⁵¹ K. H. Geib, *Z. Elektrochem.*, **47**, 275 (1941).

³⁵² K. H. Geib and W. M. Vaidya, *Proc. Roy. Soc. (London)*, **A178**, 351 (1941).

³⁵³ L. Avramenko, *Acta Physicochimica (U.R.S.S.)*, **18**, 53 (1943).

³⁵⁴ H. Neuimin and A. Terenin, *Acta Physicochimica (U.R.S.S.)*, **5**, 465 (1936).

³⁵⁵ N. Prileshajeva and A. Terenin, *Trans. Faraday Soc.*, **31**, 1483 (1935).

³⁵⁶ A. V. Yakovleva, *Acta Physicochimica (U.R.S.S.)*, **10**, 433 (1939).

³⁵⁷ H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

³⁵⁸ H. Beutler and E. Rabinowitsch, *Z. physik. Chem.*, **B8**, 403 (1930).

³⁵⁹ P. Bender, *Phys. Rev.*, **36**, 1535 (1930).

³⁶⁰ L. O. Olsen, *J. Chem. Phys.*, **6**, 307 (1933).

³⁶¹ E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, **12**, 34 (1944).

³⁶² Z. Bay and W. Steiner, *Z. physik. Chem.*, **B3**, 149 (1929).

observations could be made to give absolute values of atom concentrations.

(6) Absorption Spectra

In principle the detection and estimation of atoms and radicals in absorption is without difficulty. In practice, however, it is necessary that the concentration be fairly high for this method to be successful. (See footnote 363 for a discussion of the difficulties involved.)

Bonhoeffer and Reichardt³⁶⁴ photographed the hydroxyl bands in absorption in a flow system with steam at temperatures in the neighbourhood of 1600°, and were thus able to determine the equilibrium in the reaction.



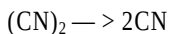
Bonhoeffer and Pearson, however, were unable to find the hydroxyl radical in absorption in the gas flowing from a discharge through water vapor.³⁶⁵ Geib and Harteck³⁶⁶ were also unable to find it spectroscopically in the reaction of hydrogen atoms with oxygen.

Oldenberg^{367,368} by using a 21-foot grating found the radical in absorption in a discharge in water vapor. He was able to detect it for as long as 1/8 sec. after the discharge was interrupted.

The hydroxyl radical has frequently been found in absorption in hydrogen and hydrocarbon flames.^{347,369-372}

Franck and Reichardt³⁷³ detected the NH radical in absorption in a flow system in decomposing ammonia at 2000°.

Kistiakowsky and Gershinowitz³⁷⁴ and White³⁷⁵ investigated the dissociation of cyanogen,



in the neighbourhood of 1200° by using absorption spectroscopy with a flow system.

³⁶³ O. Oldenberg, *J. Phys. Chem.*, **41**, 293 (1937).

³⁶⁴ K. F. Bonhoeffer and H. Reichardt, *Z. physik. Chem.*, **A139**, 75 (1928).

³⁶⁵ K. F. Bonhoeffer and T. G. Pearson, *Z. physik. Chem.*, **B14**, 1 (1931).

³⁶⁶ K. H. Geib and P. Harteck, *Trans. Faraday Soc.*, **30**, 134 (1934).

³⁶⁷ A. A. Frost and O. Oldenberg, *J. Chem. Phys.*, **4**, 642 (1936).

³⁶⁸ E. M. Stoddart, *Phil. Mag.*, **18**, 409 (1934).

³⁶⁹ L. Avramenko and V. Kondratjew, *Acta Physicochimica* (U.R.S.S.), **7**, 567 (1937).

³⁷⁰ K. F. Bonhoeffer and F. Haber, *Z. physik. Chem.*, **A137**, 263 (1928).

³⁷¹ V. Kondratjew, *Acta Physicochimica* (U.R.S.S.), **8**, 315 (1938), **10**, 791 (1939); *Uspekhi Khim.*, **8**, 195 (1939).

³⁷² V. Kondratjew and M. Ziskin, *Acta Physicochimica* (U.R.S.S.), **6**, 307 (1937); *J. Phys. Chem.* (U.S.S.R.), **9**, 542 (1937).

³⁷³ H. H. Franck and H. Reichardt, *Naturwiss.*, **24**, 171 (1936).

³⁷⁴ G. B. Kistiakowsky and H. Gershinowitz, *J. Chem. Phys.*, **1**, 432, 885 (1933).

³⁷⁵ J. U. White, *J. Chem. Phys.*, **8**, 459 (1940).

The C₂ radical was detected in absorption by means of the Swan bands in the reaction



by Klemenc, Wechsberg, and Wagner.³⁷⁶

For a review of the detection of CH and other radicals in absorption see Willey.³⁷⁷

Rabinowitch and his co-workers³⁷⁸ have measured the atom concentration in illuminated systems containing the halogens by measuring the extinction coefficients, and from these calculating the decrease in the number of molecules present, and hence indirectly the atom concentration. Hydrogen atom concentrations have also been measured by absorption spectroscopy.³⁷⁹

(c) *Miscellaneous Optical Methods*

Kohanenko³⁸⁰ has detected radicals and atoms by means of a glowing screen of zinc sulphide, as described previously.

In investigating the reaction between mercury vapor and the halogens, Ogg, Martin, and Leighton³⁸¹ used light from a resonance lamp to cast a shadow of a mercury vapor jet, and thus followed the decrease in concentration of the mercury vapor by a method analogous to the diffusion flame technique. In this way they were able to follow relatively fast reactions with activation energies of the order of 5 kcal.

Kudrjawzewa and Prileshajewa³⁸² used an ingenious method to investigate the photodecomposition of adsorbed acetone. The acetone was adsorbed on a thin metallic mirror, and a spectrum was focussed on it. The photochemically effective light formed radicals which removed the mirror at the part of the spectrum which was effective. In this way the photochemical threshold for adsorbed acetone was determined.

³⁷⁶ A. Klemenc, R. Wechsberg, and G. Wagner, *Z. physik. Chem.*, **A170**, 97 (1934).

³⁷⁷ E. J. B. Willey, *Trans. Faraday Soc.*, **30**, 230 (1934).

³⁷⁸ E. Rabinowitch, *Z. physik. Chem.*, **B33**, 275 (1936); E. Rabinowitch and H. L. Lehmann, *Trans. Faraday Soc.*, **31**, 689 (1935); E. Rabinowitch and W. C. Wood, *J. Chem. Phys.*, **4**, 358 (1936).

³⁷⁹ W. M. Preston, *Phys. Rev.*, **57**, 1074 (1940).

³⁸⁰ P. N. Kohanenko, *Acta Physicochimica* (U.R.S.S.), **9**, 93 (1938).

³⁸¹ R. A. Ogg, H. C. Martin, and P. A. Leighton, *J. Am. Chem. Soc.*, **68**, 1922 (1936).

³⁸² V. Kudrjawzewa and N. Prileshajewa, *Acta Physicochimica* (U.R.S.S.), **8**, 211 (1938).

Chapter III

Free Radicals in Thermal Decomposition Reactions

1. The Strength of Bonds in Organic Molecules

The "strength" of the R—X bond in a molecule RX is defined as the heat of the reaction



at the absolute zero. In other words, it is the heat of reaction when an isolated gas molecule decomposes to give a radical and an atom. Actually values are frequently given which are based on thermochemical data at room temperature rather than at the absolute zero. The correction involved, however, is only about 1 kcal., and since this is much less than the usual uncertainty in the data, it is rarely worth while to make the correction to 0°K.

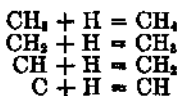
It would be out of place to enter into an extended discussion of bond strengths here. However, since a knowledge of bond strengths is of great importance in connection with the mechanism of decomposition reactions, a brief review of the subject will be given.

The early estimates of C—H and C—C bond strengths were based on thermochemical quantities. In the case of methane, for example, Rice¹ gives the following data:

	ΔH
$\text{C}_{(\text{graphite})} + 2\text{H}_{2(\text{gas})} = \text{CH}_{4(\text{gas})}$	~ 18.5 kcal.
$4\text{H}_{(\text{gas})} = 2\text{H}_{2(\text{gas})}$	~ 205 kcal.
$\text{C}_{(\text{gas})} = \text{C}_{(\text{graphite})}$	~ 154 kcal.
$\text{C}_{(\text{gas})} + 4\text{H}_{(\text{gas})} = \text{CH}_{4(\text{gas})}$	~ 377.5 kcal.

Whence the average C—H bond strength in methane is $377.5/4 = 94.4$ kcal.

This type of calculation can be used for other substances provided that the heats of formation are available, as is usually the case. It involves, however, two doubtful points. In the first place it is assumed that all the C—H bonds are equal, i.e., that the reactions



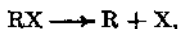
¹ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

all have equal heats. Secondly a value must be assumed for the heat of the reaction

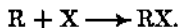


and this is a matter of considerable controversy.

Other early estimates of bond strengths were based on kinetic evidence. These usually involve first the establishment of a mechanism consisting of several elementary stages, secondly the calculation from such a mechanism of the activation energy of an elementary reaction of the type



and thirdly the assumption that the activation energy of such a reaction is equal to the strength of the bond which is broken. This is equivalent to the assumption that the activation energy is zero for the reverse reaction



While there is some doubt about this, it seems to be well established that the activation energies of such radical recombination reactions are small, and hence the assumption is not usually far wrong. In some cases information exists about the activation energy of the reverse reaction, and such an assumption is unnecessary. The main trouble with the earlier "kinetic" values of bond strengths, however, was that they were usually based on kinetic mechanisms for which the evidence was rather flimsy. Estimates of this sort will be discussed in detail in later chapters in connection with specific reaction mechanisms.

As a result of these difficulties the earlier values of bond strengths were unreliable and widely divergent. As an example of the unsatisfactory state of affairs which existed as recently as five years ago, Table IV gives data taken from a book by Rollefson and Burton² which was published in 1939.

If we confine our attention to the C—C and C—H bonds, which are by far the most important, it will be seen from the foregoing table that the values fall into two rough groups, a "high" group of 100 or more kcal. for C—H and about 80 kcal. for C—C, and a "low" group of about 92-95 kcal. for C—H and 72 kcal. for C—C. The discrepancy is even more marked if Pauling's later estimates¹³ are substituted for the ones given in the Table. These later values, which are average bond strengths based on thermochemical data, are C—H (in CH₄) = 87.3 kcal., C—C = 58.6 kcal. These seem unquestionably too low, and the reason for the discrepancy has been discussed by Baughan.¹⁴ He points out that if a value of about 104 kcal. is assumed for the first C—H in methane (*i.e.*, a value compatible with the

² G. K. Rollefson and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions*, New York, 1939.

³⁻¹² Reference notes on the opposite page.

¹³ L. Pauling, *The Nature of the Chemical Bond*, Ithaca, 1939.

¹⁴ E. C. Baughan, *Nature*, 147, 542 (1941).

TABLE IV. BOND STRENGTH DATA UP TO 1939

Bond	Strength, kcal.	Reference
C—H	100 (hydrocarbons)	1
	92.3	3
	94.8 (CH ₄)	12
	100 (CH ₄)	5
	92	6
	114	7
	102.5	8
	108	9
	103 (CH ₄)	11
C—C	79 (ethane)	1
	83	4
	84.2 (paraffins)	5
	110-115	7
	71	6
	97.6	9
	72.1 (ethane)	12
	89.5 (ethane)	1
C=C	162 (ethylene)	11
	145 (hydrocarbons)	1
	149	4
	200	7
	125	6
	151.2 (olefins and cyclic compounds)	5
C≡C	198.5 (acetylenic hydrocarbons)	5
	220.5 (acetylene)	11
	200	4, 1
	187	10

"high" group), and it is assumed that the discrepancy is due to the fact that Pauling's value is an average one for all 4 C—H bonds, then the two values could be reconciled if the average of the last 3 C—H bonds in methane were 82 kcal. This large difference between the first C—H and the others is considered by Baughan to be unlikely for two reasons. In the

³ R. S. Mulliken, *Rev. Mod. Phys.*, 4, 1 (1932).

⁴ L. Pauling, *J. Am. Chem. Soc.*, 54, 3570 (1932).

⁵ L. Pauling and J. Sherman, *J. Chem. Phys.*, 1, 606 (1933).

⁶ F. Eucken, *Handbuch der Experimental Physik: Energie und Wärmehalt*, Leipzig, 1929.

⁷ R. Mecke, *Nature*, 125, 526 (1930); *Z. physik. Chem.*, B17, 1 (1932).

⁸ F. Patat, *Z. physik. Chem.*, B32, 290 (1936).

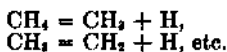
⁹ N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, 5, 203 (1937).

¹⁰ W. C. Price, *Phys. Rev.*, 45, 843 (1934), 47, 444 (1935).

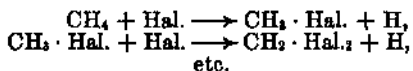
¹¹ R. G. W. Norrish, *Trans. Faraday Soc.*, 30, 103 (1934).

¹² M. Burton, *J. Chem. Phys.*, 6, 818 (1938).

first place Voge¹⁵ made an approximate quantum mechanical calculation of the energies of the successive reactions



and found no such large difference. In the second place the heats of successive substitution reactions of the type



are practically constant, and this would be unlikely if the C—H bonds in methane varied greatly.

Baughan therefore rules out this explanation and suggests that the source of error in Pauling's estimates is the assumed value for the heat of sublimation of graphite. This has been the subject of considerable discussion, and it has generally been considered that the value is either — 168.8 kcal. or — 123.6 kcal. The latter value has been strongly favored on spectroscopic grounds,¹⁶ and is the one used by Pauling. More recently, however, it has been suggested by Penney that the higher value may be correct.¹⁷ If the higher value is adopted, Pauling's C—H value of 87.3 kcal. becomes 98.6 kcal., and his C—C value of 58.6 kcal. becomes 81.2 kcal. The corrected values are thus in fair agreement with the "high" group.

Baughan's argument is, however, by no means compelling. The C—H bond strength in C—H is about 80 kcal. on the basis of spectroscopic evidence.¹⁷⁰ It is therefore possible with the low value of the heat of sublimation of graphite for the CH₃—H bond to have a value of 102 kcal., the C—H bond 80 kcal., and the other two about 84 kcal. Voge's calculations are hardly reliable enough to be taken very seriously. Further, the constancy of substitution heats is not a powerful argument, since it merely means that the C—H and C—Hal. bond strengths run parallel, as might be expected. It may therefore be concluded that a "high" value of 102 kcal. or so is not unreasonable no matter which value of the heat of sublimation of graphite is accepted.

Of the kinetic values given in Table IV, the higher ones appear to be more reliable than the others. The work of Trenner, Morikawa, and Taylor and of Patat appears to be on much more certain ground than the other investigations. Further, the values given by Rice are the activation energies of the split into free radicals, as determined by the mirror method, and are thus much more direct than the values obtained in other investigations.

¹⁵ H. H. Voge, *J. Chem. Phys.*, 4, 581 (1936).

¹⁶ G. Herzberg, *Chem. Rev.*, 20, 145 (1937).

¹⁷ W. G. Penney, *Trans. Faraday Soc.*, 35, 835 (1939).

^{17a} G. Herzberg, *Molecular Spectra and Molecular Structure I. Diatomic Molecules*, New York, 1939.

The main uncertainty in Rice's values is the assumption of the equality of activation energies and bond strengths.

Further strong support for the higher values comes from three recent investigations by different methods. Polanyi and his collaborators¹⁸ investigated the pyrolysis of a series of iodides in a flow system. A very low iodide pressure was used together with a carrier gas, and the flow rate was high. Under these circumstances they conclude that secondary reactions are unimportant, and that the measured activation energies are those of the split

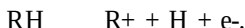


These activation energies are assumed to be equal to the corresponding RI bond strengths, which seems justifiable since much evidence points to an activation energy of about zero for the reverse reaction. Combining these bond strengths with thermochemical data, they arrive at the strengths of various C—H, C—C, and other bonds. The values thus obtained are given in Table V.

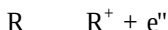
TABLE V. BOND STRENGTHS FROM THE PYROLYSIS OF IODIDES (Polanyi *et al.*)
Values in kcal.

R	R—I	R—Br	R—H	R—CH ₃	R—OH
CH ₃	54.0	68.5	102.5	87.0	86.5
C ₂ H ₅	52.0	67.0	97.5	85.0	87.0
<i>n</i> -C ₃ H ₇	50.0	64.5	95.0	82.0	86.0
<i>n</i> -C ₄ H ₉	49.0	63.5	94.0	81.0	85.5
<i>iso</i> -C ₃ H ₇	46.5	61.0	89.0	78.0	84.5
<i>tert</i> -C ₄ H ₉	45.0	60.0	86.0	75.5	85.0

Stevenson has arrived at bond strength values by an entirely different method.¹⁹ By electron impact the "appearance potentials" of ionized radicals are measured. This is equivalent to measuring the heat of the reaction



If the ionization potential of the radical is known, *i.e.*, the heat of the reaction



a combination of the two values yields the heat of the reaction



¹⁸ E. T. Butler and M. Polanyi, *Nature*, **146**, 129 (1940); *Trans. Faraday Soc.*, 39, 19 (1943); E. C. Baughan and M. Polanyi, *Nature*, **146**, 685 (1940); *Trans. Faraday Soc.*, 37, 648 (1941); E. C. Baughan, *Nature*, **147**, 542 (1941); E. C. Baughan, M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.*, 37, 377 (1941).

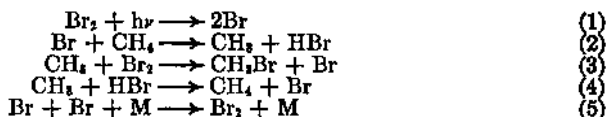
¹⁹ D. P. Stevenson, *J. Chem. Phys.*, 10, 291 (1942); *J. Am. Chem. Soc.*, 65, 209 (1943); D. P. Stevenson and J. A. Hippie, *J. Am. Chem. Soc.*, **64**, 1588, 2766 (1942); J. A. Hippie and D. P. Stevenson, *Phys. Rev.* 63, 121 (1943).

i.e., the strength of the R—H bond in the molecule under investigation. By combining these values with thermochemical data other bond strengths can be determined as well. The interpretation of the electron impact results involves certain assumptions, and the results are thus not unequivocal. They appear, however, to be very reasonable. In this way Stevenson arrives at the bond strengths shown in Table VI.

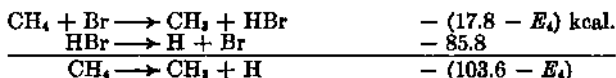
TABLE VI. BOND STRENGTHS FROM ELECTRON IMPACT DATA

R	Values in kcal.				
	R—H	R—CH ₃	R—C ₂ H ₅	R—C ₂ H ₃	R—Cl
H	103.8	—	—	—	—
CH ₃	101.4	83.4	—	—	—
C ₂ H ₅	96.8	81.1	79.1	—	—
C ₂ H ₃	91.0	79.1	76.1	76.5	—
Cl	102.8	80.7	79.5	71.5	57.6

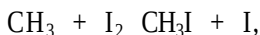
Further kinetic information comes from recent papers on the photobromination of methane and ethane.²⁰ For the photobromination of methane strong evidence is presented that the mechanism is



This work is discussed in detail in sections X-9 and X-35. Reaction (2) is unquestionably the slow rate-determining stage, so that the experimental activation energy may be considered to be that of (2), i.e., $E_2 = 17.8$ kcal. Hence, since (4) is the reverse of (2) we have



The indications are that E_1 is small. In the first place the temperature dependence of inhibition of the reaction by HBr indicated that $E_4 - E_z \sim 2$ kcal., and since E_3 is very small, E_4 is therefore ca. 2 kcal. Secondly, the yield of CH₄ in the photolysis of CH₃I—HBr mixtures, which is presumably due to (4), gives E_4 about 0.8 kcal. greater than the activation energy of the reaction



for which much evidence indicates $E = 0$. Combining the results by the two methods Kistiakowsky *et al.* put

$$E_4 = 1.5 + 1 \text{ kcal.}$$

²⁰ H. G. Andersen, G. B. Kistiakowsky, and E. R. Van Artsdalen, *J. Chem. Phys.*, 10, 305 (1942); E. R. Van Artsdalen, *J. Chem. Phys.*, 10, 653 (1942); H. G. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, 11, 6 (1943).

Whence the C—H bond strength in methane becomes

$$103.6 - 15 \pm 1 = 102 \pm 1 \text{ kcal.}$$

While this value is of course dependent on the assumptions made, the mechanism appears to be well established, and the agreement of the above result with the estimates of Stevenson and of Butler and Polanyi seems rather definitely to establish the "high" value for the C—H bond strength in methane.

A similar investigation of the photobromination of ethane,^{20a} although not as thorough as that of methane, yields with fair certainty a value of 98 ± 2 kcal. for the C—H bond strength in ethane. Combining these results with ordinary thermochemical data, Van Artsdalen obtains the values given in Table VII.*

TABLE VII. BOND STRENGTHS FROM THE KINETICS OF PHOTOBROMINATION REACTIONS

<i>Values in kcal.</i>			
R	R—H	R—CH ₃	R—C ₂ H ₅
CH ₃	102	85.6	—
C ₂ H ₅	98	83.8	82.4

There is thus excellent agreement between the values of Polanyi, Stevenson, and Kistiakowsky *et al.*, as shown by Table VIII, and the bond strengths given in the table may be accepted with considerable confidence.

TABLE VIII. COMPARISON OF BOND STRENGTH VALUES

<i>Values in kcal.</i>			
Bond	Kistiakowsky	Polanyi	Stevenson
CH ₃ —H	102	102.5	101.4
C ₂ H ₅ —H	98	97.5	96.8
CH ₃ —CH ₃	85.6	87.0	83.4
CH ₃ —C ₂ H ₅	83.8	85.0	81.1
C ₂ H ₅ —C ₂ H ₅	82.4	—	79.1

Unsaturated Hydrocarbons

The only reliable information concerning the C—H bond strength in ethylene, and the strength of C—C bonds attached to the vinyl radical appears to be the values found by Stevenson and given in Table VI.

For acetylene, Henkin and Burton^{20c} have calculated the C=C bond strength on the basis of a value of 125.1 kcal. for the heat of sublimation of graphite, and Herzberg's value^{17a} of 80 kcal. for the C—H bond in C—H. Combining these with standard thermochemical data, they get

$$\text{C}_2\text{H}_2 = 2\text{CH} - 137.9 \text{ kcal.}$$

* In a later paper^{20b} a correction is applied to bring the CH₃—H value to 0°K, and the value 101 kcal. is obtained.

^{20a} H. G. Andersen and E. R. Van Artsdalen, *J. Chem. Phys.*, 12, 479 (1944).

^{20b} G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, 12, 469 (1944).

^{20c} H. Henkin and M. Burton, *J. Chem. Phys.*, 8, 297 (1940).

This is considerably lower than former estimates of $\text{Gs}=\text{C}$ bond strengths, but appears to be reliable.

If we combine this with Herzberg, Herzfeld, and Teller's value Δ of

$$\text{C}_2 = 2\text{C} - 90 \text{ kcal.},$$

we get

$$\text{C}_2\text{H}_2 - \text{C}_2 + 2\text{H} - 208 \text{ kcal.},$$

i.e. an average value of 104 kcal. for the two $\text{C}-\text{H}$ bonds in acetylene.

Other Bonds

Conclusions as to many other bond strengths will be discussed in later sections in connection with specific kinetic mechanisms.

2. Free Radicals in Organic Decomposition Reactions

As discussed in Section (II-6) Rice and his co-workers^{*} investigated the decomposition of a wide variety of organic compounds by a modification of the Paneth technique. It was found that free radicals could be detected in the decomposition of almost all gaseous organic substances investigated, including hydrocarbons, ketones, aldehydes, alcohols, ethers, amines, etc. On this evidence Rice suggested that the majority of organic substances decompose by a mechanism involving free radicals.

Rice and his co-workers also determined the activation energies of the split into free radicals by the mirror technique. The values obtained for a number of substances are given in Table IX. For a discussion of the reliability of these results see (III—5).

TABLE IX. ACTIVATION ENERGIES OF THE DISSOCIATION OF ORGANIC MOLECULES INTO RADICALS

Substance	E , kcal.
Methane	100
Ethane	79.5
Propane	71.5
n-Butane	65.4
n-Pentane	64.0
n-Heptane	63.2
Dimethyl carbonate	74.2
Acetone	70.9
Acetaldehyde	69.4
Ethyl alcohol	68.6
Diethyl ether	68.6
Dimethyl ether	81.1
Ethylene oxide	44.0
Trimethyl amine	50.8
Dimethyl amine	52.0

As we have seen, the value for methane agrees well with recent estimates of the $\text{C}-\text{H}$ bond strength, while that for ethane is in fair agreement with the

^{20d} G. Herzberg, K. F. Herzfeld, and E. Teller, *J. Phys. Chem.*, 41, 325 (1937).

C—C bond strength in ethane. The other values will be referred to frequently in later sections dealing with specific reactions.

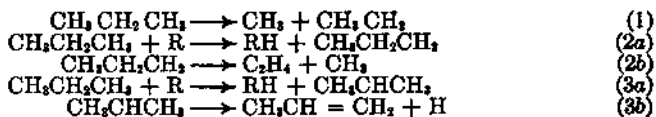
On account of the low pressures, fast flow, etc., which must be used in such experiments, it is necessary to work at temperatures which are from 200° to 300° higher than those at which the ordinary thermal decomposition sets in. Hence while it is certain that radicals are present in the decompositions when they are carried out at very high temperatures, tests by the Paneth method do not *prove* the presence of radicals during ordinary thermal decomposition at lower temperatures.

The theory has met with its greatest success in predicting the products of organic decomposition reactions,¹ especially those of the hydrocarbons. The observed activation energies of the decomposition reactions of most organic substances lie between 35 and 70 kcal. Rice points out that if two reactions have activation energies differing by 4 kcal., then the relative rates at 600° are in the ratio $e^{\frac{4000}{2 \times 873}}$ to 1, or approximately 9 to 1. Similarly for a difference of 10kcal. the rates will be in the ratio of 500 to 1. It follows, therefore, that if there are two or more possible modes of decomposition of a compound, and if one of these has an activation energy 10 kcal. or more lower than that of any of the others, it alone will occur to an appreciable extent.*

As may be seen from Tables IV and VIII, the C—C bond in hydrocarbons is much weaker than the C=C, C≡C, and C—H bonds. Rice therefore concludes that if the thermal decomposition of a hydrocarbon occurs through free radicals, the split will always be at a C—C bond and never at a C—H or a double or triple bond. Thus in the case of propane, for example, the primary reaction can only be



Now radicals higher than methyl and ethyl decompose relatively easily into unsaturated compounds and C_2H_5 , CH_3 , or H. Reactions of radicals with molecules usually have an activation energy much lower than that of reaction (1). In the case of propane we thus have the following scheme, R denoting a methyl radical or a hydrogen atom,

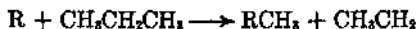


* This argument is usually correct. It has exceptions, however, since in some cases the variation in the frequency factor A in the Arrhenius equation,

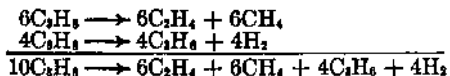
$$k = Ae^{-E/RT}$$

is sufficient to offset a difference in E. In most cases, however, for decomposition reactions the values of A are the same to within one power of 10 and equal to about 10^{18} .

(It should be noted that the assumption that the n-propyl radical decomposes to give C_2H_4 and CH_3 , while the iso-propyl gives C_3H_6 and H is entirely arbitrary. Also a fundamental postulate of all the Rice mechanisms is that reactions like (2a) and (3a) occur readily, but that reactions such as



do not occur to an appreciable extent.) On the basis of chance we would expect reaction (2a) to be faster than reaction (3a) in the ratio of 3 to 1, since there are six primary hydrogen atoms to two secondary. There is, however, evidence that secondary hydrogen atoms are somewhat less strongly bound than primary.²¹ On this basis Rice estimates that reaction (2a) : reaction (3a) :: 6 : 4. Hence, since (2a) is followed by (26) and (3a) by (36), the rates of production of C_2H_4 and C_3H_6 should be in the ratio 6:4. If the chains are long, C_2H_6 formation will be negligible since C_2H_5 radicals are not regenerated in the chain-carrying steps. This leaves CH_3 and H as the chain-carrying radicals, and since their rates of production are also in the ratio 6 : 4, we have for the overall decomposition:



This agrees reasonably well with experimental work on the pyrolysis of propane.²² In general the predictions of the theory are fairly accurate as far as the products of pyrolytic reactions are concerned.

3. The Rice-Herzfeld Mechanisms

If the free-radical theory of organic decomposition reactions is to be accepted, however, it must account not only for the products of organic decompositions, but also for the kinetics of such processes. It is an experimental fact that the majority of organic decomposition reactions follow a first-order rate law, and it is therefore necessary for the theory to answer two questions: (a) If the measured process is really the summation of a complex series of reaction steps, how is it that the overall reaction follows a first-order rate law? (6) If, as is postulated, most reactions occur by the breaking of a C—C bond, how is it that experimental activation energies for decomposition reactions are usually far smaller than the strength of this bond?

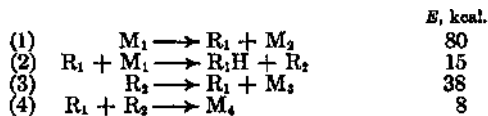
Rice and Herzfeld²³ answered these questions by showing that mechanisms could be devised on a free-radical basis which would lead to a first-

²¹ See, e.g., J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, 7, 390 (1939); A. Kossiakoff and F. O. Rice, *J. Am. Chem. Soc.*, 66, 590 (1943). The detailed discussion of the evidence on this point will be deferred till later chapters.

²² See, e.g., F. E. Frey and H. J. Hepp, *Ind. Eng. Chem.*, 25, 441 (1933).

²³ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, 56, 284 (1934).

order rate. Further, by a suitable choice of the activation energies of the part reactions, the apparent activation energy of the overall reaction could be made to agree perfectly with the experimental value.* As an example, consider the following scheme for the decomposition of a hydrocarbon molecule M_1 :



The molecule M_1 is assumed to decompose into a radical R_1 and a molecule M_2 . The radical R_1 reacts with a fresh molecule of the reactant, abstracts a hydrogen atom, and forms the stable substance R_1H and the radical R_2 . R_2 then decomposes into the radical R_1 and a molecule M_3 . We thus have a chain process, since steps (2) and (3) can repeat over and over again. The chain is finally broken when the radicals combine to form a stable molecule by reaction (4).

If we set up the equations giving the concentrations of the radicals in the steady state, we have, assuming long chains,

$$\frac{d}{dt}[R_1] = 0 = k_1[M_1] - k_2[R_1][M_1] + k_3[R_2] - k_4[R_1][R_2]$$

$$\frac{d}{dt}[R_2] = 0 = k_2[R_1][M_1] - k_3[R_2] - k_4[R_1][R_2]$$

Whence, we obtain

$$[R_1] = \frac{k_1}{4k_2} + \sqrt{\left(\frac{k_1}{4k_2}\right)^2 + \frac{k_1k_3}{2k_2k_4}}$$

If it is assumed that k_1 is very small, then we have approximately

$$[R_1] = \sqrt{\frac{k_1k_3}{2k_2k_4}}$$

Now the overall rate of decomposition of M_1 is given by

$$-\frac{d}{dt}[M_1] = k_1[M_1] + k_2[R_1][M_1] \quad (A)$$

Substituting for $[R_1]$

$$-\frac{d}{dt}[M_1] = k_1[M_1] \left(1 + \sqrt{\frac{k_2k_3}{2k_1k_4}} \right)$$

* It should be emphasized that the primary purpose of Rice and Herzfeld's paper was to show that free-radical mechanisms *could* be devised which were not inconsistent with experimental data. For this reason they assigned numerous activation energies to elementary reactions on a purely speculative basis. Later work has made it possible to evaluate many of these activation energies in a fairly direct way, and as might be expected the experimental values sometimes differ considerably from those assumed by Rice and Herzfeld. Also, as we shall see in this chapter, there are grave doubts as to the validity of some of the mechanisms themselves. However, considering the almost **purely speculative** basis by which these mechanisms were arrived at, the activation energies assumed by Rice and Herzfeld and by Rice * have, on the whole, proved **amazingly accurate**.

If k is small, i.e., if the primary step is slow compared with the overall rate, this becomes approximately

$$-\frac{d}{dt} [M_1] = k_1[M_1] \sqrt{\frac{k_2k_3}{2k_1k_4}} = [M_1] \sqrt{\frac{k_2k_3k_1}{2k_4}}$$

Hence the overall reaction is of the first order. In equation (A) it will be seen that the overall rate is made up of two parts ($k_1 [M_1]$), which is the rate of the primary step, and ($k_2[R_1][M_1]$), which is the rate of disappearance of M_1 by the chain steps. The ratio of these is evidently the average chain length, i.e.,

$$\text{Chain length} = \frac{k_2[R_1][M_1]}{k_1[M_1]} = \sqrt{\frac{k_2k_3}{2k_1k_4}}$$

The temperature coefficient of the reaction is obviously given by

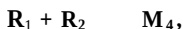
$$E_{\text{overall}} = \frac{1}{2}(E_1 + E_2 + E_3 - E_4)$$

Using the values given above for the activation energies of the part reactions, we get

$$E_{\text{overall}} = 62.5 \text{ kcal.},$$

which is much below the 80 kcal. assumed for the strength of the C—C bond. It thus follows that on the basis of a free-radical chain mechanism it is *possible* to explain in a general way the kinetics of the decomposition of organic compounds. The explanation involves certain rather definite assumptions about the rates of the part reactions, and the truth or falsity of such assumptions can only be demonstrated by experiment. Later in this chapter we will discuss the experimental evidence in detail for a number of substances.

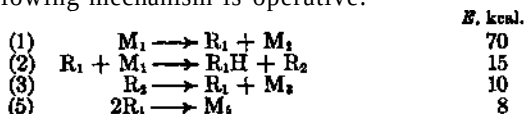
It should be emphasized at this point that the prediction of a first-order overall rate is dependent on the assumption made regarding the method of termination of the reaction chains. The above scheme assumes that they end by the radical recombination reaction



and this, as we have seen, leads to a first-order rate. Suppose, however, that it is assumed that radical recombination occurs by



i.e., that the following mechanism is operative:



As before, we have

$$\begin{aligned} \frac{d}{dt} [R_1] &= 0 = k_1[M_1] - k_2[R_1][M_1] + k_3[R_2] - k_4[R_1]^2 \\ \frac{d}{dt} [R_2] &= 0 = k_2[R_1][M_1] - k_3[R_2] \end{aligned}$$

Whence

$$[R_1] = \sqrt{\frac{[M_1]k_1}{k_5}},$$

and the overall rate of decomposition is

$$-\frac{d}{dt}[M_1] = k_1[M_1] + k_2[R_1][M_1] = k_1[M_1]\left(1 + k_2\sqrt{\frac{[M_1]}{k_1k_5}}\right)$$

Or, approximately,

$$-\frac{d}{dt}[M_1] = [M_1]^{\frac{3}{2}}k_2\sqrt{\frac{k_1}{k_5}}$$

The reaction thus has an order of 1.5 instead of 1.

Similarly it can be shown that if the chains terminate by



the order of the overall reaction will be 0.5.

In any given case, the mechanism of chain termination will be dependent on the magnitude of E_2 and E_3 . The chain carrying steps are reactions (2) and (3). Reaction (2) produces R_2 and destroys R_1 , while reaction (3) produces R_1 and destroys R_2 . The magnitudes of E_2 and E_3 thus largely determine the relative concentrations of R_1 and R_2 , and these concentrations are mainly responsible for one particular radical recombination reaction swamping out the others. The prediction of a first-order rate is dependent on reaction (4) being the main chain terminating process, and this thus necessitates that the ratio E_3/E_2 shall fall within a certain range.

Free-radical mechanisms of this sort are, of course, highly speculative, and could hardly have been taken seriously in the absence of other evidence. Striking support for the fundamental idea of free-radical chain reactions was, however, immediately forthcoming. Frey²⁴ was able to start chains in butane at temperatures below its normal decomposition range by adding methyl radicals (from the decomposition of mercury dimethyl). Similarly Allen and Sickman²⁵ showed that chain decomposition of acetaldehyde could be caused by methyl radicals from the decomposition of azomethane. Leermakers²⁶ also produced sensitized chain decomposition of methyl ether at temperatures below 400° by photolysing added acetone. Many other examples of induced decompositions have been referred to in Chapter II. All these observations prove that free radicals *can* cause chain decomposition of a large number of organic substances. They do not, however, necessarily prove that such free-radical chain decomposition occurs in the normal pyrolysis of the substances concerned.

Further evidence for the chain character of a large number of decomposi

²⁴ F. E. Frey, *Ind. Eng. Chem.*, 26, 198 (1934).

²⁵ A. O. Allen and D. V. Sickman, *J. Am. Chem. Soc.*, 66, 2031 (1934); D. V. Sickman and A. O. Allen, *J. Am. Chem. Soc.*, 56, 1251 (1934).

²⁶ J. A. Leermakers, *J. Am. Chem. Soc.*, 56, 1899 (1934).

tion reactions is furnished by the nitric oxide inhibition method. (See Chapter II.) On the assumption that maximum inhibition by nitric oxide corresponds to the complete suppression of chains normally present, chain lengths of from two to twenty may be calculated for the decomposition of a number of substances. This is definite evidence for the presence of chains, but in most cases the chain lengths thus obtained are far too small to be in accord with the Rice-Herzfeld mechanisms. In some cases it seems probable that there may be a few long chains rather than a large number of short ones, *i.e.*, that the Rice-Herzfeld mechanisms may hold for a small fraction of the total reaction, the remainder of the substance decomposing by a molecular mechanism.

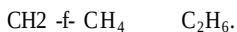
It may be concluded that it is rather definitely established that free radicals play some part in the decomposition of a large number of organic substances. The importance of the role of free radicals is, however, still a matter of controversy. The status of the Rice-Herzfeld mechanisms is also a question which is difficult to answer, although there is no question that Rice's theories have pointed the way to a great deal of fruitful work. In the following sections we will discuss in detail a number of the more important decomposition reactions from the point of view of free-radical mechanisms.

4. Methane

Following early work by a number of investigators, Kassel²⁷ made a thorough investigation of the thermal decomposition of methane. He concluded that the reaction was homogeneous and of the first order, with an overall activation energy of 79 kcal., and suggested as possible initial steps the reactions



In view of the fact that (1) is endothermic to an extent much greater than 79 kcal., he concluded that (2) must be the primary step, followed by



The resultant ethane was then assumed to decompose to ethylene and hydrogen, with various secondary reactions following. In support of this mechanism Storch²⁸ showed that the earliest product which could be detected was ethane. This was done by decomposing methane on a hot carbon filament at low pressures in a bulb cooled in liquid nitrogen. It should be noted, however, that Storch's results might have been due to a catalytic decomposition of methane on carbon, rather than to a homogeneous reaction.

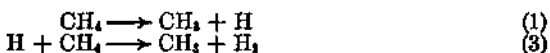
²⁷ L. S. Kassel, *J. Am. Chem. Soc.*, 54, 3949 (1932).

²⁸ H. H. Storch, *J. Am. Chem. Soc.*, 54, 4185 (1932).

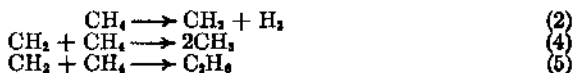
Rice and Dooley²⁹ investigated the primary process in the methane decomposition by the mirror technique. Using tellurium mirrors they found that $\text{CH}_3\text{Te} \cdot \text{TeCH}_3$ was formed, and not $(\text{TeCH}_2)_n$, and so concluded that the primary process involved methyl rather than methylene radicals. The activation energy of the split into radicals was 100 ± 6 kcal. As discussed in Chapter II, Belchetz and Rideal³⁰ obtained results contrary to those of Rice and Dooley, and concluded that the primary process was reaction (2). It appears probable, however, that the carbon filament was a complicating factor in their work, and that their conclusions are not applicable to the homogeneous decomposition.

If Rice and Dooley's detection of the methyl radical is accepted as valid, then as they point out there are two opposing mechanisms for its formation.

Rice and Dooley

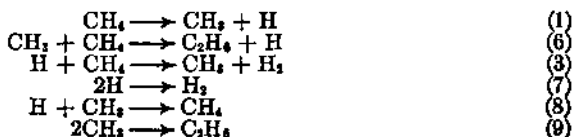


Belchetz and Rideal



If reaction (2) is the correct primary step rather than reaction (1), then either (4) or (5) must have an activation energy less than 12 kcal. to account for the absence of methylene radicals at the mirror in the experiments of Rice and Dooley. They consider this to be much too low, and hence they favor reaction (1) as the primary step. No hydrogen telluride was formed in their experiments, as would be the case if hydrogen atoms reached the tellurium mirror, and they therefore conclude that hydrogen atoms must disappear from the system rapidly by wall recombination or by reaction (3). This is reasonable since (3) has an activation energy of ca. 13 kcal., and would thus be very fast at 800° .

Kassel³¹ has also discussed the question in some detail. In his work on the thermal decomposition of methane, discussed above, the primary split was assumed to be that postulated by Belchetz and Rideal. He sets up the following chain sequence on the basis of Rice and Dooley's mechanism:



²⁹ F. O. Rice and M. D. Dooley, *J. Am. Chem. Soc.*, 56, 2747 (1934).

³⁰ L. Belchetz and E. K. Rideal, *Trans. Faraday Soc.*, 30, 170 (1934); *J. Am. Chem. Soc.*, 57, 1168 (1935).

³¹ L. S. Kassel, *J. Am. Chem. Soc.*, 57, 833 (1935).

Kassel then shows that on the basis of this mechanism it is not possible to explain the observed kinetics of the methane decomposition unless $[H]$ is at least 10^4 times greater than $[CH_3]$. On the grounds that it does not seem possible that such a factor could be overcome by wall recombination of hydrogen atoms to such an extent that they do not reach the mirror in appreciable quantities, Kassel rules out reaction (1) and concludes that the initial step is

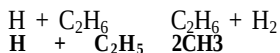


as postulated by Belchetz and Rideal, and that the reaction



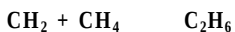
is probably fast enough to keep the concentration of methylene radicals down to such a low value that they could not be detected by the Rice technique.

This argument is, however, inconclusive. In the first place it is based primarily on the Kassel mechanism for the methane decomposition which is largely speculative, and in particular offers no explanation of the observed induction period. In the second place the free-radical chain mechanism set up for the purpose of the discussion has many objectionable features. Thus Kassel uses the value $E_s = 25$ kcal. This is now known to be much too high and the more reliable value of $E_z \sim 13$ kcal. will lower the ratio of $[H][CH_3]$ necessary for the operation of the mechanism by a factor of about 10. Secondly since the wall has little effect on methyl radicals, but much care in "poisoning" it is necessary to get H-atoms through even a short, wide tube, it is by no means certain that wall recombination would not offer an explanation of the non-arrival of H-atoms at the mirror in Rice and Dooley's experiments. Thirdly, reaction (6) has much too high an activation energy to be of importance. (See section VI-29.) And finally once ethane has accumulated the reactions



will become important as a source of methyl radicals. Kassel's objections to the Rice and Dooley mechanism are therefore not to be considered seriously.

An investigation of the properties of the methylene radical, prepared by the decomposition of diazomethane and of ketene, was made by Pearson, Purcell, and Saigh.³² They found that methane had little effect on the life of the radical, and hence that the reaction



or



³² T. G. Pearson, R. H. Purcell, and G. S. Saigh, *J. Chem. Soc.*, 1938, 409.

is slow at room temperature. They suggest that it occurs readily at high temperatures, however, and that the methyl radicals found by Rice and Dooley were the result of the secondary reaction



However, if this is the case reaction (4) must have an activation energy of not over 12 kcal. to explain Rice and Dooley's results. As we have seen Rice and Dooley consider that this is much too low, and Kassel estimated it at 44 kcal. The experimental evidence regarding the activation energy is rather questionable (see section VI-23), but on the whole it seems probable that the reaction only occurs to an appreciable extent at temperatures of 200° to 300° or more, and hence that the activation energy is considerably higher than 12 kcal.³³

Rice³⁴ has attempted to repeat Belchetz and Rideal's work. He confirmed the previous conclusion of Rice and Dooley that methyl radicals could be detected in the decomposition, but no methylene.

In a brief note Eltenton³⁵ has discussed experiments in which radicals have been detected and their relative concentrations determined by means of a mass spectrometer. By a suitable choice of potential it is possible to avoid complications due to the formation of radicals in the ionization chamber. In the case of methane, methyl radicals were the only ones detected when the gas was flowed through a hot quartz reaction chamber. Similarly, only methyl was formed on a hot carbon filament contrary to the results of Belchetz and Rideal. Methylene radicals when present in other reactions were readily detectable.

On the whole, the evidence thus seems definitely to favor a primary free radical split in the methane decomposition, and this split appears to lead to methyl rather than to methylene radicals. Not much can, however, be said with certainty about the succeeding steps. It appears likely, however, that chain processes are not of major importance. Thus Hobbs and Hinshelwood³⁶ investigated the inhibition of the methane decomposition by nitric oxide. They found that the results were complicated by a reaction between nitric oxide and methane. Applying corrections for this they obtained definite evidence of inhibition, the apparent chain lengths being 4.7 at 850° and 100 mm. of methane, and 2.9 at the same temperature with 200 mm. of methane. This is definite evidence for chains, but the average chain length is too short for mechanisms of the Rice type to be applicable.

³³ C. E. H. Bawn, *Trans. Faraday Soc.*, 36, 898 (1939); C. Rosenblum, *J. Am. Chem. Soc.*, 63, 3322 (1941).

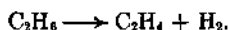
³⁴ F. O. Rice, *J. Am. Chem. Soc.*, 61, 213 (1939).

³⁵ G. C. Eltenton, *J. Chem. Phys.*, 10, 403 (1942).

³⁶ J. E. Hobbs and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A167, 447 (1938).

5. Ethane

A great deal of work has been done on the kinetics of the ethane decomposition from a free radical point of view, and the reaction has been one of the main proving grounds for the Rice mechanisms. The first kinetic treatment of the reaction was that of Pease.³⁷ Using a flow system at 650° in a preliminary investigation he concluded that the reaction was homogeneous and probably first order, and that the overall reaction was



The results of Frey and Smith,³⁸ obtained by the static method at 575°, are in excellent agreement with those of Pease. The first reasonably thorough investigation was that of Marek and McCluer,³⁹ who also used a flow method. Recalculation of their results by Paul and Marek⁴⁰ led to the equation for the first order rate constant

$$\log_{10} k = 16.06 - \frac{77,000}{2.3RT} \text{ sec.}^{-1}$$

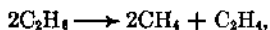
There is no doubt that their value of the activation energy was not very accurate on account of the non-uniformity of the temperature of their reaction vessel.

A more thorough investigation of the kinetics of the reaction by the static method led Sachsse⁴¹ to the conclusion that the high-pressure first-order rate constants were given by

$$\log_{10} k = 14.1 - \frac{69,800}{2.3RT} \text{ sec.}^{-1}$$

He also found that in addition to ethylene and hydrogen a small amount of condensable products was formed. This conclusion is confirmed by the work of Storch and Kassel.⁴²

An investigation at high pressures by Dinzes, Zharkova, Zherko, and Frost⁴³ indicated the formation of some methane as well. They suggested that this was due to the concurrent reaction



the influence of which would increase with increased pressure, since it is a second-order reaction.

Dinzes and Frost⁴⁴ investigated the thermal decomposition by the static

³⁷ R. N. Pease, *J. Am. Chem. Soc.*, 60, 1179 (1928).

³⁸ F. E. Frey and D. F. Smith, *Ind. Eng. Chem.*, 20, 948 (1928).

³⁹ L. F. Marek and W. B. McCluer, *Ind. Eng. Chem.*, 23, 878 (1931).

⁴⁰ R. E. Paul and L. F. Marek, *Ind. Eng. Chem.*, 26, 454 (1934).

⁴¹ H. Sachsse, *Z. physik. Chem.*, B31, 87 (1935).

⁴² H. H. Storch and L. S. Kassel, *J. Am. Chem. Soc.*, 69, 1240 (1937).

⁴³ A. I. Dinzes, V. R. Zharkova, A. V. Zherko, and A. V. Frost, *J. Gen. Chem. (U.S.S.R.)*, 7, 1063 (1937).

⁴⁴ A. I. Dinzes and A. V. Frost, *J. Gen. Chem. (U.R.S.S.)*, 3, 747 (1933); *Compt. Rend. Acad. Sci., (U.S.S.R.)*, 4, 153 (1933), 6, 513 (1934).

method with the object of making an accurate check of the unimolecular character of the reaction. The reaction was followed by the pressure change and by analysis at 678° and at pressures from 1.7 to 22.3 mm. It was found that the reaction did not follow a first-order equation well, but that the course of an individual experiment could be expressed accurately by the equation

$$k = \frac{1}{t} \left(\log \frac{1}{1-x} - Bx \right),$$

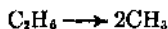
where x and t have their usual significance, and B is a constant. From the complex character of the rate equation they concluded that the reaction is probably a chain process. The form of the rate equation obviously suggests inhibition by the products of the reaction. However, it is unwise to draw too many conclusions from what happens in the later stages of a decomposition, and only initial rates have very much significance. Thus at 678° the ethylene formed would almost certainly undergo a series of further complex changes, and it would hardly be expected that a first order rate equation would hold throughout the reaction. Evidence of further complexity is furnished by the observation that the reaction is inhibited by the addition of propylene.⁴⁵

Rice and Dooley,⁴⁶ using the Paneth technique, found that lead mirrors were removed by the products of the ethane decomposition at 850° to 950°. By means of standard mirrors they measured the temperature coefficient of the primary split into radicals and found the values given in Table X.

TABLE X. DISSOCIATION OF ETHANE INTO FREE RADICALS

Distance from end of furnace, cm.	2.5	2.1	15	1.0	0.7
Ratio of time of mirror removal at 906° to that at 960°.	3.14	3.31	3.73	3.88	4.08
Activation energy, kcal.	61.6	64.5	71.0	73.0	76.0

By extrapolation to the end of the furnace, they obtain a value of 79.5 ± 3 kcal. for the activation energy of the assumed reaction



The limits of error assigned seem rather narrow, since it is very doubtful where the real "end of the furnace" actually is. In this connection Forsyth^{47a} found that in a similar apparatus the effective end of the furnace was displaced about 4 cm. outside. There thus appears to be some question about the accuracy of the activation energies of free-radical splits as determined by the Rice technique, and in the opinion of the writer the values given might well be uncertain to ± 10 kcal. Rice and Dooley did not

⁴⁵ A. I. Dinzes, A. D. Stepukhovitch, D. A. Kyvatkovskii, and A. V. Frost, *J. Gen. Chem.* (U.R.S.S.), 7, 1754 (1937).

⁴⁶ F. O. Rice and D. M. Dooley, *J. Am. Chem. Soc.*, 65, 4245 (1933).

^{47a} J. S. A. Forsyth, *Trans. Faraday Soc.*, 37, 312 (1941).

identify the products of the reaction, and hence obtained no direct proof that the radicals formed were methyls. However, this appears to be the only reasonable assumption.

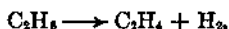
Belchetz and Rideal⁴⁷ using the technique previously described, found no evidence of radical formation and concluded that the primary reaction was



with an activation energy of 94.6 kcal. They suggest that it is possible that the reaction proceeds through the intermediate formation of ethylidene radicals,



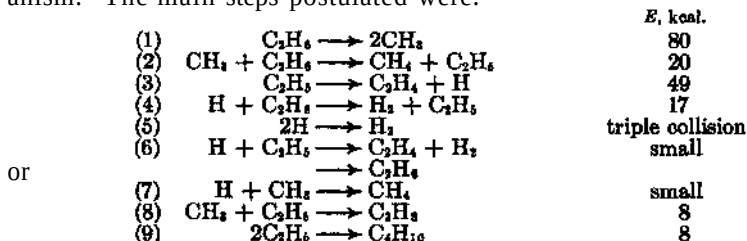
but if so they isomerize to ethylene so rapidly that they cannot be detected. However, there seems to be no doubt from Rice and Dooley's work that radicals of some sort are formed, and these cannot arise from ethylene and hydrogen in secondary reactions in any plausible way. Further, if the direct molecular split into hydrogen and ethylene is the true mechanism, Belchetz and Rideal's activation energy of 94.6 kcal. cannot be reconciled with the observed activation energy of ca. 70 kcal., since if the primary process is



no chain decomposition can be postulated. There seems therefore to be no doubt that the primary split into radicals is that postulated by Rice and Dooley. Actually, as discussed in Chapter II, Belchetz and Rideal's findings are probably vitiated by heterogeneous processes occurring on the surface of the carbon filament by means of which the pyrolysis was brought about.

Eltenton³⁶ has recently shown by means of a mass spectrometer that methyl and ethyl radicals can be detected in the ethane decomposition at pressures from 10^{-2} to 120 mm.

There thus seems to be no doubt that methyl radicals are formed in the decomposition of ethane at high temperatures: this is not proof, however, of their presence in the ordinary pyrolysis of ethane at lower temperatures. Rice and Herzfeld²³ have suggested that the kinetics of the ordinary pyrolysis can be satisfactorily explained on the basis of a free-radical mechanism. The main steps postulated were:



⁴⁷ L. Belchetz and E. K. Rideal, *J. Am. Chem. Soc.*, 57, 1168 (1935).

The activation energies allotted to the various steps were partly based on experimental data, but were mainly frankly assigned to give agreement with the free-radical mechanism. Assuming reactions (5), (7), (8), and (9) to be negligible, the customary steady-state treatment gives

$$E_{\text{overall}} = \frac{1}{2}(E_1 + E_2 + E_4 - E_6) = 73 \text{ kcal.},$$

in good agreement with the experimental value of Marek and McCluer. E_1 is the experimental value obtained by Rice and Dooley, and E_6 is probably small. $E_3 + E_4$ is merely adjusted to make the mechanism agree with experiment.

For the overall reaction rate the Rice-Herzfeld scheme leads to the expression

$$\begin{aligned} \frac{-d}{dt} [\text{C}_2\text{H}_6] &= k[\text{C}_2\text{H}_6] \\ \log k &= \frac{1}{2} \log \frac{k_1 k_3 k_4}{2k_5}, \end{aligned}$$

i.e., the reaction is of the first order as found experimentally. The calculated chain length is about 100.

It should be emphasized that the successful prediction of a first-order rate is dependent on the assumption that reactions (5), (7), (8), and (9) are negligible compared with (6). Third body restrictions probably are sufficient to allow reactions (5) and (7) to be neglected. Reactions (8) and (9) are much harder to dispose of. Rice and Herzfeld estimate that for the mechanism to hold k_9/k_6 must be $\leq 10^{-3}$. To account for this they assume $E_9 = 8 \text{ kcal.}$, and assign a steric factor to the reaction of 0.1. Reaction (8) is ruled out on the same basis. It must be admitted that this is entirely arbitrary. At any rate, provided certain assumptions were made, the Rice-Herzfeld scheme showed that it was possible to account for the kinetics of the ethane decomposition on a free-radical basis. This does not, of course, prove that the reaction does occur in this way, and actually information has been obtained from a variety of sources which bears on this point.

Patat and Sachsse^{48,49} showed by means of the para-ortho hydrogen conversion that the concentration of atomic hydrogen in a system containing decomposing ethane is much less than that predicted by the Rice-Herzfeld mechanism. Their experimental value at 590° was $[\text{H}] = 10^{-11}$ mole/liter, as compared with a predicted value of $10^{-9.2}$. However, as pointed out in Chapter II, these calculations are to be regarded with some reserve.

Direct measurement of the value of E_4 by Steacie and Phillips⁶⁰ and by Trenner, Morikawa, and Taylor⁵¹ shows that the value assigned by Rice and Herzfeld is much too high. (See VI-9.) With the experimental value

⁴⁸ F. Patat and H. Sachsse, *Z. Elektrochem.*, 41, 493 (1935).

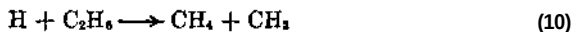
⁴⁹ H. Sachsse, *Z. physik. Chem.*, B31, 79 (1935).

⁵⁰ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 4, 461 (1936).

⁶¹ N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, 5, 203 (1937).

of about 9 kcal. in place of the 17 kcal. assumed by Rice and Herzfeld it is no longer possible to exclude reactions (8) and (9) as chain-breaking steps, and the scheme no longer predicts a first-order rate or the correct value of the activation energy.^{52,63}

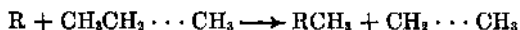
Furthermore, work on the reaction of hydrogen atoms with ethane,⁵¹⁻⁵⁴ and on the mercury photosensitized reactions of ethane^{50, 55, 56} showed methane was readily formed in systems containing hydrogen atoms and ethane, and suggested that the reaction



was faster than reaction (4). If this were so, it would have serious consequences for all the Rice mechanisms since all of Rice's ideas are based on the assumption that reactions of the type

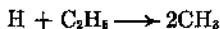


occur readily, but that hydrocarbon chain breaking reactions of the type



do not occur to any appreciable extent.

It was suggested by Rice and Teller,⁵⁷ however, that the facts could be explained without the postulation of (10), provided that we assume the ready occurrence of



This assumption is strongly supported by work on the reaction of hydrogen atoms with propane⁵⁸ and butane.⁵⁹ (Sections VI-12 and VI-15.) It has also received theoretical support.⁶⁰

It appears that the decomposition of ethane cannot be sensitized to any significant extent by free radicals. Sickman and Rice⁶¹ found that methyl radicals from decomposing azomethane would sensitize the reaction slightly. However, Echols and Pease⁶² obtained no decomposition of ethane at 425° in the presence of radicals from decomposing ethylene oxide. Similarly Steacie and Shane⁶³ found chain lengths of only about 0.3 with radicals

⁵² E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 5, 275 (1937).

⁶³ H. Sachsse, *J. Chem. Phys.*, 5, 199 (1937).

⁶⁴ E. W. R. Steacie, *J. Chem. Phys.*, 6, 37 (1938).

⁶⁶ E. W. R. Steacie and N. W. F. Phillips, *Can. J. Research*, **B16**, 303 (1938).

⁶⁶ E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research*, **B16**, 314 (1938).

⁶⁷ F. O. Rice and E. Teller, *J. Chem. Phys.*, 6, 489 (1938).

⁶⁸ E. W. R. Steacie and N. A. D. Parlee, *Trans. Faraday Soc.*, 36, 854 (1939); *Can. Research*, **B17**, 371 (1939).

⁶⁹ E. W. R. Steacie and E. A. Brown, *J. Chem. Phys.*, 8, 734 (1940).

⁶⁰ E. Gorin, W. Kauzman, J. Walter, and H. Eyring, *J. Chem. Phys.*, 7, 633 (1939).

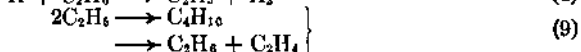
⁶¹ D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, 4, 608 (1936).

⁶² L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, 58, 1317 (1936).

⁶⁸ E. W. R. Steacie and G. Shane, unpublished work.

from decomposing ethylene oxide, mercury dimethyl and mercury diethyl at temperatures around 475°. Such experiments are, however, rather inconclusive since at the low temperatures used in sensitization experiments the equilibrium is so far over on the ethane side that the percentage decomposition to be expected is very small.

The above discussion indicates that while there is considerable indirect support for the idea that radicals participate in the ethane decomposition, there is little doubt that the mechanism proposed by Rice and Herzfeld is untenable in its original form. An investigation by Kuchler and Theile,⁶⁴ however, made a fundamental change in the situation. They reinvestigated the kinetics of the decomposition and obtained a value of 77 kcal. for the activation energy. They suggested that the Rice-Herzfeld mechanism could be made to yield a first-order rate law even if the chain terminating step is the recombination of two ethyl radicals, provided it is assumed that the initial step is bimolecular rather than unimolecular, as assumed by Rice and Herzfeld, i.e.,



or

where X is usually an ethane molecule. This leads to the rate equation

$$-\frac{d}{dt} [\text{C}_2\text{H}_6] = k_3 \left(\frac{2k_{12}}{k_9} \right)^{\frac{1}{2}} [\text{C}_2\text{H}_6] = k [\text{C}_2\text{H}_6]$$

The overall activation energy is then given by

$$E_{\text{overall}} = E_1 + \frac{1}{2}(E_{12} - E_9)$$

Rice and Herzfeld⁶⁵ have discussed this mechanism in detail. They conclude that the overall activation energy of 77 kcal. found by Kuchler and Theile can be accounted for in a way which is not incompatible with thermochemical data. Their treatment involves a number of assumptions regarding bond strengths, etc. The values which they assume are not what would probably be regarded as the "best" values to-day. We will therefore not consider their discussion, but will consider the mechanism instead in the light of the bond strength values given in Table VIII.

We are concerned with three activation energies, E_{12} , E_3 , and E_9 . If Q is the strength of the C—C bond in ethane, and E_{12} is the activation energy of the recombination of 2 methyls, i.e., the reverse of reaction 12, then

$$Q = E_{12} - E_{12}'$$

⁶⁴ L. Ktichler and H. Theile, *Z. physik. Chem.*, B42, 359 (1939).

⁶⁶ F. O. Rice and K. F. Herzfeld, *J. Chem. Phys.*, 7, 671 (1939).

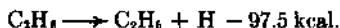
If, as seems reasonable, we assume that the activation energy of the recombination of two ethyls does not differ appreciably from that for two methyls, then

$$E_{12}' \sim E_6$$

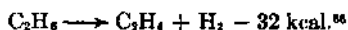
Hence

$$E_{12} - E_3 \sim Q$$

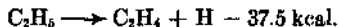
We also need the heat of reaction (3). If we take the strength of the C—H bond in ethane as 97.5 kcal., then



Now



Whence we get



The activation energy of the reverse of reaction (3) is very small, certainly not over 5 kcal. Hence $E_3 \sim 43$ kcal. Using 87.0 kcal. for Q , we therefore have

$$E_{\text{overall}} = 43 + \frac{1}{2} \times 87 = 86.5 \text{ kcal.}$$

This is far too high. If we put $E_3 = 39$, which is about as low as seems possible, and accept Rice and Dooley's value of $E_n = 80$ kcal., which

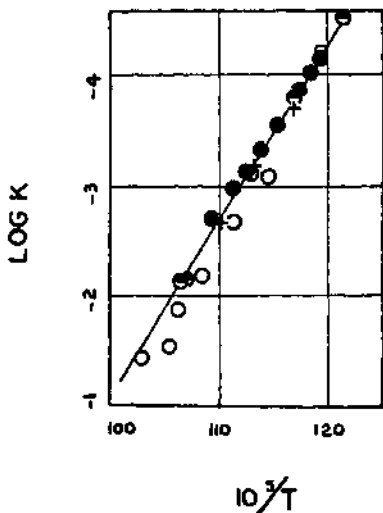


Figure 8. Comparison of results on decomposition of ethane.

Sachse, +
Marek and McCluer, ○
Storch and Kassel, □
Kuchler and Theile, ●
Steacie and Puddington, ●

seems certainly too low we can get $E_{\text{overall}} 79$ kcal. in fair agreement with Kuchler and Theile's observed value. However, this involves a considerable straining of values, and it would seem impossible to reconcile the Kuchler-Theile modification of the Rice-Herzfeld mechanism with any value of Overall much below 80 kcal.

⁶⁶ F. R. Bichowsky and F. D. Rossini, *Thermo-Chemistry of Chemical Substances*, New York, 1936.

Steacie and Shane⁶⁷ reinvestigated the thermal decomposition, and confirmed the previous lower estimates of the activation energy. Their value was 68.7 kcal. It should be emphasized that all investigations of the ethane decomposition are relatively inaccurate on account of difficulties associated with the occurrence of the back reaction. A comparison of the results of different workers is given in Table XI, and the results are given in Figure 8 in the form of a $\log k - 1/T$ plot. This shows that the results of Marek and McCluer are definitely out of line with those of other workers. A "best" line through the remaining points definitely favors the lower value of the activation energy, and makes it very unlikely that the true value lies above 72 kcal.

The lower value of the activation energy is also supported by a comparison of the activation energies of the decomposition reactions of the lower straight chain paraffins. Thus with Steacie and Shane's value for ethane we have

Substance	E, kcal.
CH ₄	79.5 ⁶⁸
C ₂ H ₆	68.7 ⁶⁷
C ₃ H ₈	83.3 ⁶⁹
n-C ₄ H ₁₀	58.7 ⁷⁰

TABLE XI. SUMMARY OF RESULTS OF DIFFERENT OBSERVERS

Temp., °K.	Observer	Mean value of rate constant, sec. ⁻¹
824	Kuchler and Theile	0.28 X 10 ⁻⁴
838	Storch and Kassel	0.60
838	Steacie and Puddington	0.68
845	Steacie and Puddington	0.89
853	Steacie and Puddington	1.16
856	Sachsse	1.83
856	Kuchler and Theile	1.5
868	Steacie and Puddington	2.76
873	Marek and McCluer	7.9
880	Steacie and Puddington	4.62
886	Sachsse	7.4
887	Kuchler and Theile	7.8
889	Steacie and Puddington	7.43
898	Marek and McCluer	21.0
898	Steacie and Puddington	10.5
910	Sachsse	20.8
913	Steacie and Puddington	17.1
922	Marek and McCluer	66.4
934	Kuchler and Theile	73
938	Kuchler and Theile	75
941	Marek and McCluer	136
948	Marek and McCluer	294
973	Marek and McCluer	361

⁶⁷ E. W. R. Steacie and G. Shane, *Can. J. Research*, **B18**, 203 (1940).

⁶⁸ L. S. Kassel, *J. Am. Chem. Soc.*, **54**, 3949 (1932).

⁶⁹ E. W. R. Steacie and I. E. Puddington, *Can. J. Research*, **B16**, 411 (1938).

⁷⁰ E. W. R. Steacie and I. E. Puddington, *Can. J. Research*, **B16**, 176 (1938).

This gives a much more regular gradation of values than would a higher value for the activation energy of the ethane decomposition.

If we accept the lower value for the activation energy, it would appear to rule out the Kuchler-Theile mechanism. Indeed, the lower the activation energy, the more stringent are the requirements for a free-radical mechanism. Thus if the activation energy of the overall reaction were equal to that of the primary split into radicals, all that would be necessary for a free-radical mechanism would be to postulate secondary reactions which were fast compared with the primary step. The primary step would then be rate-controlling, and the activation energy would be accounted for without the necessity of postulating reaction chains. The order of the reaction would also be accounted for, since if the primary step were first order the overall reaction would also be first order. If, however, the activation energy of the overall reaction is much lower than that of the primary step, then the process can only be accounted for on a free-radical basis by the assumption of long reaction chains.

It is also of interest to compare the falling-off in the velocity constants with diminishing pressure for the decomposition reactions of the lower paraffins; very roughly we have the values given in Table XII.

TABLE XII

Substance	Approximate pressure at which $k_{\infty}/k = 1.5$
C_2H_6	70-90 mm.
C_3H_8	60-80
$n-C_4H_{10}$	170-220
$iso-C_4H_{10}$	40-60

If the paraffin decompositions were ordinary first order reactions, we would expect the more complex molecules to show the falling-off in rate at much lower pressures than the simpler ethane molecule. The complete lack of regularity here seems strong evidence that at least some of the decompositions proceed by complex mechanisms.

A number of workers have investigated the inhibition of the ethane decomposition by nitric oxide. Staveley⁷¹ found that small amounts of nitric oxide caused marked inhibition of the reaction at 620°. The mean chain length varied from 20.6 at 50 mm. ethane pressure to 6.4 at 500 mm. He concluded that only a small fraction of the activated ethane molecules decompose primarily into radicals, the great majority rearranging directly into ethylene and hydrogen. He postulated very few chains, but with lengths of the order of 10^5 to 10^7 units.

Hobbs and Hinshelwood⁷² made an investigation of the effect of nitric

⁷¹ L. A. K. Staveley, *Proc. Roy. Soc. (London)*, A162, 557 (1937).

⁷² J. E. Hobbs and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A167, 447 (1938).

oxide on the ethane decomposition at 600°. They concluded that the chain length varied from 9.8 at 57 mm. to 4.1 at 454 mm. (Table XIII). The apparent chain length was found to be proportional to $[\text{C}_2\text{H}_6]^{0.35}$.

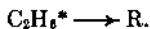
TABLE XIII. VARIATION OF APPARENT CHAIN LENGTH
WITH ETHANE PRESSURE AT 600°

Ethane pressure, mm.	Mean Chain Length
57	9.8
100	6.5
300	5.9
454	4.1

It is possible to draw certain conclusions as to mechanism from the effect of ethane concentration on inhibition. Since the general argument used here is frequently employed by Hinshelwood and his collaborators, we will develop the argument employed by Hobbs and Hinshelwood rather fully.

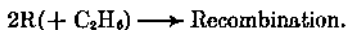
Let us assume the mechanism of the reaction, in a general way, to be as follows. Let the concentration of activated ethane molecules which give rise to radicals be a , and let the concentration of normal ethane molecules be n . Then the following steps will play a part in the reaction.

- (1) Activated ethane molecules form radicals.



The rate of this step is given by k_1a . a is an unknown function of the concentration of ethane (i.e., the order of the reaction which forms radicals is unknown). We can put $a = n^x$. x is presumably between 1 and 2.

- (2) Recombination of radicals takes place.



This may be binary, or ternary with ethane molecules acting as third bodies. We may therefore put the rate as

$$k_2[\text{R}]^2n^y,$$

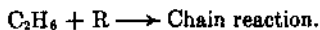
where $y = 0$ for binary recombination and $y = 1$ for ternary recombination. If both mechanisms operate, y will be between 0 and 1 and will be expected to vary with the ethane pressure.

(3) A rearrangement reaction may also be considered in which ethane gives products without the intermediate formation of radicals. The rate of this will be given by

$$k_3f_2(n),$$

where $f_2(n)$ is an unknown function of the ethane concentration.

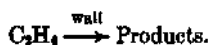
(4) Reaction chains will presumably be propagated by a reaction between a radical and an ethane molecule



The rate will be given by

$$k_4[\text{R}]n.$$

(5) A surface reaction may also be important,



The rate of this may be denoted by s .

(6) In the presence of nitric oxide the chains will almost certainly be broken by a bimolecular reaction between a radical and NO,



with the rate $fo[\text{R}][\text{NO}]$.

In the stationary state we have

$$\frac{d[\text{R}]}{dt} = 0 = k_1 a - k_2 [\text{R}]^2 n^y - k_3 [\text{R}][\text{NO}].$$

Whence

$$[\text{R}] = \frac{-k_3[\text{NO}] + \{(k_3[\text{NO}])^2 + 4k_1k_2an^y\}^{\frac{1}{2}}}{2k_2n^y}.$$

Let p be the rate of the reaction, p_0 that in the absence of NO, and p_0 the rate corresponding to maximum inhibition.

The total rate of the reaction is

$$p = k_3 f_1(n) + k_4 [\text{R}]n + s.$$

Substituting for $[\text{R}]$

$$p = s + k_3 f_1(n) + \frac{k_4 n}{2k_2 n^y} [-k_3[\text{NO}] + \{(k_3[\text{NO}])^2 + 4k_1k_2an^y\}^{\frac{1}{2}}]$$

and p_0 , the rate when $[\text{NO}] = 0$ will be

$$p_0 = s + k_3 f_1(n) + \frac{k_4 n}{2k_2 n^y} (4k_1k_2an^y)^{\frac{1}{2}}.$$

When $[\text{NO}]$ is large, the limiting rate p_{∞} is given by

$$p_{\infty} = s + k_3 f_2(n).$$

Whence we get

$$\frac{p - p_{\infty}}{p_0 - p_{\infty}} = \{(\gamma[\text{NO}])^2 + 1\}^{\frac{1}{2}} - \gamma[\text{NO}], \quad (1)$$

where

$$\gamma = \frac{k_3}{(4k_1k_2)^{\frac{1}{2}}} [\text{C}_2\text{H}_6]^{-\frac{x+y}{2}}. \quad (2)$$

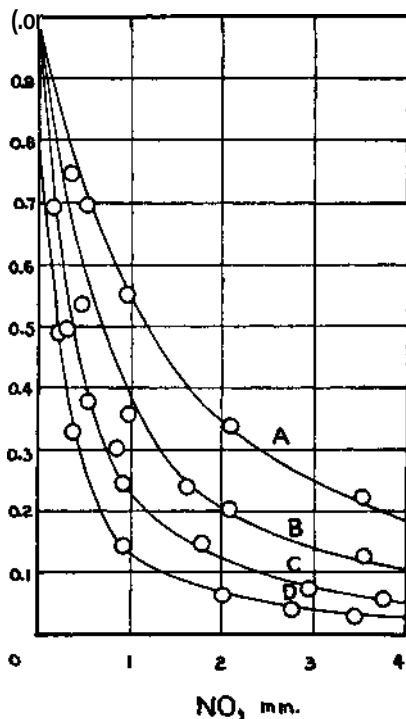
When $[\text{C}_2\text{H}_6]$ is constant, γ is constant, while for varying ethane y will vary as indicated.

This treatment is made use of as follows: A curve is plotted giving the variation of $\frac{p - p_{\infty}}{p_0 - p_{\infty}}$ with the nitric oxide pressure, for various ethane pressures. (See Figure 9.) It is found that the experimental points are excellently fitted by equation (1) if values of γ are chosen as follows:

Figure 9. Inhibition of ethane decomposition by nitric oxide.

A, 454 mm., $y = 0.65$
 B, 300 mm., $y = 1.15$
 C, 100 mm., $y = 2.10$
 D, 57 mm., $y = 3.60$

$$\frac{P - P_{\infty}}{P_0 - P_{\infty}}$$



Ethane pressure,
mm.

454	0.65
300	1.15
100	2.10
57	3.60

From equation (2)

$$\log \gamma = \text{Const.} - \frac{x+y}{2} \log [C_2H_6].$$

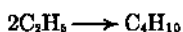
Hence by plotting $\log \gamma$ against $\log [C_2H_6]$ we can determine the value of $x + y$. This gives

$$x + y \sim 1.66.$$

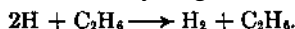
Now x cannot be less than 1, and is almost certainly between 1 and 2. Hence since y cannot be negative it must be between zero and 0.66. This suggests recombination by both binary and ternary collisions. Hobbs and Hinshelwood show that if we put $y = 0.66$ it leads to the experimental result that the apparent chain length is proportional to $C_2H_6]^{-0.36}$, and that any other value gives less exact agreement. They therefore adopt the values $x = 1$, $y = 0.66$.

There are two possible ways in which these results may be explained
 (a) A single chain-ending process, the order of which varies with the pres-

sure owing to the formation of an activated complex the average life of which is comparable with the time between collisions, (b) Two independent chain-ending processes one involving binary collisions and one ternary. The latter seems the more likely alternative, and it seems probable that the binary collision process is the recombination of two free radicals, such as



while the ternary process involves hydrogen atoms, *i.e.*,



If this is so, then instead of the rate expression for the recombination

$$k_2\text{R}^2[\text{C}_2\text{H}_6]^y,$$

we should have the more exact expression.

$$k_2\text{R}^2 + k_2'\text{R}^2[\text{C}_2\text{H}_6].$$

If we express $[\text{C}_2\text{H}_6]$ in mm., then

$$k_2 + k_2'[\text{C}_2\text{H}_6]$$

will vary approximately in the : $k[\text{C}_2\text{H}_6]^0$ ⁵⁸ ;

if $\frac{k_2'}{k_2} = 1.32 \times 10^{-2}$.

On this basis the ratio of binary to ternary recombination processes is unity at 76 mm. pressure, the binary processes predominating at lower pressures, and the ternary at higher. It should be noted that if this argument is correct the chain-ending processes are not those postulated by Rice and Herzfeld, and their mechanism would no longer predict a first order rate. As we have seen, there is other evidence which points to the same conclusion. However, the treatment of the inhibition results given of Hobbs and Hinshelwood is rather elaborate, and it is a matter of some doubt how much reliance may be placed on their detailed conclusions regarding the chain-ending process.

The inhibition of the ethane decomposition has also been investigated by Steacie and Shane,⁷³ who obtained results in general agreement with those of Hobbs and Hinshelwood. Their investigation was primarily concerned with the evaluation of the activation energy of the inhibited reaction, and they found a value of 77.3 kcal., in fair agreement with the results of Staveley who obtained 74.5 kcal. The normal non-chain reaction thus definitely has an activation energy considerably greater than that of the overall reaction. It is, however, undoubtedly less than that of the chain-initiating split into radicals, and hence most ethane molecules which decompose do not form free radicals. Those molecules which do form radicals,

⁷³ E. W. R. Steacie and C. Shane, *Can. J. Research*, **B18**, 351 (1940).

however, appear to initiate long chains, and hence most of the ethane decomposing does so via the chain process.

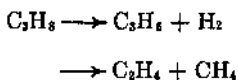
The inhibition was also investigated by Gray, Travers, and White⁷⁴ by an analytical method. They found an initial retardation of pressure increase in the decomposition which they interpreted as due to a rapid initial reaction between ethane and nitric oxide without a pressure increase. They further postulated that this ethane-nitric oxide reaction has a lower activation energy than the primary decomposition process, thus replacing the latter. However, in view of the general agreement of other workers, the results of Gray, Travers, and White seem open to question.

Work on inhibition thus furnishes support for the idea that the decomposition of ethane is complex, and that chain processes are involved to some extent. However, the chain lengths found are much too short to be in accord with mechanisms of the Rice-Herzfeld type. All in all the evidence indicates that the ethane decomposition proceeds partially by a direct molecular rearrangement and partially by a free-radical mechanism. In spite of the large amount of work on the reaction the mechanism of the chain part of the decomposition is still open to question. It appears probable, however, that the chain part of the reaction proceeds by a mechanism of the general type proposed by Rice and Herzfeld. There is no question, however, that the Rice-Herzfeld mechanism is definitely untenable when applied to the total reaction.

6. Propane and the Butanes

The behaviour of propane and the butanes is, in general, similar to that of ethane. There is considerable evidence that free-radical processes participate in these reactions. As with ethane, however, it appears to be unlikely that the whole reaction occurs by a free-radical chain mechanism. The evidence is much more sketchy, however, and it is not possible to draw very definite conclusions.

Early papers^{75,76} on the propane decomposition showed that the reaction was homogeneous and of the first order, the main course being



or

together with reactions leading to the formation of smaller amounts of ethane and butane.

⁷⁴ J. T. Gray, M. W. Travers, and F. T. White, *Proc. Roy. Soc. (London)*, **A167**, 15 (1938).

⁷⁵ R. N. Pease, *J. Am. Chem. Soc.*, **50**, 1779 (1928).

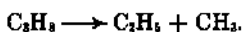
⁷⁶ F. E. Frey and D. F. Smith, *Ind. Eng. Chem.*, **20**, 948 (1928).

⁷⁷ R. N. Pease and E. S. Durgan, *J. Am. Chem. Soc.*, **62**, 1262 (1930).

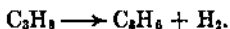
⁷⁸ V. Schneider and P. K. Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931).

The kinetics of the reaction have been investigated by a number of workers.^{79,82} The activation energy is about 63 kcal. Dinzes and Frost⁸² found that the first order rate constants fell off badly during the course of an experiment, and they developed an equation for the rate constant similar to that given for ethane. In view of the complexity of the reaction they concluded that it proceeded by a free-radical mechanism. Steacie and Puddington^M arrived at the same conclusion on the grounds that the rate constants fell off with pressure in a way which was much too pronounced for the simple unimolecular decomposition of a molecule as complex as propane.

Rice and his co-workers^{84, 85} detected free radicals in the decomposition of propane at high temperatures, and obtained a value of 71.5 kcal. for the activation energy of the reaction



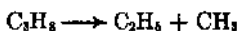
Rice¹ points out, however, that the values of the activation energies of the split into radicals may be somewhat low in the case of large molecules, since we may have a primary dehydrogenation to form an olefin and hydrogen,



The C—C bond in propylene which attaches the methyl group to the rest of the molecule is weak, and hence some methyl radicals may arise by



He therefore suggests that the true activation energy of the reaction



is higher than that found, and is probably about 79 kcal. He also⁸⁶ suggested a mechanism for the decomposition similar to the Rice-Herzfeld mechanism for ethane.

Belchetz and Rideal⁸⁷ were unable to detect free radicals in the decomposition, as discussed elsewhere, but it appears certain that their work was affected by heterogeneous processes occurring on the surface of the carbon filament used in their work.

In a very rough qualitative investigation Evering⁸⁸ found that the de-

⁷⁹ L. F. Marek and W. B. McCluer, *Ind. Eng. Chem.*, 23, 878 (1931).

⁸⁰ R. E. Paul and L. F. Marek, *Ind. Eng. Chem.*, 26, 454 (1934).

⁸¹ F. E. Frey and H. J. Hepp, *Ind. Eng. Chem.*, 25, 441 (1933).

⁸² W. A. I. Dinzes and A. V. Frost, *J. Gen. Chem. (U.S.S.R.)*, 3, 747 (1933); *Compt. Rend. Acad. Sci. (U.R.S.S.)*, 4, 153 (1933), 5, 513 (1934).

⁸³ E. W. R. Steacie and I. E. Puddington, *Can. J. Research*, B16, 411 (1938).

⁸⁴ F. O. Rice, W. R. Johnston, and B. L. Evering, *J. Am. Chem. Soc.*, 54, 3529 (1932).

⁸⁵ F. O. Rice and W. R. Johnston, *J. Am. Chem. Soc.*, 56, 214 (1934).

⁸⁶ F. O. Rice, *J. Am. Chem. Soc.*, 55, 3035 (1933); *Trans. Faraday Soc.*, 30, 152 (1934).

⁸⁷ L. Belchetz and E. K. Rideal, *J. Am. Chem. Soc.*, 57, 2466 (1935).

⁸⁸ B. L. Evering, *J. Am. Chem. Soc.*, 61, 1400 (1939).

composition products from propane removed lead mirrors with the production of lead tetramethyl.

Patat⁸⁹ determined the hydrogen atom concentration during the decomposition by means of the para-ortho hydrogen conversion. As with ethane, he found a concentration of hydrogen atoms far too small to agree with the Rice-Herzfeld type of mechanism.

There is much evidence to show that the decomposition of propane can be sensitized by free radicals. Sickman and Rice⁹⁰ found that methyl radicals from the decomposition of azomethane caused some decomposition of propane. Echols and Pease⁹¹ showed that radicals from ethylene oxide decomposed propane at 425°. The chain length was calculated by comparing the amount of olefin formed with the amount of carbon monoxide resulting from the ethylene oxide decomposition. They obtained a mean chain length of 0.55. This is probably too low by a factor of about 3, since the indications are that on the average only about 0.3 methyl radical results from the decomposition of one molecule of ethylene oxide. In any case it is, of course, only an average chain length, and it is possible that there are a few long chains rather than many short ones. It should also be remarked that short chain lengths at temperatures much below the normal decomposition temperature do not necessarily mean that there are not long chains at higher temperatures, since an essential chain propagating step may be too slow at the lower temperature.

Hobbs and Hinshelwood⁹² investigated the inhibition of the propane decomposition by nitric oxide. The results were very similar to those for ethane. The apparent chain length at 550° varied from 3.3 at 501 mm. pressure to 10.1 at 23 mm. (Table XIV).

TABLE XIV. VARIATION OF APPARENT CHAIN LENGTH
WITH PROPANE PRESSURE AT 550°

Propane pressure, mm.	Chain length
23	10.1
50	9.9
103	7.5
211	4.9
306	4.1
501	3.3

They point out that the apparent chain lengths are really dependent on three different activation energies, viz., of the radical forming process, the rearrangement process, and the chain-propagating process. They conclude very roughly that the activation energies of the chain-propagating

⁸⁹ F. Patat, *Z. physik. Chem.*, **B32**, 274 (1936).

⁹⁰ D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, **4**, 608 (1936).

⁹¹ L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, **58**, 1317 (1936).

⁹² J. E. Hobbs and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A167**, 447 (1938).

process are 10 kcal. for methane and ethane, 9 kcal. for propane, and 6 kcal. for hexane. (Note that in the Rice-Herzfeld mechanism for ethane reaction (4) is the chain-propagating process, and $E_4 \sim 9$ kcal.)

Further evidence for the free-radical nature of the decomposition comes from the work of Rice and Polly⁹³ who found that the reaction was strongly inhibited by propylene.

All in all, the status of the propane decomposition appears to be similar to that of ethane. Much evidence of the participation of radicals exists, but it appears certain that the rearrangement reaction is also occurring to a large extent.

A considerable amount of work has been done on the decomposition of the butanes, mostly on n-butane. Early work served to show^{94,97} that the reactions were homogeneous and approximately first order, and that their main course could be represented by

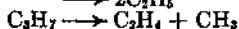


Reactions (2) and (3) are the predominant ones with n-butane, and (1) and (2) with iso-butane.

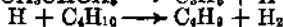
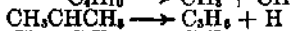
Paul and Marek⁹⁸ studied the kinetics of the two decompositions. They obtained activation energies of 73.9 kcal. for n-butane and 66.0 for iso-butane. Their work, however, was rather rough. A more thorough investigation of the two reactions " gave the values 58.7 kcal. for n-butane and 63.5 kcal. for iso-butane.

It was shown that free radicals could be detected in the high temperature decomposition of the butanes by Rice, Johnston, and Evering,⁸⁴ and the activation energy of the free-radical split was found to be 65.4 kcal. for n-butane by Rice and Johnston.⁸⁵ As pointed out in the case of propane, this value is probably too low owing to primary unsaturation followed by the decomposition of the olefin thus produced. Rice assumes that the decompositions proceed by the following mechanisms:

n-butane



iso-butane



etc.

⁹⁸ F. O. Rice and O. L. Polly, *J. Chem. Phys.*, 6, 273 (1938).

⁹⁴ R. N. Pease, *J. Am. Chem. Soc.*, 50, 1779 (1928).

⁹⁶ R. N. Pease and E. S. Durgan, *J. Am. Chem. Soc.*, 62, 1262 (1930).

⁹⁷ C. D. Hurd and L. U. Spence, *J. Am. Chem. Soc.*, 51, 3353 (1929).

⁹⁷ A. Cambron, *Can. J. Research*, 7, 646 (1932).

⁹⁸ R. E. Paul and L. F. Marek, *Ind. Eng. Chem.*, 26, 454 (1934).

⁹⁹ E. W. R. Steacie and I. E. Puddington, *Can. J. Research*, B16, 176, 260 (1938).

In a rough qualitative investigation Evering⁸⁸ found that decomposing w-butane removed lead mirrors, and he identified lead tetramethyl in the products. This furnishes further evidence for the production of methyl radicals in the butane decomposition.

As in the case of ethane and propane, Belchetz and Rideal obtained results completely at variance with those of Rice and his collaborators, and concluded that the initial reaction was a direct molecular rearrangement into butane and hydrogen. In this case also the evidence strongly favors Rice's results, and it is probable that Belchetz and Rideal's results were complicated by heterogeneous processes on the surface of the carbon filament. It may therefore be assumed that the detection of radicals in the high temperature decomposition of the butanes is valid.

As far as the products of the reactions are concerned, the Rice mechanisms for the butanes are in fair agreement with experiment, as shown by Table XV.

TABLE XV. COMPARISON OF PRODUCTS OF THE BUTANE DECOMPOSITIONS WITH THOSE PREDICTED BY THE RICE THEORY

Product	n-butane		iso-butane	
	observed," per cent	calculated, per cent	observed," per cent	calculated per cent
C ₂ H ₄	15.2	21	0.9	0
C ₂ H ₆	14.1	21	0.9	0
CaHe	33.9	29	14	24
CH ₄	33.9	29	14	24
H ₂	2.9	0	35	26
iso-C ₄ H ₈	0	0	35	26

There is considerable evidence to show that the decomposition of the butanes can be sensitized by free radicals. Heckert and Mack¹⁰⁰ found that the decomposition of n-butane was sensitized by radicals from the decomposition of ethylene oxide. Echols and Pease¹⁰¹ investigated this in more detail. Their experiments were carried out at 425° and a pressure of 500 mm. The ratio of unsaturated substances produced from butane to the carbon monoxide produced from the decomposition of ethylene oxide gave a measure of the chain length, as shown by Table XVI.

TABLE XVI. SENSITIZED DECOMPOSITION OF n-BUTANE BY ETHYLENE OXIDE

Substance	Initial ratio	Products
	$\frac{\text{Hydrocarbon}}{(\text{CH}_2)_2\text{O}}$	$\frac{\text{C}_n\text{H}_m}{\text{CO}}$
iso-butane	1.7	0.75
n-butane	1.6	1.2
	4.1	4.5
	8.0	12.0

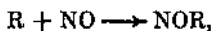
¹⁰⁰ W. W. Heckert and E. Mack, *J. Am. Chem. Soc.*, 61, 2706 (1929).

¹⁰¹ L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, 68, 1317 (1936).

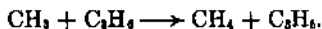
These results prove definitely that chains (of rather short length) can be set up in the decomposition of the butanes. The chain length becomes appreciable at high ratios of hydrocarbon to ethylene oxide.

Other evidence on the sensitization of the decomposition of n-butane comes from the work of Frey¹⁰² who found that the addition of 1 per cent of dimethyl mercury to n-butane at 525° brought about the decomposition of 20 equivalents of butane.

Further evidence for the participation of free radicals in the decomposition comes from experiments on its inhibition. Rice and Polly⁹³ found that the decomposition of n-butane at 512° was strongly retarded by propylene. In general its action is less efficient as an inhibitor than is nitric oxide. This may be due as Rice and Polly suggest to the fact that nitric oxide combines with and removes the chain carriers



while propylene probably reacts with the chain carrier and replaces it with the allyl radical, which might be less efficient as a chain carrier, viz.,



Stearie and Folkins¹⁰³ investigated the inhibition by nitric oxide of chains which had been set up in n-butane at 450° by the addition of ethylene oxide. They concluded that a certain amount of residual chain decomposition occurred at all NO concentrations, the chain length being about 4 for the maximally inhibited reaction, and hence that maximum inhibition of the decomposition of n-butane in the ordinary way does not necessarily correspond to complete suppression of chains.

In a later paper¹⁰⁴ the same authors investigated the inhibition by NO of the normal decomposition of n-butane. Their results were similar to those of other workers with propane and ethane. Chain lengths of 3 to 6 were found, and as with other hydrocarbons the inhibition decreased with increasing butane pressure. This suggests a mechanism of chain termination similar to that for ethane, i.e., by ternary collisions. The temperature coefficient of the inhibited reaction varied strongly with the pressure. The apparent activation energies, taken from initial rates, are shown in Table XVII.

TABLE XVII. APPARENT ACTIVATION ENERGY OF INHIBITED DECOMPOSITION OF n-BUTANE

Initial C ₄ H ₁₀ pressure, cm.	60	32	16	8
Apparent <i>E</i> , kcal.	64.0	71.1	85.2	93.9

¹⁰² F. E. Frey, *Ind. Eng. Chem.*, 26, 198 (1934).

¹⁰³ E. W. R. Steacie and H. O. Folkins, *Can. J. Research*, **B17**, 105 (1939).

¹⁰⁴ E. W. R. Steacie and H. O. Folkins, *Can. J. Research*, **B18**, 1 (1940).

If these are extrapolated to infinite pressure, we obtain for the high pressure rate a value of 57.2 kcal., as compared with 58.7 for the normal reaction.

The products of the inhibited reaction were found to be the same as those of the normal reaction (Table XVIII).

TABLE XVIII. PRODUCTS OF *n*-BuTANE DECOMPOSITION

Product, mole per cent	525° <i>butane pressure</i> = 60 cm.						Percent decomposition
	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₄ H ₈	
No nitric oxide added	6.7	29.9	13.8	14.4	27.1	8.1	26.6
2 cm. nitric oxide added	7.1	25.3	14.1	14.4	29.6	9.2	25.9

This makes it difficult to consider a mechanism in which there is both a molecular rearrangement and a chain reaction consisting of relatively few, but very long, chains. In such a case complete suppression of chains would leave only the molecular decomposition. It seems very unlikely, however, that both mechanisms should lead to identical products, since it would be necessary to have three separate molecular splits, to C₄H₈ + H₂, C₃H₆ + CH₄, and C₂H₄ + C₂H₆, combined in exactly the right proportions to duplicate the products of the chain reaction.

They therefore suggest that the normal decomposition involves a large number of relatively short chains, and that the addition of nitric oxide merely diminishes the chain length without completely suppressing the chain reaction. Under these circumstances, provided that the residual chain length is appreciable, there is no reason to expect much alteration in the products of the reaction.

Echols and Pease made a detailed investigation of both the normal¹⁰⁵ and the inhibited¹⁰⁶ reaction. They paid attention to the later phases of the reaction, as well as the initial stage and concluded that it was highly complex. The order was about 1.3 in the early stages, and there was a strong retardation by the products in the later stages. This retardation was mainly due to propylene.

The reaction was found to be inhibited by nitric oxide, the apparent chain length being about 20. The inhibition was only transitory, however, and the rate became normal after about 15 per cent reaction. They suggested that the transient effect was due to an equilibrium



¹⁰⁵ L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, **61**, 208 (1939).

¹⁰⁶ L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, **59**, 766 (1937), **60**, 1701 (1938), **61**, 1024 (1939).

the complex RNO dissociating and "feeding-back" radicals to the system. The reaction was also found to be inhibited by propylene in the same transitory manner.

To sum up, it would appear that as with ethane there is definite evidence for the participation of radicals in the propane and butane decompositions, but it appears to be very unlikely that the entire decomposition proceeds by a free-radical chain mechanism.

7. Dimethyl Ether

A large number of investigations have been made with a variety of ethers. The most thoroughly investigated are dimethyl ether and diethyl ether, and we will confine our attention almost entirely to these.

The decomposition of dimethyl ether¹⁰⁷ leads to the products represented by the equation



It is approximately of the first order, and the limiting high pressure rate constants are given by

$$\log k = 13.2 - \frac{58,500}{2.3 RT} \text{ sec.}^{-1}.$$

Free radicals were detected in the decomposition by the Paneth technique by Rice and Johnston.¹⁰⁸ They estimated the activation energy of the split into radicals to be 81.1 kcal. This is somewhat lower than the usual estimates of the C—O bond strength in ethers; thus Baughan, Evans, and Polanyi¹⁰⁹ estimate 87 kcal. Rice and Herzfeld¹¹⁰ suggested the following chain mechanism for the reaction:

		<i>E</i> , kcal.
(1)	$\text{CH}_3\text{OCH}_3 \longrightarrow \text{CH}_3 + \text{CH}_3\text{O}$	80
(2)	$\text{CH}_3\text{O} + \text{CH}_3\text{OCH}_3 \longrightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{OCH}_3$	15-25
(3)	$\text{CH}_3\text{O} \longrightarrow \text{HCHO} + \text{H}$	20-45
(4)	$\text{H} + \text{CH}_3\text{OCH}_3 \longrightarrow \text{H}_2 + \text{CH}_2\text{OCH}_3$	10-15
(5)	$\text{CH}_3 + \text{CH}_3\text{OCH}_3 \longrightarrow \text{CH}_4 + \text{CH}_2\text{OCH}_3$	15
(6)	$\text{CH}_2\text{OCH}_3 \longrightarrow \text{CH}_3 + \text{HCHO}$	38
(7)	$2\text{CH}_3 \longrightarrow \text{C}_2\text{H}_6$	8
(8)	$\text{CH}_3 + \text{CH}_2\text{OCH}_3 \longrightarrow \text{C}_2\text{H}_5\text{OCH}_3$	8
(9)	$2\text{CH}_2\text{OCH}_3 \longrightarrow (\text{CH}_3\text{OCH}_2)_2$	8

This leads in the usual way to

$$\log k = 14.5 - \frac{62,500}{2.3 RT} \text{ sec.}^{-1}$$

in reasonable agreement with experiment. The calculated chain length is of the order of 10^5 . (In a later estimate¹ Rice puts $E_1 = 80$ kcal., $E_6 = 25$ kcal.)

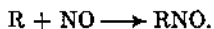
¹⁰⁷ C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc. (London)*, **A115**, 215 (1927).

¹⁰⁸ F. O. Rice and W. R. Johnston, *J. Am. Chem. Soc.*, **56**, 214 (1934).

¹⁰⁹ E. C. Baughan, M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

¹¹⁰ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

There is a considerable variety of evidence for the existence of chains in the reaction. Pease¹¹¹ found the reaction to be retarded by an increase in the surface-volume ratio of the reaction vessel, as frequently occurs with chain reactions in which the chains end by wall recombination. The reaction is also inhibited by nitric oxide.¹¹² The chain length calculated in the usual way is about 17 at 813°K. It appears from these results that about 1 collision in 1500 of nitric oxide with radicals is effective in breaking the chains, corresponding to an activation energy of 10 to 12 kcal. for the reaction



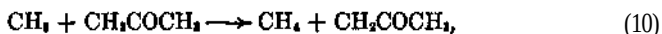
The decomposition is also inhibited by propylene,¹¹³ although as usual much larger quantities are required than is the case with nitric oxide.

The reaction has been investigated by the para-ortho hydrogen method by Patat.¹¹⁴ In this case very considerable catalysis of the conversion occurs, but as usual he concludes that only a small fraction of the decomposition proceeds via radicals. He calculates that the fraction is about 10^{-3} if the chains end by radical recombination in the gas phase, or about $10^{-1.6}$ if the recombination is heterogeneous. These calculations are open to the objections previously discussed (II-7).

Leermakers¹¹⁵ showed that the decomposition of methyl ether could be sensitized by free radicals. He photolysed acetone, as a source of methyl radicals, in the presence of dimethyl ether at temperatures from 270° to 400°. The methane produced in the ether decomposition was used as a measure of the rate, and it was found that the results could be expressed by

$$\frac{d}{dt} [CH_4] = k \sqrt{\frac{I_{abs}}{[CH_3COCH_3]}} [CH_3OCH_3].$$

The temperature coefficient of methane production corresponded to an activation energy of 16 kcal. At low light intensities and low acetone concentrations quantum yields up to 230 were obtained at 400°. Leermakers used a mechanism for the acetone decomposition which is discussed under that heading (III—14), and combined it with one of the Rice-Herzfeld type for the ether decomposition, *i.e.*, he assumed that methyl radicals from the acetone photolysis either react with acetone



¹¹¹ R. N. Pease, *J. Am. Chem. Soc.*, **59**, 425 (1937).

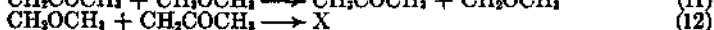
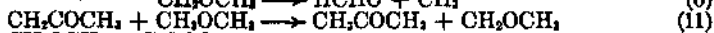
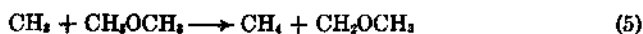
¹¹² L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A159**, 192 (1937), **A164**, 335 (1936); P. F. Gay and M. W. Travers, *Nature*, **138**, 546 (1936).

¹¹³ F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

¹¹⁴ F. Patat, *Z. physik. Chem.*, **B32**, 294 (1936).

¹¹⁵ J. A. Leermakers, *J. Am. Chem. Soc.*, **56**, 1899 (1934).

or else react with ether and we then have



This gives general agreement with experiment if we assume $E_h = 15$ kcal., $E_6 = 35$ kcal., $E_{11} = 20$ kcal, and $E_{12} = 10$ kcal. E_5 and E_6 are in good agreement with the values assumed by Rice and Herzfeld.

Leermakers' work gives definite proof that methyl radicals can set up long chains in methyl ether. It does not, however, necessarily prove that such chains are the predominant process in the ordinary decomposition.

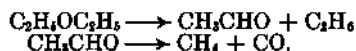
Klute and Walters^{115a} have investigated the decomposition of dimethyl ether at 523°, sensitized by the addition of 1 per cent of diacetyl. The sensitization was quite efficient. The sensitized decomposition was largely inhibited by the addition of nitric oxide. The inhibition was not complete, however, since the inhibited sensitized rate was still considerably greater than the rate of the inhibited unsensitized decomposition.

8. Diethyl Ether

The decomposition of diethyl ether has been much investigated. The original investigation of Hinshelwood¹¹⁶ showed that the overall reaction was mainly



together with a certain amount of condensation products and of ethane. At least a part of the reaction appeared to proceed via acetaldehyde, viz.,



The reaction was approximately of the first order, the rate constants falling sharply, however, at lower pressures. Hinshelwood found an activation energy of 53 kcal. The reaction was somewhat inhibited by the products.

Rice has suggested a chain mechanism for the reaction, which is, in general, identical with that given above for methyl ether. There are a large number of rather varied investigations which support the idea that the reaction is complicated. It is obviously not a simple unimolecular change, since the rate-pressure curve is complex. The reaction has been investigated over an unusually wide range of pressure, viz., from 0.1 mm.¹¹⁷ to about 300 atmospheres,¹¹⁸ and even at the highest pressure the rate is still increasing with increasing pressure. From this it seems certain that

^{115a} C. H. Klute and W. D. Walters, *J. Am. Chem. Soc.*, 67, 550 (1945).

¹¹⁶ C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A114**, 84 (1927).

¹¹⁷ O. K. Rice and D. V. Sickman, *J. Am. Chem. Soc.*, 56, 1444 (1934).

¹¹⁸ D. M. Newitt and M. A. Vernon, *Proc. Roy. Soc. (London)*, **A136**, 307 (1932); E. W. R. Steacie and E. Solomon, *J. Chem. Phys.*, 2, 503 (1934); E. W. R. Steacie, W. H. Hatcher, and S. Rosenberg, *J. Chem. Phys.*, 4, 220 (1936).

chains are involved to some extent at least, and that they predominate at higher pressures.

Further evidence for the complexity of the reaction is furnished by the fact that mixtures of dimethyl and diethyl ether decompose at a rate faster than the sum of their rates alone, as would be the case if radicals from one ether set up chains in the other.¹¹⁹ The decomposition is catalysed by iodine¹²⁰ and by chlorine.¹²¹

Rice and Johnston¹⁰⁸ detected free radicals in the reaction by the Paneth technique, and estimated the activation energy of the split into radicals to be 68.6 kcal. This seems rather low. Radicals have also been detected in a similar way by Forsyth.¹²²

Fletcher and Rollefson¹²³ determined the amount of acetaldehyde present at various stages of the reaction. Their results indicate that at least a part of the acetaldehyde formed decomposes more rapidly than is normally the case, and they conclude that its decomposition is catalysed by radicals from the ether decomposition. This was verified by adding small amounts of ether to acetaldehyde and determining the rate of decomposition of the latter at temperatures from 490° to 550°. This appears to be a proof of the presence of radicals in the decomposition of ether even at low temperatures. Fletcher and Rollefson conclude, however, that the mechanism is probably a mixed one involving both a molecular rearrangement and a free-radical chain reaction.

The same authors¹²⁴ showed that the decomposition of ethyl ether could be sensitized by the addition of ethylene oxide. Thus at 441° 5 per cent of ethylene oxide in the presence of 180 mm. of ether increased the rate of decomposition of the latter by a factor of 20. They conclude: "If the chain length of the ethylene oxide catalysed reaction is not very different from that of the chains in the normal ether decomposition, it is apparent that the proportion of free radicals produced directly from ether is only about 1/400 of the proportion from ethylene oxide; considerably less than one ether molecule in a thousand, therefore, forms a free radical. Extrapolation of the ether decomposition inhibited by nitric oxide indicates that some 15 per cent of the ether decomposes by a non-chain reaction, so that it follows that in the uncatalysed reaction there is an appreciable amount of decomposition which takes place neither to free radicals nor by a chain

¹¹⁹ L. S. Kassel, *J. Am. Chem. Soc.*, 54, 3641 (1932); E. W. R. Steacie, *J. Phys. Chem.*, 36, 1562 (1932), *J. Chem. Phys.*, 1, 313 (1933).

¹²⁰ K. Clusius and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A128**, 82 (1930); R. F. Faull and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 1755 (1936).

¹²¹ S. Bairstow, *Trans. Faraday Soc.*, 29, 1227 (1933); H. P. Meissner and H. J. Schumacher, *Z. physik. Chem.*, **A185**, 447 (1940).

¹²² J. S. A. Forsyth, *Trans. Faraday Soc.*, 37, 312 (1941).

¹²³ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2129 (1936).

¹²⁴ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2135 (1936).

reaction, but rather by a direct molecular rearrangement. Further, the chains must be few and long rather than numerous and short."

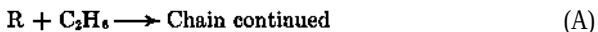
The decomposition is also induced by radicals from the decomposition of diacetyl.¹²⁵ Thus at 499° the rate was increased by a factor of 4 by 1 per cent of diacetyl in 190 mm. of ether. The decomposition promoted by diacetyl is inhibited by propylene,¹²⁶ proving that the catalysis by diacetyl proceeds by a free-radical mechanism.

Leermakers¹¹⁵ in addition to his investigation of the acetone photo-sensitized decomposition of dimethyl ether also made some measurements with diethyl ether. The results are not very complete, but they indicate definitely (i) that methyl radicals from the photodecomposition of acetone react with ethyl ether and set up its chain decomposition, and (ii) that the chains are much shorter than they are with methyl ether, the maximum length being about 20 at the same temperatures.

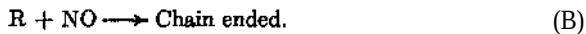
It was shown by Staveley and Hinshelwood¹²⁷ that the reaction is inhibited by nitric oxide in a manner similar to that of the other ethers. The apparent chain length was about 4.4 at 540°. The activation energy of the inhibited reaction was much higher than that of the normal reaction, viz., 67 kcal. as compared with 53 kcal. A more detailed investigation of the inhibited reaction was made by Hobbs,¹²⁸ with special emphasis on the effect of the ether pressure. The "inhibition curve," i.e., the curve obtained

by plotting $\frac{\rho - \rho_\infty}{\rho_0 - \rho_\infty}$ * against the concentration of nitric oxide was found to be independent of the ether pressure, as shown by Figure 10. This is strikingly different from the behaviour of ethane.

Hobbs discusses the mechanism of the reaction in some detail on the basis of this result. With ethane the amount of nitric oxide required for a given degree of inhibition increases with increasing ethane concentration. This has been explained as due to a competition between the two processes



and



With increase in ethane pressure the first process will obviously be favored at the expense of the second. With ethyl ether, however, the amount of nitric oxide required to produce a given degree of inhibition is independent of the ether pressure. Reaction (B) thus appears to be competing with a

* See section (III-5).

¹²⁵ F. O. Rice and W. D. Walters, *J. Am. Chem. Soc.*, **63**, 1701 (1941).

¹²⁶ F. O. Rice and F. C. Kelton, unpublished work, quoted from (125).

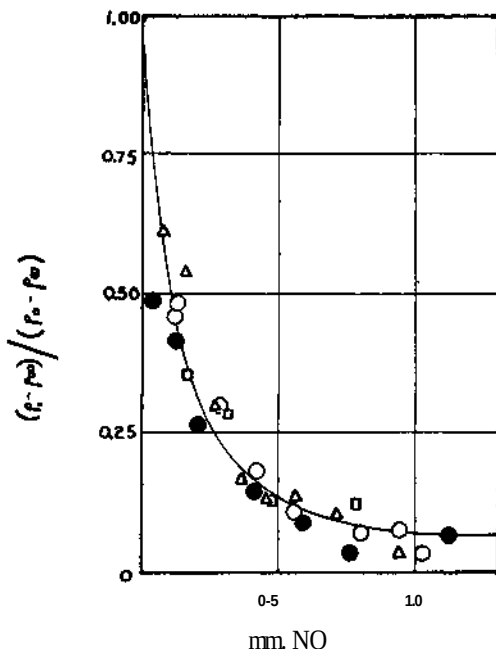
¹²⁷ L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A154**, 335 (1936), **A159**, 192 (1937); *J. Chem. Soc.*, **1937**, 1568.

¹²⁸ J. E. Hobbs, *Proc. Roy. Soc. (London)*, **A167**, 456 (1938).

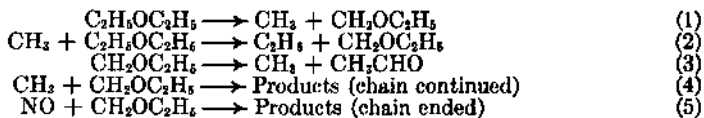
process which is independent of the ether concentration. Since surface effects do not appear to be important, he concludes that the alternative process is the decomposition of the radical itself.

Figure 10. Inhibition of diethyl ether decomposition by nitric oxide.

Ether pressure = 51 mm. — □
 = 103 mm. — ○
 = 200 mm. — ●
 = 400 mm. — △

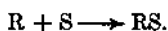


This effect can be readily explained on the assumption that the mechanism of the chain part of the decomposition is that suggested by Rice and Herzfeld:¹¹⁰



To make the discussion more general, let us, following Hobbs' treatment, denote the large radical $\text{CH}_2\text{OC}_2\text{H}_5$ which is removed by nitric oxide by S, the small radical CH_3 which reacts with the ether by R, and the ether by A.

In order to explain the difference in behaviour between ethane and ether it is necessary to assume that with ethane nitric oxide removes R, but that with ether it removes S. The Rice-Herzfeld mechanism for the ether decomposition assumes that chain-breaking occurs by the reaction



In order that this shall be the predominant chain ending process in the uninhibited reaction, R must react with ether at a rate which is fast compared with the decomposition of S. The concentration of S will then be

large compared to R, and NO will tend to react with S by reaction (5), rather than with R by the reaction



In the case of ethane, however, R apparently builds up in the system and chains are broken normally by



or in the presence of nitric oxide by reaction (6).

Following the above mechanism for the ether decomposition, we have in the steady state:

$$\frac{d}{dt} [\text{R}] = k_1[\text{A}] + k_3[\text{S}] - k_2[\text{R}][\text{A}] - k_4[\text{R}][\text{S}] = 0.$$

$$\frac{d}{dt} [\text{S}] = k_1[\text{A}] + k_2[\text{R}][\text{A}] - k_3[\text{S}] - k_4[\text{R}][\text{S}] - k_5[\text{S}][\text{NO}] = 0.$$

Whence

$$[\text{R}] = \frac{-k_2k_3[\text{NO}] + [(k_2k_3[\text{NO}])^2 + 8k_2k_4(k_1k_3[\text{NO}] + 2k_1k_3)]^{\frac{1}{2}}}{4k_2k_4}.$$

In addition to the chain reaction there is a rearrangement process and perhaps a surface reaction: the rate of these two processes combined may be put equal to $k'f(\text{A})$. The total rate is then

$$\rho = k'f(\text{A}) + k_2[\text{R}][\text{A}],$$

and hence

$$\rho = k'f(\text{A}) + \frac{k_2[\text{A}]}{4k_2k_4} \{[(k_2k_3[\text{NO}])^2 + 8k_2k_4(k_1k_3[\text{NO}] + 2k_1k_3)]^{\frac{1}{2}} - k_2k_3[\text{NO}]\}.$$

ρ_0 is the rate when $[\text{NO}] = 0$, hence

$$\rho_0 = k'f(\text{A}) + \frac{k_2[\text{A}]}{4k_2k_4} (16k_1k_3k_4)^{\frac{1}{2}}.$$

The rate of the chain reaction is the second term of this equation, i.e.,

$$[\text{A}](k_1k_2k_3/k_4)^{\frac{1}{2}},$$

and is thus proportional to the first power of the ether concentration.

ρ_0 is the limiting rate for large values of $[\text{NO}]$, and is obviously equal to the first term above, i.e.,

$$\rho_\infty = k'f(\text{A}).$$

Hence

$$\frac{\rho - \rho_\infty}{\rho_0 - \rho_\infty} = \frac{\{[(k_2k_3[\text{NO}])^2 + 8k_2k_4(k_1k_3[\text{NO}] + 2k_1k_3)]^{\frac{1}{2}} - k_2k_3[\text{NO}]\}}{4(k_1k_2k_3k_4)^{\frac{1}{2}}}.$$

The quantity used in plotting the inhibition curve, $(\rho - \rho_\infty)/(\rho_0 - \rho_\infty)$, is thus independent of the ether pressure.

The mean chain length of the reaction, as determined by inhibition experiments, is given by

$$\frac{\rho_0}{\rho_\infty} = \frac{k'f(\text{A}) + [\text{A}](k_1k_2k_3/k_4)^{\frac{1}{2}}}{k'f(\text{A})}.$$

It has been found that the rate of the maximally inhibited reaction, p_{00} , is first order, i.e.,

$$k'f(A) = k''[A].$$

Hence p_0/p_∞ is independent of $[A]$, i.e., the mean chain length is independent of the ether concentration as found experimentally.

It will be apparent from the above discussion that the dependence or independence of the inhibition curve on the concentration of the substrate furnishes some very definite information concerning the mechanism of the reaction.

Smith and Hinshelwood¹²⁹ have investigated the relative efficiencies of propylene and of nitric oxide as inhibitors of the ethyl ether decomposition. The results, at 550°, showed that, within the experimental error, the same limiting rate was produced by both inhibitors, although the quantity of propylene required for a given degree of inhibition was about 15 times greater than that of nitric oxide. (See Table XIX.) This strengthens the conclusion that both inhibitors are really giving complete inhibition, rather than setting up stationary states where the added substances start and stop chains with equal efficiency.

There is, however, one distinct difference in the behaviour of the two inhibitors. With nitric oxide, as we have seen, the inhibition curve is independent of the ether pressure. With propylene, however, the inhibition is strongly dependent on the ether pressure, as shown by Figure 11. It thus appears that while nitric oxide reacts almost entirely with the larger radical $\text{CH}_3\text{OC}_2\text{H}_5$, propylene reacts with CH_3 as well. Smith and Hinshelwood suggest that this is due to the comparative slowness of the reaction



Propylene thus reacts to a considerable extent with methyl radicals in spite of the fact that they are present in smaller amount. This explanation is consistent with the relatively low efficiency of propylene as an inhibitor.

The ethyl ether decomposition has recently been reinvestigated in some detail by Davoud and Hinshelwood.¹³⁰ They corrected the former results of Hinshelwood and his co-workers for the presence of undecomposed acetaldehyde during the reaction, and confirmed the findings of Fletcher and Rollefson that the acetaldehyde decomposes at about twice its normal rate. No appreciable difference was found between the products of the normal and of the inhibited reaction. They also confirmed Hobbs' results on inhibition of the reaction by nitric oxide.

¹²⁹ J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 237 (1942).

¹³⁰ J. G. Davoud and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A171**, 39 (1939), **A174**, 50 (1940).

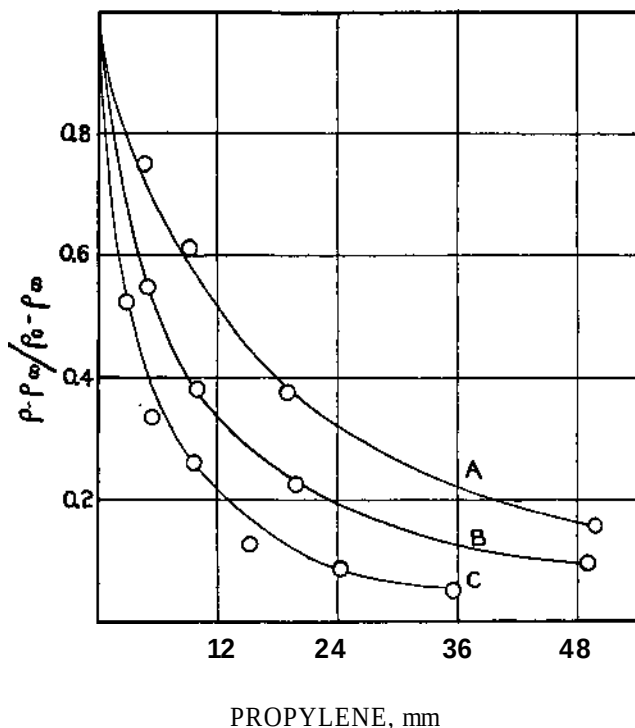


Figure 11. Inhibition of diethyl ether decomposition by propylene.

A, Ether pressure = 300 mm. B, Ether pressure = 100 mm. C, Ether pressure = 35 mm.

TABLE XIX. COMPARISON OF INHIBITION OF DIETHYL ETHER DECOMPOSITION BY NITRIC OXIDE AND BY PROPYLENE

Temperature = 550°			
Initial ether pressure = 100 mm.			
Propylene pressure, mm.	$1/t_{50} \times 10^3$, sec. ⁻¹	Nitric oxide pressure, mm.	$1/t_{10} \times 10^3$, sec. ⁻¹
0	6.53	0	6.54
5	4.35	0.37	5.80
10	3.60	0.90	3.17
20	2.88	2.00	2.53
50	2.25	3.50	2.05
100	2.02	4.97	1.94
200	2.17	7.1	1.91
300	2.28	14.3	1.92

It will be evident from the above discussion that the status of free-radical mechanisms in the decomposition of ethyl ether is fairly clear. The reaction is evidently composite, and there seems to be little doubt that a part of the total reaction proceeds by a rearrangement mechanism and the re-

mainder by a free-radical chain process. The chain reaction appears to follow a mechanism of the Rice-Herzfeld type.

9. Other Ethers

Information on other ethers from a free radical point of view is somewhat fragmentary. The results are summarized very briefly below.

Methyl Ethyl Ether

The reaction is inhibited by nitric oxide,¹²⁷ the mean chain length calculated in the usual way being 8.4 at 540°. Rice, Walters, and Ruoff¹³¹ have shown that the decomposition can be induced by the thermal decomposition of azomethane at 299°, up to 17 molecules of ether being decomposed per methyl radical produced from azomethane (assuming that two methyl radicals are formed for each azomethane molecule decomposed).

Ethyl Propyl Ether

This decomposition is also inhibited by nitric oxide,¹²⁷ the apparent chain length being 3.2 at 540°.

Dipropyl Ether

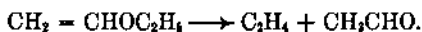
The decompositions of both di-n-propyl and di-iso-propyl ether are inhibited by nitric oxide.¹²⁷ The apparent chain lengths are 2.7 and 1.4 respectively.

Methyl Butyl Ether

The thermal decomposition of methyl-n-butyl ether was investigated by Magram and Taylor.¹³² The reaction is similar to those of the other ethers. The butyraldehyde formed as an intermediate presumably undergoes a free-radical sensitized decomposition as is the case with acetaldehyde in the decomposition of diethyl ether. The reaction is inhibited by nitric oxide, the apparent chain length at 536° being 5.0.

Vinyl Ethyl Ether

The decomposition of vinyl ethyl ether¹³³ yields mainly ethylene and acetaldehyde, *i.e.*,



The decomposing ether can sensitize the decomposition of acetaldehyde and the polymerization of ethylene, showing that free radicals are formed in the reaction. Nitric oxide, however, was found to have practically no

¹³¹ F. O. Rice, W. D. Walters, and P. M. Ruoff, *J. Chem. Phys.*, 8, 259 (1940).

¹³² S. J. Magram and H. A. Taylor, *J. Chem. Phys.*, 9, 755 (1941).

¹³³ S. N. Wang and C. A. Winkler, *Can. J. Research*, 21B, 97 (1943).

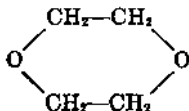
inhibitory effect on the reaction. Wang and Winkler conclude that the decomposition occurs mainly by a rearrangement mechanism, but that some free radicals are formed, and that these initiate a sensitized decomposition of the acetaldehyde formed in the reaction.

Divinyl Ether

The decomposition is complex and can be induced by azomethane.¹³⁴

Dioxane

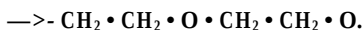
This is a cyclic ether,



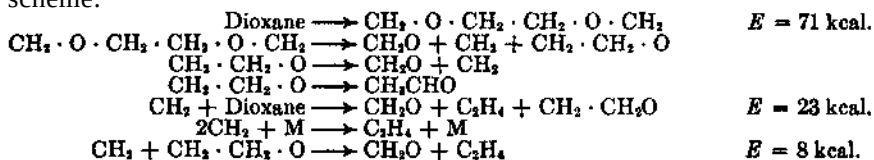
The decomposition has been investigated by Klichler and Lambert.¹³⁶ The reaction is very strongly inhibited by nitric oxide. It is, however, not catalysed by methyl radicals from the decomposition of azomethane. The para-ortho hydrogen method also gives negative results. It therefore appears that chains are present, but that alkyl radicals are not the carriers, and the reaction is thus an unusual and interesting one. The primary process is presumably a ring opening, and we thus have two possibilities:



or



Klichler and Lambert suggest the former, and the following reaction scheme:

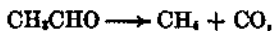


This gives general agreement with experiment, but is completely speculative.

Radicals, perhaps methylene, have been detected by the Paneth technique in the dioxane decomposition by Forsyth.⁴⁷⁰

10. Acetaldehyde

Early work on the reaction¹³⁶ showed that the predominant products are those corresponding stoichiometrically to the equation



¹³⁴ H. A. Taylor, *J. Chem. Phys.*, 4, 116 (1936).

¹³⁶ L. Klichler and J. D. Lambert, *Z. physik. Chem.*, B37, 285 (1937).

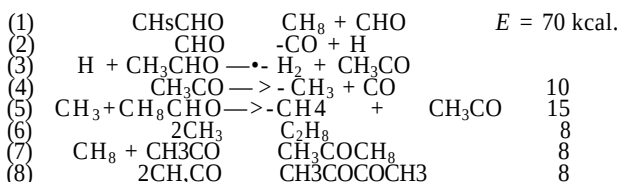
¹³⁸ For comprehensive discussions of earlier work see M. Letort, *Thesis*, Paris, 1937; H. J. Schumacher, *Chemische Gasreaktionen*, Leipzig, 1938.

and that the decomposition is almost entirely homogeneous. The order of the reaction is approximately 1.5. The activation energy calculated from the results at higher pressures is about 48 kcal.

Hinshelwood and his co-workers¹³⁷ have investigated the pressure dependence of the rate constants of the reaction in great detail. They conclude that the rate-pressure curve is segmented, and attribute this to the operation of different modes of activation within the molecule. While the segmented nature of the curves does not appear to be beyond dispute, there is no question that the rate-pressure curves for most aldehydes are of an unusual form, and this suggests that the reactions may be complex.

Travers and Seddon¹³⁸ have also investigated the reaction. They conclude that the process is much more complex than had previous workers, and their results differ widely from those of Hinshelwood and his collaborators. Their technique involved the use of small sealed bulbs which were held at elevated temperatures for a definite time and then quenched and analysed. They were thus always using fresh surfaces, and it appears certain that surface effects played a decisive part in their work, which will therefore not be further considered.

It was suggested by Rice and Herzfeld that the facts could be explained on the basis of the following free-radical chain mechanism:



They also assumed that the activation energy of the reverse of (1) is 8 kcal., and that of the reverse of (8) is 45 kcal. Steps (4) and (5) thus constitute the chain, with methyl and acetyl radicals as the carriers. The activation energies indicated were merely assigned^{1,139} to make the mechanism agree with experiment, with the exception of E_1 which comes from an experimental determination by Rice, Johnston, and Evering⁸⁴ by the Paneth technique.

In view of the rapid decomposition of the acetyl radicals, reactions (7) and (8) will not be of much importance compared with (6) as chain-ter-

¹³⁷ C. J. M. Fletcher and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **AM1**, 41 (1933); C. N. Hinshelwood, C. J. M. Fletcher, F. H. Verhoek, and C. A. Winkler, *Proc. Roy. Soc. (London)*, **AM6**, 327 (1934); C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **AM9**, 355 (1935).

¹³⁸ M. W. Travers, *Proc. Roy. Soc. (London)*, **AM6**, 248 (1934); *Nature*, **134**, 569 (1934); M. W. Travers and R. V. Seddon, *Nature*, **137**, 906 (1936); *Proc. Roy. Soc. (London)*, **A156**, 234 (1936).

¹³⁹ F. O. Rice, *J. Am. Chem. Soc.*, **56**, 488 (1934).

minating reactions and may be neglected. On this basis the usual steady-state treatment leads to an order of 3/2, in agreement with experiment. It also gives

$$E_{\text{overall}} = \frac{1}{2}(E_1 - E_6 + E_5) = 46 \text{ kcal.}$$

There is ample evidence that free radicals play some role in the reaction. As mentioned above, methyl radicals have been detected in the decomposition by the Paneth method by Rice, Johnston, and Evering. They have also been detected by the same method by Letort.¹³⁶ Leermakers¹⁴⁰ has also detected the methyl radical in the photodecomposition, as have & number of other workers under various conditions.¹⁴¹

The thermal decomposition has recently been reinvestigated by the Paneth method by Burton, Ricci, and Davis.¹⁴² By the use of radioactive lead mirrors they made the test sensitive enough so that the experiments could be carried out at 500°, instead of having to be performed at temperatures much higher than those usually employed in the pyrolysis. They were able to prove the presence of radicals, but the difficulties involved were such that the results can only be classed as qualitative. The significant feature of the work, however, is that radicals were detected when acetaldehyde was decomposed at temperatures in the range in which investigations of the pyrolysis have been carried out. Morris¹⁴³ has criticized the work of Burton, Ricci, and Davis on the grounds that a very small amount of oxygen, even 0.001 per cent, would have been sufficient to have set up enough chains to lead to a positive Paneth test. Morris attempted to answer the question of the occurrence of radicals at temperatures around 500° by decomposing mixtures of CH₃CHO and CD₃CDO and examining the products by infra-red absorption. It would be expected that in the absence of radicals only CEU and CD₄ would be produced, but that in the event of appreciable radical production mixed methanes CH₃D, CH₂D₂, etc., would be formed.

He found that with acetaldehyde purified in the ordinary way mixed methanes were formed in amounts corresponding to the occurrence of about 50 per cent of the reaction by a chain mechanism. If, however, the acetaldehyde were purified by treatment with hydroquinone and subsequent distillation, the rate decreased to about 1/2 the normal rate and mixed methanes were no longer formed in appreciable quantities (i.e., not over 10 to 20 per cent). The impurity was not oxygen, since the rate of decomposition of the "treated" acetaldehyde increased when the acetaldehyde was allowed to stand for some time after distillation following the hydroquinone treat-

¹⁴⁰ J. A. Leermakers, *J. Am. Chem. Soc.*, 66, 1537 (1934).

¹⁴¹ T. G. Pearson, *J. Chem. Soc.*, **1934**, 1718; T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, **1935**, 1151; M. Burton, *J. Am. Chem. Soc.*, 62, 265 (1940), 60, 212 (1938).

¹⁴² M. Burton, J. E. Ricci, and T. W. Davis, *J. Am. Chem. Soc.*, 62, 265 (1940).

¹⁴³ J. C. Morris, *J. Am. Chem. Soc.*, 63, 2535 (1941), 66, 584 (1944).

ment. He suggests that the "inhibition" of the acetaldehyde decomposition by nitric oxide is also due to the removal of an impurity, and therefore concludes that pure acetaldehyde decomposes entirely by a molecular mechanism. He explains the order of 1.5 or so for the acetaldehyde decomposition on the basis of a "fall-off" first order reaction rather than a complex mechanism.

The rate of decomposition of deuterio-acetaldehyde was found to be slower than that of ordinary acetaldehyde in the ratio 1.3 to 1.4. The deuterio-acetaldehyde decomposition was somewhat less affected by treatment of the substance with hydroquinone.

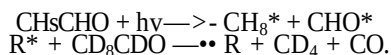
It is well known that the acetaldehyde decomposition is catalysed by traces of oxygen. In agreement with this Morris found mixed methanes to be formed in the presence of traces of oxygen.

Morris was unable to reach definite conclusions concerning the nature of the "impurities" responsible for promoting a chain decomposition of acetaldehyde. It should be pointed out that it is possible that the function of the hydroquinone is not to purify the acetaldehyde but rather to contaminate it with traces of substances which inhibit its chain decomposition. This investigation cannot, therefore, be regarded as an entirely conclusive demonstration of the lack of chain processes in the thermal decomposition of pure acetaldehyde.

Garrison and Burton¹⁴⁴ have suggested that the discrepancy between the results of Burton, Ricci, and Davis and those of Morris could be explained if the chain-continuing step were not that postulated by Rice and Herzfeld,



which would lead to exchange but rather a sort of induced predissociation



This would give a free-radical mechanism but would not lead to exchange.

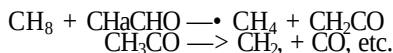
There is also ample evidence that the addition of free radicals to acetaldehyde can cause its induced decomposition, obviously by a free-radical chain mechanism of some sort. Allen and Sickman¹⁴⁵ showed that azomethane caused the induced decomposition at temperatures in the neighbourhood of 300°, chain lengths up to 500 being found. The azomethane is undoubtedly acting as a source of methyl radicals. The order of the induced decomposition under these circumstances is approximately unity, and the activation energy of the induced reaction is 39.5 kcal.

The decomposition of acetaldehyde induced by free radicals from the decomposition of ethylene oxide has been investigated by Fletcher and

¹⁴⁴ W. M. Garrison and M. Burton, *J. Chem. Phys.*, **10**, 730 (1942).

¹⁴⁵ A. O. Allen and D. V. Sickman, *J. Am. Chem. Soc.*, **56**, 2031 (1934); D. V. Sickman and A. O. Allen, *J. Am. Chem. Soc.*, **56**, 1251 (1934).

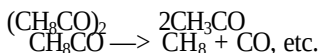
Rollefson.¹⁴⁶ At 441° with 20 mm. of ethylene oxide and 180 mm. of acetaldehyde chains up to 300 molecules long occurred, presumably by



The decomposition is also induced by radicals from diethyl ether,¹⁴⁷ ethyl bromide,¹⁴⁸ and ethyl iodide.¹⁴⁸

Winkler and Wang¹³³ have shown that the acetaldehyde decomposition can be induced by radicals from the decomposition of vinyl ethyl ether at temperatures from 389° to 412°. The induced reaction is strongly inhibited by small amounts of nitric oxide.

Rice and Walters¹⁴⁹ found that the reaction could be induced by diacetyl at 499°. The mechanism is presumably



The induced reaction is not appreciably inhibited by nitric oxide,¹¹⁵⁰ possibly owing to catalysis by nitric oxide masking its inhibiting effect. (See V-7.)

Blacet and Taurog¹⁶⁰ showed that methyl radicals from the photodecomposition of azomethane sensitized the acetaldehyde decomposition at room temperature.

Rollefson and Faull¹⁵¹ found that the reaction was accelerated by iodine. This is probably due to the formation of an alkyl iodide which decomposes to give radicals, which then sensitize the reaction. Mitchell and Hinshelwood¹⁶² have pointed out that there is a definite parallelism between those organic substances the decompositions of which are catalysed by iodine, and those which are catalysed by free radicals. The reaction is similarly catalysed by bromine.¹⁶³ It is also catalysed by traces of oxygen.^{148, 164} This is probably due to the oxidation of acetaldehyde with the formation of free radicals, which then cause the sensitized decomposition of further acetaldehyde. It is also catalysed by NO,¹⁶⁵ N₂O,¹⁵⁶ and H₂S.¹⁶⁷

¹⁴⁶ C. J. M. Fletcher, *J. Am. Chem. Soc.*, 58, 534 (1936); C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2135 (1936).

¹⁴⁷ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2129 (1936); M. W. Travers and C. G. Silcocks, *Nature*, **139**, 1018 (1937).

¹⁴⁸ J. G. Roof and F. Daniels, *J. Am. Chem. Soc.*, 62, 2912 (1940); J. G. Roof, *J. Am. Chem. Soc.*, 66, 358 (1944).

¹⁴⁹ F. O. Rice and W. D. Walters, *J. Am. Chem. Soc.*, 63, 1701 (1941).

¹⁵⁰ F. E. Blacet and A. Taurog, *J. Am. Chem. Soc.*, 61, 3024 (1939).

¹⁵¹ G. K. Rollefson and R. F. Faull, *J. Am. Chem. Soc.*, 69, 625 (1937).

¹⁶² J. W. Mitchell and C. N. Hinshelwood, *Proc Roy. Soc.*, **A159**, 32 (1937).

¹⁶³ W. Brenschede and H. J. Schumacher, *Ber.*, **70B**, 452 (1937).

¹⁵⁴ M. Letort, *J. Chim. Phys.*, 34, 265, 355, 428 (1937).

¹⁵⁵ F. H. Verhoek, *Trans. Faraday Soc.*, **31**, 1527 (1935).

¹¹¹ F. H. Verhoek, *Trans. Faraday Soc.*, **31**, 1533 (1935); E. W. R. Steacie and R. D. McDonald, *Can. J. Research*, 12, 711 (1935).

¹⁵⁷ W. L. Roth and G. K. Rollefson, *J. Am. Chem. Soc.*, 64, 1707 (1942).

Another line of attack is that of Patat and Sachsse¹⁵⁸ who used the para-ortho hydrogen method with acetaldehyde at 550°. The result qualitatively was that the conversion was catalysed in the presence of decomposing acetaldehyde, thus proving the presence of atoms or radicals. Quantitatively, however, the H-atom concentration was found to be about 2 powers of ten lower than that predicted by the Rice-Herzfeld mechanism. However, the calculation is too much dependent on the exact values of assigned activation energies to have much quantitative meaning. Nevertheless it does seem to indicate that the number of atoms and radicals present in decomposing acetaldehyde is smaller than is predicted by the mechanism.

Experiments have been made on the effect of inert foreign gases, hydrogen¹⁵⁹ and helium,¹⁶⁰ on the decomposition. In both cases the reaction is accelerated to some extent. This points to collisional activation of an ordinary unimolecular decomposition, since in the case of a chain reaction it would be expected that the addition of a foreign gas would retard the reaction by favoring three body recombination of chain carriers.

The rates of decomposition of ordinary and of deuterioacetaldehyde have been compared by Smith.¹⁶¹ The deuterio compound was found to decompose more slowly by an amount corresponding to a difference in the activation energies of ca. 1.5 kcal. It does not seem possible to obtain much information regarding the mechanism from this observation, although Smith suggests that the main step involves breaking a C—H or C—D bond. He also found that ethylene exerted no inhibitory effect on the decomposition and hence concluded that the reaction does not involve chains. In the free-radical sensitized decomposition ethylene does have an inhibitory effect.¹⁶² Thus in a mixture of 100 mm. of acetaldehyde and 100 mm. of ethylene, the rate of the reaction sensitized by ethylene oxide was reduced to 31 per cent of its value in the absence of ethylene. This is, however, a rather small change for such a large amount of inhibitor.

Rice and Polly,¹⁶³ found that the oxygen-induced decomposition of acetaldehyde was strongly inhibited by ethyl nitrite at 300°. At 500°, however, it had very little effect, and under some circumstances actually produced an induced decomposition itself. They also found that propylene inhibited the decomposition.

¹⁵⁸ F. Patat and H. Sachsse, *Naturwiss.*, **23**, 247 (1935); *Z. physik. Chem.*, **B31**, 105 (1935); H. Sachsse, *Z. Elektrochem.*, **41**, 493 (1935); F. Patat, *Z. physik. Chem.*, **B32**, 294 (1936).

¹⁵⁹ C. N. Hinshelwood and P. J. Askey, *J. Chem. Soc.*, **1936**, 812; C. J. M. Fletcher and C. N. Hinshelwood, *Trans. Faraday Soc.*, **30**, 614 (1934).

¹⁶⁰ C. J. M. Fletcher, *J. Am. Chem. Soc.*, **58**, 2646 (1936).

¹⁶¹ J. R. E. Smith, *Trans. Faraday Soc.*, **35**, 1328 (1939).

¹⁶² C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2135 (1936).

¹⁶³ F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

The original investigation of the effect of nitric oxide on the reaction¹⁶⁴ showed no appreciable inhibition, and was thus definite evidence against the participation of free radicals. A recent investigation by Smith and Hinshelwood,¹⁶⁶ however, makes a fundamental change in the situation. They summarized the evidence for and against the chain theory, and pointed out that lack of inhibition constituted the main evidence against

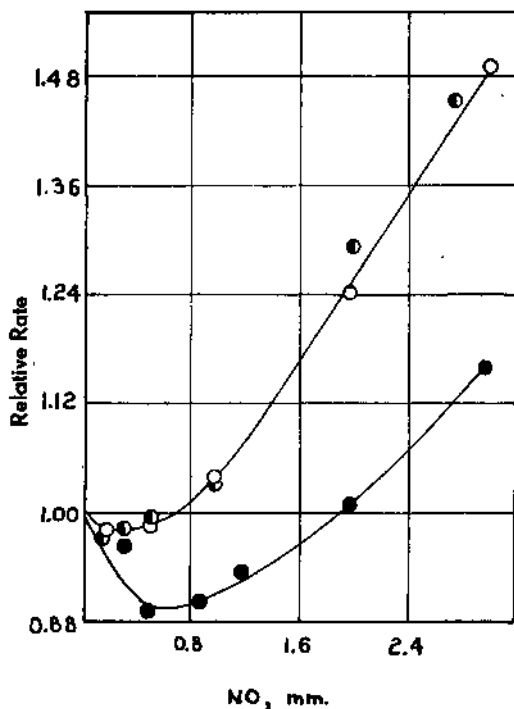


Figure 12. Effect of nitric oxide on the decomposition of acetaldehyde.

50 mm. acetaldehyde — ●
 150 mm. acetaldehyde — ◐
 400 mm. acetaldehyde — ○

the chain theory. They therefore made a more detailed investigation of the effect of nitric oxide and of propylene on the acetaldehyde decomposition. The result of Rice and Polly was confirmed that the reaction is inhibited by propylene, but as usual large amounts of propylene were required for maximum inhibition.

With nitric oxide it was found that at higher pressures the first millimeter or two of nitric oxide added had no appreciable effect on the rate: larger amounts of nitric oxide caused a large *increase* in rate. At pressures of 50 mm. or less, however, appreciable inhibition occurred, followed again by catalysis at higher nitric oxide concentrations. (See Figure 12.) It appears,

¹⁶⁴ L. A. K. Staveley and C. N. Hinshelwood, *Nature*, **137**, 29 (1936); *J. Chem. Soc.*, **1936**, 812.

¹⁶⁵ J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 237 (1942).

therefore, that the strong catalytic effect of nitric oxide is masking the inhibition, and the discrepancy between the results with propylene and nitric oxide is thus removed.

It was also proved that the lack of appreciable inhibition by nitric oxide at higher pressures was not due to a rapid destruction of nitric oxide by acetaldehyde. This was done by showing that nitric oxide inhibits the decomposition of mixtures of acetaldehyde and diethyl ether.

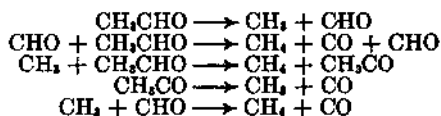
If it is assumed that the maximally inhibited reaction represents the chain-free part of the process, then its characteristics are found to be much simpler than those of the total reaction. The order is almost 2, and the variation of activation energy with pressure no longer exists. Thus for the chain-free reaction the results in Table XX were obtained:

TABLE XX. EFFECT OF PRESSURE ON APPARENT ACTIVATION ENERGY OF MAXIMALLY INHIBITED DECOMPOSITION OF ACETALDEHYDE

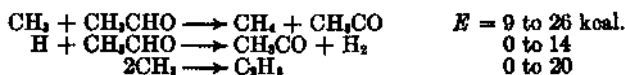
Pressure, mm.	<i>E</i> , kcal.
75	47.8
200	46.2
350	47.0

The inhibition curves with propylene vary with the initial aldehyde pressure. This suggests a mechanism of the ethane type rather than the ethyl ether type. If it is assumed that at higher pressures chains end by a termolecular process, the reaction will be first order. At lower pressures a bimolecular process is postulated, leading to a 3J2 order reaction.

Various other free-radical mechanisms could, of course, be constructed which, with suitable assumptions about activation energies, etc., could be made to yield the 3J2 order and the observed overall activation energy. An example is that proposed by Leermakers:¹⁴⁰

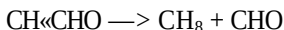


However, the Rice-Herzfeld mechanism seems more plausible. Letort¹³⁶ has discussed the possible free-radical mechanisms in detail, and he concludes that it is possible to reconcile Patat and Sachsse's results with the Rice-Herzfeld scheme provided that the activation energies of the following reactions lie within the limits indicated:



The limits seem reasonable.

Taylor and Burton¹⁶⁶ have discussed the mechanism from the standpoint of the possible potential energy surfaces. They suggest that the chain starting step



is not in competition with a simple unimolecular rearrangement



but rather with a bimolecular reaction



Burton, Taylor, and their co-workers in a number of papers¹⁶⁷ have discussed the mechanism of the reaction. The discussion, however, was based on bond strength values which were later withdrawn and is therefore not relevant to the issue.

Grahame¹⁶⁸ in commenting on the G—C bond strength in acetaldehyde points out that in the photolysis of acetaldehyde, using the Rice-Herzfeld scheme,

$$E_{\text{photo}} - E_5 - \frac{1}{2}E_6 = 8.6 \text{ kcal.}$$

If it is assumed that the thermal reaction proceeds by a chain process similar to the photolysis, then

$$E_{\text{thermal}} - E_6 - \frac{1}{2}E_6 + \pm E_1 = 45.5 \text{ kcal.}$$

Whence

$$E_1 = 73.8 \text{ kcal.}$$

This is therefore a maximum value for the C—C bond in acetaldehyde.

Burton, Taylor, and Davis¹⁶⁹ have discussed the chain mechanism in some detail. However, they point out in a later note that their paper contains an arithmetical error which vitiates most of their conclusions.¹⁷⁰ They do point out, however, that from Allen and Sickman's work on the azomethane induced reaction we have

$$E_5 - \frac{1}{2}E_6 = 14 \text{ kcal.,}$$

in contrast to Grahame's value of 8.6 kcal. However, in the induced reaction the chain carriers can only be CH₃ and the unstable CH₃CO, while in the photolysis we also have to consider the possible chain-carrying role of CHO. In any case, considering possible complications due to the surface, etc., it seems to the writer that the experimental error might well cover the difference between the two values.

¹⁶⁸ H. A. Taylor and M. Burton, *J. Chem. Phys.*, **7**, 414 (1939).

¹⁶⁷ M. Burton, *J. Chem. Phys.*, **6**, 818 (1938); *J. Chem. Phys.*, **7**, 1072 (1939); H. A. Taylor and M. Burton, *J. Chem. Phys.*, **7**, 675 (1939).

¹⁶⁸ D. C. Grahame, *J. Chem. Phys.*, **7**, 680 (1939).

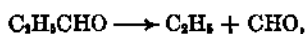
¹⁶⁹ M. Burton, H. A. Taylor, and T. W. Davis, *J. Chem. Phys.*, **7**, 1080 (1939).

¹⁷⁰ M. Burton, H. A. Taylor, and T. W. Davis, *J. Chem. Phys.*, **10**, 146 (1942).

In conclusion, as with the previous examples, the evidence favors a mixed free-radical chain and rearrangement mechanism. The Rice-Herzfeld mechanism appears to be rather well established for the free-radical chain part of the process. In view of Morris' work, however, it is possible that with perfectly pure acetaldehyde no free-radical processes occur.

11. Propionaldehyde

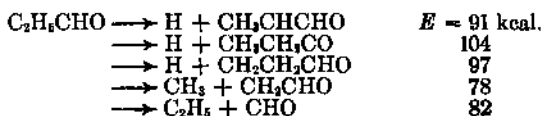
The thermal decomposition of propionaldehyde is in general similar to that of acetaldehyde.¹⁷¹ Rice has suggested a chain mechanism for the reaction of the same type as that for acetaldehyde, the primary step being



with perhaps also



He suggests the following activation energies for the possible primary steps:



On this basis the chain mechanism may differ somewhat from that for acetaldehyde, since the last two primary steps may both occur.

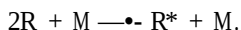
Patat and Sachsse,¹⁵⁸ by the para-ortho hydrogen method, concluded that, as in other cases, the radical concentration during the decomposition is considerably less than that predicted by the Rice-Herzfeld mechanism, viz., $10 \sim 10^{10.0}$ instead of $10 \sim 8.7$ mole per litre under their experimental conditions.

The decomposition, like that of acetaldehyde is catalysed by iodine.¹⁶¹

The reaction is inhibited by nitric oxide,¹⁶⁴ but the apparent chain length thus determined is only about 2. The activation energy of the induced reaction is about 5 kcal. less than that of the normal decomposition. Smith and Hinshelwood¹⁶⁶ reinvestigated the inhibition of the propionaldehyde decomposition in some detail. They showed first that the pressure change was a true measure of the extent of the reaction in the presence of propylene. Then, using the pressure change as a measure of the reaction, they compared the inhibitory action of nitric oxide with that of propylene. The results, at 550°, showed that the same limiting rate was produced by both inhibitors, although the quantity of propylene required for a given degree of inhibition was about 100 times larger than that of nitric oxide. This strengthens the conclusion that both substances are really giving complete inhibition. Further evidence along these lines is furnished by the fact that

¹⁷¹ C. N. Hinshelwood and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A113**, 221 (1936); C. A. Winkler, C. J. M. Fletcher, and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A146**, 345 (1934).

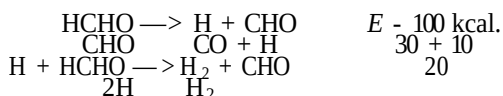
mixtures of propylene and nitric oxide also give the same limiting rate as that with either alone. It was also found that the fully inhibited reaction with propylene is of an order between the first and the second. This suggests that the chain ending mechanism in the decomposition is of the type



12. Other Aldehydes

Formaldehyde

The thermal decomposition of formaldehyde is complicated by side reactions involving condensation, etc.,¹⁷² and it is difficult to obtain much definite information about it. The Rice type of mechanism, using values of activation energies given by Rice,¹ is



The reaction has been investigated by the para-ortho hydrogen method by Patat and Sachsse.¹⁷³ They concluded that practically no hydrogen atoms were present during the decomposition, and that it must proceed almost entirely by a direct rearrangement



The same conclusion was reached by Steacie and Alexander¹⁷⁴ by the following method. Mixtures of deutero-acetone and ordinary dimethyl ether were decomposed at 590°. It was found that the hydrogen in the products contained no deuterium within the experimental error, which was rather large. Now methyl ether decomposes largely via formaldehyde. If the formaldehyde thus produced decomposed by a mechanism of the Rice-Herzfeld type hydrogen atoms would be produced, and these by reaction with deutero-acetone would form HD.

Fletcher and Rollefson¹⁷⁵ have shown that formaldehyde formed as an intermediate step in the decomposition of dimethyl ether at 504° decomposes 15 times faster than would be expected from its normal rate of decomposition alone. Since the decomposition of dimethyl ether undoubtedly involves radicals, it appears probable that the result is due to a methyl radical sensitized decomposition of formaldehyde. This explanation is not

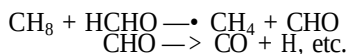
¹⁷² C. J. M. Fletcher, *Proc. Roy. Soc. (London)*, **A146**, 357 (1934).

¹⁷³ F. Patat and H. Sachsse, *Nach. Ges. Wiss. Göttingen*, **111**, 1, 41 (1935); H. Sachsse, *Z. Elektrochem.*, **41**, 493 (1935).

¹⁷⁴ E. W. R. Steacie and W. A. Alexander, *J. Chem. Phys.*, **5**, 372 (1937) [*Can. J. Research*, **B15**, 295 (1937)].

¹⁷⁵ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **68**, 2129 (1936).

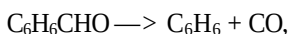
in accord with the work of Steacie and Alexander, however, since sensitized decomposition of formaldehyde would almost certainly proceed by



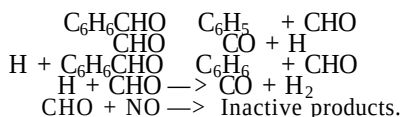
Hydrogen atoms would thus be formed, contrary to their conclusions.

Benzaldehyde

Smith and Hinshelwood¹⁷⁶ have investigated the thermal decomposition of gaseous benzaldehyde. The predominant overall reaction is



but diphenyl is also formed to some extent. The order of the reaction is approximately unity, and the rate constants fall off at pressures below 100 mm. The reaction is inhibited by nitric oxide, and the inhibited reaction has a variable order between 1 and 2. The inhibition curves are identical for various initial aldehyde pressures. On the basis of the previous discussion, this means that the mechanism must involve two kinds of radical, one of which can only propagate the chain after itself decomposing to give a smaller radical, and the chains are broken by recombination of the two different kinds of radical. They therefore propose the mechanism:



Acrolein

The thermal decomposition of acrolein is complicated.¹⁷⁷ It can be induced by iodine at temperatures 100° below the normal decomposition temperature. The rate of the sensitized decomposition is proportional to the square root of the iodine concentration, indicating an atomic mechanism in which free-radical chains are undoubtedly involved. The decomposition can also be sensitized by ethylene oxide,¹⁶² the rate at 470° being increased by a factor of 4 in the presence of 10 per cent of ethylene oxide.

13. A Comparison of the Aldehyde Decompositions

Smith and Hinshelwood¹⁶⁵ have compared the decompositions of various aldehydes in the light of their work on inhibition. They conclude that the maximally inhibited reactions are all approximately of the second order.

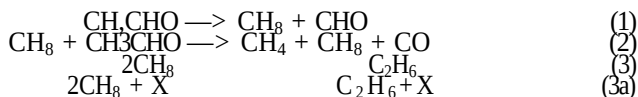
By using the difference between the reciprocals of the times-to-half-value for the normal and inhibited reactions as a measure of the rate of the

¹⁷⁶ J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A175**, 131 (1940).

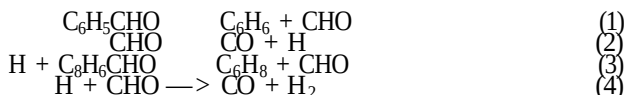
¹⁷⁷ H. W. Thompson and J. J. Frewing, *J. Chem. Soc.*, **1935**, 1443.

chain part of the processes they conclude that the chain reactions of acetaldehyde, propionaldehyde and benzaldehyde are all first order at higher pressures. For the chain processes they point out that there are two main types of mechanism possible:

A



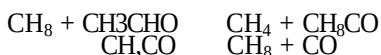
B



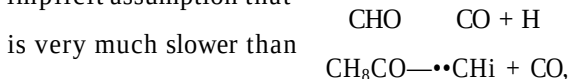
The main differences between these are: (a) In B one of the rate-controlling steps is the spontaneous decomposition of one of the participating radicals: this does not occur in A; and (6) The chain-ending step in A is the recombination of two like radicals, while in B two unlike radicals combine. Mechanism A with (3) as the chain-ending step leads to a reaction of the 3J2 order, with (3a) it yields a first order rate equation. As we have seen previously it leads to inhibition curves which are dependent on the aldehyde concentration. Mechanism B leads to a first-order rate and to inhibition curves independent of the aldehyde concentration.

With acetaldehyde and propionaldehyde the inhibition curves are dependent on the initial pressure, and the order at higher pressures is approximately the first. This suggests mechanism A with chain breaking mainly occurring by three body collisions at higher pressures. With benzaldehyde, on the other hand, the inhibition curves are independent of the aldehyde concentration, pointing to mechanism B. Smith and Hinshelwood suggest that in all probability both mechanisms come into play to some extent with each substance.

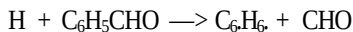
The above discussion gives a consistent picture of the aldehyde decompositions. It may be pointed out, however, that reaction A (2) is of course really a pair of consecutive reactions



The main difference in the two mechanisms thus really results from the implicit assumption that



so that all acetyl radicals decompose instantaneously, but some formyl radicals survive long enough to allow the chains to end by B(4). Also the reaction



seems unlikely compared with



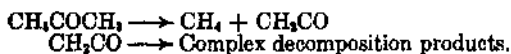
so that the mechanism of the benzaldehyde decomposition is by no means to be regarded as established.

14. Acetone

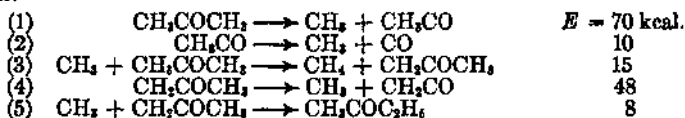
The thermal decomposition of acetone has been investigated by a number of workers.¹⁷⁸ The reaction is predominantly homogeneous and of the first order, the limiting high pressure rate constants being given by

$$k = 10^{15} e^{-18000/RT} \text{ sec.}^{-1}.$$

It apparently proceeds in stages with the intermediate formation of ketene, i.e.,



Rice and Herzfeld suggested the following chain mechanism for the reaction:



This yields a first-order rate equation in the usual way. The overall activation energy is given by

$$E_{\text{overall}} \approx \frac{1}{2}(E_1 + E_2 + E_4 - E_5) = 62.5 \text{ kcal.},$$

as compared with the experimental value of 68 kcal. The predicted chain length is ca. 300. Rice later estimated¹ $E_1 = 84 \text{ kcal.}$ However, this was frankly assigned to make the mechanism agree with experiment, and yields

$$E_{\text{overall}} = 69.5 \text{ kcal.}$$

Allen¹⁷⁹ investigated the reaction at very low temperatures and very small percentage conversions, so that the decomposition of ketene would not be a complicating factor. He found pronounced induction periods: packing the reaction vessel eliminated the induction period and retarded the reaction. This strongly suggests a chain mechanism. Schumacher¹⁸⁰ points out, however, that the reaction might involve very short chains, and that the effects obtained by Allen might thus be explained without the Rice mechanism being operative. Davoud and Hinshelwood¹⁸¹ suggest

¹⁷⁸ C. N. Hinshelwood and W. K. Hutchison, *Proc. Roy. Soc. (London)*, **A111**, 245 (1926); F. O. Rice and R. E. Vollrath, *Proc. Nat. Acad. Sci. (Washington)*, **16**, 702 (1929); C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A149**, 340 (1935); J. R. Huffman, *J. Am. Chem. Soc.*, **58**, 1815 (1936).

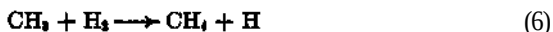
¹⁷⁹ A. O. Allen, *J. Am. Chem. Soc.*, **68**, 1052 (1936).

¹⁸⁰ H. J. Schumacher, *Chemische Gasreaktionen*, Leipzig, 1938.

¹⁸¹ J. G. Davoud and C. N. Hinshelwood, *Nature*, **144**, 909 (1939).

that the complications found by Allen may be due to effects of a secondary nature, such as the polymerization of ketene formed in the reaction.

Patat and Sachsse,¹⁵⁸ have investigated the acetone decomposition by the para-ortho hydrogen method. As in other cases, the results obtained are uncertain since they depend on the detailed mechanism assumed, and especially on the relative rates of the reactions



and



If we adopt Rice's estimates of the activation energies of these reactions, viz., $E_6 = 23$ kcal., $E_7 = 15$ kcal., Patat and Saehsse's results lead to a value of $[\text{CH}_3] = 10^{-9.96}$ atm., while the Rice mechanism predicts $10^{-8.1}$. Patat and Sachsse point out that to obtain agreement between the mechanism and their experiments it is necessary for $E_6 - E_7$ to be equal to 15 kcal. This is impossible, since present estimates of E_e put it well below 15 kcal. Nevertheless it is noteworthy that the difference between the calculated and observed values is less for acetone than for other substances. As will be seen later, other evidence seems to indicate that long chains are not set up in acetone by free radicals. Hence Patat and Saehsse's results may be considered as evidence for the production of radicals in the primary step of the acetone decomposition without necessarily implying that chains are involved. It may also be noted that the difference between the strength of the C—C bond in acetone and the overall activation energy of the decomposition is relatively small, and hence it would not be difficult to explain the facts on a free radical mechanism involving very short chains.

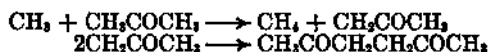
There have been a considerable number of investigations of the induced decomposition of acetone. Leermakers¹⁸² found that the quantum yield of the acetone photolysis, unlike that of acetaldehyde, did not increase appreciably with rise in temperature up to 400°, the quantum yield at the highest temperature being only about 1.3. Hence the acetone photolysis at high temperatures is not a chain reaction. It was, however, possible to produce the sensitized decomposition of methyl ether by photolysing acetone in its presence. It may thus be concluded that methyl radicals are formed in the photolysis of acetone, but that these are incapable of propagating chains at temperatures up to 400°. This does not, however, rule out the possibility of chain propagation at the higher temperatures employed in the investigations of the thermal decomposition.

The same conclusion was reached by Rice, Rodowskas, and Lewis¹⁸³ who decomposed dimethyl mercury in the presence of acetone in the temperature range 350° to 400°. No decomposition of the acetone occurred, but

¹⁸² J. A. Leermakers, *J. Am. Chem. Soc.*, 56, 1899 (1934).

¹⁸³ F. O. Rice, E. L. Rodowskas, and W. R. Lewis, *J. Am. Chem. Soc.*, 56, 2497 (1934).

acetyl acetone was formed in amounts corresponding to that of the dimethyl mercury. Chain processes, therefore, do not occur below 400°, but at temperatures in the range 350° to 400° we probably have the reactions



At still lower temperatures methyl radicals apparently do not attack acetone. They were unable to detect methyl or other radicals by the Paneth technique with tellurium mirrors, using acetone at 700° and 200 mm. pressure. However, at such high pressures an effect would hardly be expected.

Fletcher and Rollefson¹⁴⁶ indirectly arrived at a similar conclusion. They found that the thermal decomposition of acetaldehyde at temperatures around 465° was induced by methyl radicals from the decomposition of ethylene oxide, and this induced decomposition was somewhat inhibited by the addition of acetone. This indicates that methyl radicals combine fairly readily with acetone at this temperature, but that they are not regenerated by a chain process.

Gantz and Walters¹⁸⁴ have shown that the decomposition of acetone is catalysed by iodine at temperatures around 500°, and that the iodine disappears during the early stages of the reaction, indicating a "chemical" mechanism for the catalysis. The resulting iodine-catalysed reaction is inhibited by ethylene, propylene, and nitric oxide, presumably indicating that the catalysed reaction involves chains. Methyl iodide and ethyl iodide also catalyse the acetone decomposition, but iso-propyl iodide is ineffective.¹⁸⁵ These results seem to indicate that at temperatures approaching those of the normal decomposition chains are possible in acetone.

The sensitization of the thermal decomposition of acetone also occurs with diacetyl.¹⁸⁶ At 526° and low diacetyl concentrations (about 0.1 per cent) up to 40 molecules of acetone were decomposed per molecule of decomposed diacetyl. It was also found that at lower temperatures, the induction period which normally occurs was eliminated by the presence of diacetyl. Oxygen and ethylene oxide also produced an appreciable acceleration of the decomposition, although their effect was much less than that of diacetyl. Azomethane, azoisopropane, trimethylamine, diethyl ether, dimethyl ether, acetyl acetone, and acetyl acetone were all ineffective.

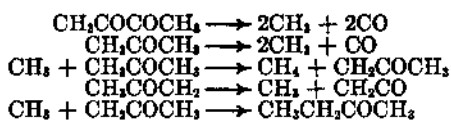
Since diacetyl was an effective sensitizer, Rice and Walters investigated the possibility of the induction period in the normal decomposition being due to the accumulation of diacetyl, but this was found not to be the case.

¹⁸⁴ G. M. Gantz and W. D. Walters, *J. Am. Chem. Soc.*, 62, 996 (1940), 63, 3412 (1941).

¹⁸⁶ Cf. S. Bairstow and C. N. Hinshelwood, *J. Chem. Soc.*, 1933, 1147; R. F. Faull and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 1755 (1936); Weiler, *Diss. Johns Hopkins University*, 1930.

¹⁸⁸ F. O. Rice and W. D. Walters, *J. Am. Chem. Soc.*, 63, 1701 (1941).

The acceleration by diacetyl must be due to radicals produced by its decomposition: these are presumably methyl radicals, since acetyl radicals are too unstable to have any appreciable effect at high temperatures. It should be noted that the temperatures used in Rice and Walters' investigation were higher than those used by other investigators who tried to sensitize the reaction, and it is possible that methyl radicals can set up chains in acetone at these, but not at lower temperatures. It is, however, peculiar that ethylene oxide should be so much less effective than diacetyl, and that azomethane and the ethers should be totally ineffective. Rice and Walters suggest that the mechanism of sensitization by diacetyl is probably



Early experiments on the inhibition of the acetone decomposition were inconclusive. Rice and Polly¹⁶³ found considerable inhibition of the reaction by propylene; 50 mm. of propylene reduced the rate of decomposition of about 150 mm. of acetone by a factor of about 4 at 550°. On the other hand Staveley and Hinshelwood¹⁸⁷ found that nitric oxide had no inhibiting effect on the reaction.

Smith and Hinshelwood^{187a} have recently reinvestigated the inhibition of the reaction by propylene and by nitric oxide. In the case of propylene, since the acetone decomposition occurs at temperatures at which propylene is itself decomposing to a slight extent, the reaction was followed analytically. The rate of the reaction was measured by the reciprocal of the time for 50 per cent reaction, and considerable inhibition by propylene was found. The results are given in Table XX A.

TABLE XX A. DECOMPOSITION OF ACETONE IN THE PRESENCE OF PROPYLENE AT 570°

Partial pressure of C ₂ H ₆ , mm.	1/T ₅₀ × 10 ³ , sec. ⁻¹			
	50 mm. acetone	100 mm. acetone	200 mm. acetone	300 mm. acetone
0	1.64	1.90	2.08	1.98
2	1.20			
5	0.96	1.35	1.60	—
10	0.81	1.14	1.42	1.67
20	0.70	0.96	1.32	1.46
50	0.60	0.72	1.05	1.21
100	0.53	0.69	0.91	1.03
150	—	—	0.80	—
170	—	0.58	—	0.83
200	—	—	0.76	—
estimated limiting rate	0.50	0.55	0.60	0.60

¹⁸⁷ L. A. K. Staveley and C. N. Hinshelwood, *Nature*, **137**, 29 (1936); *J. Chem. Soc.*, **1937**, 1568.

^{187a} J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A183**, 33 (1944).

Since these results were inconsistent with those of Staveley and Hinshelwood with nitric oxide, nitric oxide was reinvestigated as an inhibitor, with the results given in Table XX B. Inhibition undoubtedly occurs, but at high nitric oxide concentrations this is masked by catalysis by nitric oxide. If it were not for the catalysis, it appears probable that the limiting rates for the two inhibitors would coincide. It thus appears to be definitely established that the normal decomposition involves free radical chains. A large amount of inhibitor is required, however, for a relatively small amount of inhibition, and chain processes thus do not appear to play a predominant role.

TABLE XX B. DECOMPOSITION OF 100 MM. OF ACETONE AT 570°
IN THE PRESENCE OF NITRIC OXIDE

Partial pressure of nitric oxide, mm.	$1/T_{10} \times 10^4$, sec. ⁻¹
0.0	1.90
0.5	1.85
1.0	1.77
2.0	1.68
5	1.56
10	1.46
20	1.40
36	1.71

Smith and Hinshelwood adopt the mechanism suggested by Rice and Herzfeld, in which chain termination occurs by the reaction



In view of the fact that the "inhibition curves" with propylene do not coincide for different acetone pressures, they suggest that propylene attacks the CH_3 radical rather than CH_3COCH_3 . The activation energy of the reaction in the presence of excess propylene is 62.6 kcal., about 6 kcal. less than that of the normal uninhibited decomposition.

They point out that very much more nitric oxide is required to produce appreciable inhibition than is the case with other chain reactions, such as the decomposition of diethyl ether. This is explainable if the mean chain length in the acetone decomposition is relatively short, so that far more chain breaking processes occur for a given number of molecules decomposed.

The relative efficiency of nitric oxide as an inhibitor, compared with propylene, is very much less here than in other cases. (See Table X X C.)

This suggests that nitric oxide has a much greater advantage in attacking large radicals than it has with methyl. The magnitude of the effect is, however, surprising.

Klute and Walters^{115a} have recently found that at 523° the diacetyl sensitized decomposition of acetone is not inhibited by nitric oxide. It seems probable that, as with the normal decomposition, inhibition by nitric oxide is being masked by catalysis.

TABLE XX C. RELATIVE EFFICIENCIES OF NITRIC OXIDE AND PROPYLENE AS INHIBITORS

Decomposition	Ratio of amounts of CaHe and NO to produce a given amount of inhibition	Probable radicals removed by inhibitor
Acetone	~ 1	CH ₃
Acetaldehyde	~ 5	CH ₃
Diethyl ether	14	CH ₃ , CH ₂ OC ₂ H ₅
Propionaldehyde	100	C ₂ H ₅

Summing up the evidence on the acetone decomposition, it may be concluded that:

- (1) Radicals are formed in the decomposition at least to some extent.
- (2) A plausible chain mechanism for the decomposition can be devised.
- (3) Chains are not propagated at low temperatures by the introduction of radicals.
- (4) Chains can be propagated under some circumstances at higher temperatures.
- (5) Results on inhibition indicate that chains occur but that the mean chain length is quite short.

15. Higher Ketones

The decomposition of methyl ethyl ketone resembles that of acetone in every way. It has been reported that the thermal decomposition is not catalysed by iodine or by chlorine.^{180,188} In later work Gantz and Walters¹⁸⁹ found that the decomposition is catalysed by iodine, although to an extent considerably less than that of acetone. Rice suggests a chain mechanism for the reaction similar to that of acetone, but somewhat more complicated since ethyl radicals may be involved in addition to methyl and acetyl, and in addition to the acetyl radical, CH₃COCH₂, we have possibilities such as CH₃CH₂COCH₂, CH₃CHCOCH₂, and CH₃CH₂COCH₂.

The decomposition of diethyl ketone is also catalysed by iodine.¹⁸⁹

The thermal decomposition of acetophenone is not inhibited by nitric oxide, nor is it sensitized by radicals from the decomposition of diethyl ether.¹⁹⁰

¹⁸⁸ S. Bairstow and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A142, 77 (1933).

¹⁸⁹ G. M. Gantz and W. D. Walters, *J. Am. Chem. Soc.*, 63, 3412 (1941).

¹⁹⁰ J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A176,468 (1940).

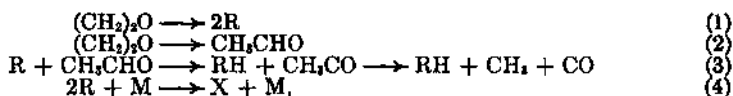
16. Ethylene Oxide

The decomposition of ethylene oxide was investigated by Heckert and Mack¹⁹¹ in the temperature range 380° to 444°. They showed that the reaction was first order, the rate at high pressures being given by

$$k_d = 6.3 \times 10^{14} e^{-15200/RT} \text{ sec.}^{-1}.$$

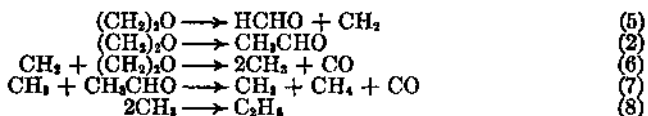
The products were approximately 50% CO, 36% CEU, 7% C_2H_6 , and 7% H_2 .

The mechanism of the reaction has been discussed by Sickman¹⁹² who concluded that its complexities could be explained on the assumption that the mechanism is



where R represents a free radical, X a molecule, and M is any third body. All the experimental facts are readily interpreted on this basis if we assume that k_1 is much smaller than k_2 , *i.e.*, that most ethylene oxide molecules isomerize to acetaldehyde, which then undergoes a radical sensitized decomposition, and that relatively few ethylene oxide molecules give free radicals by reaction (1). It should be noted that the sensitized decomposition of acetaldehyde will not affect the radical concentration, since each radical removed by reaction (3) is regenerated.

Fletcher and Rollefson^{193,194} re-investigated the reaction with special emphasis on the role of free radicals. Their work led them to postulate a mechanism of the type suggested by Sickman, but of a more detailed nature:



This mechanism is in good agreement with their rate measurements, analyses for formaldehyde and acetaldehyde, etc. By assuming that all the hydrogen found in the products comes from the decomposition of formaldehyde formed by reaction (5), and that all the ethane comes from reaction (8), they calculate that 14 per cent of the ethylene oxide decomposes by reaction (5). Whence, since each methylene gives rise to two methyls, they calculate that 0.3 methyls are formed for each ethylene oxide molecule decomposed.

¹⁹¹ W. W. Heckert and E. Mack, *J. Am. Chem. Soc.*, 61, 2706 (1929).

¹⁹² D. V. Sickman, *J. Chem. Phys.*, 4, 297 (1936).

¹⁹³ C. J. M. Fletcher, *J. Am. Chem. Soc.*, 68, 534 (1936).

¹⁹⁴ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 68, 2135 (1936).

While it cannot be said that this mechanism is established, it is undoubtedly plausible, and all the evidence indicates that by no means all the ethylene oxide decomposes by way of free radicals. It seems very unlikely that Fletcher and Rollefson's estimate of the fraction of ethylene oxide molecules giving rise to radicals is too low, although it may well be too high, since hydrogen and ethane may arise in other ways.

The fact that ethylene oxide has frequently been used as a sensitizer (see II-3) is further proof that free radicals are formed in its decomposition. Methyl radicals have been detected in the decomposition by Rice and Johnston,²¹ and the activation energy of the split into radicals is 44.0 kcal.

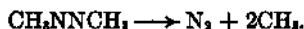
Thompson and Meissner¹⁹⁵ investigated the decomposition of propylene oxide, and found that the reaction was very similar to that of ethylene oxide. The inhibition by nitric oxide was very slight. The reaction was, however, very strongly catalysed by iodine, the rate at 452° and 200 mm. pressure being increased by a factor of nearly 40 by 12 mm. of iodine.

17. Azo and Diazo Compounds

Much work has been done on the decomposition of azomethane, so that here we will merely outline the main findings. (For an extended discussion see Schumacher.¹⁹⁶) The decomposition is complicated, but the main overall reaction results in the formation of nitrogen and hydrocarbons. Small amounts of other products are also formed.. The reaction is a classical example of a unimolecular change, the limiting high pressure rate constants being given by

$$\begin{aligned} k_{\infty} &= 3.13 \times 10^{14} e^{-52500/RT} \text{ sec.}^{-1} \text{ (Ramsperger)} \\ &= 8 \times 10^{15} e^{-50900/RT} \text{ sec.}^{-1} \text{ (Rice and Sickman }^{197, 198}) \end{aligned}$$

It has been shown in a number of cases, examples of which are given in Section II—3, that decomposing azomethane can induce the decomposition of other substances. This suggests that the decomposition process proceeds by way of free radicals, i.e.,



Experimental proof that at least part of the decomposition proceeds in this manner comes from the work of Leermakers¹⁹⁹ and of Rice and Evering²⁰⁰ who showed that mirrors were removed when azomethane was decomposed by the usual Paneth-Rice technique. The evidence favors the idea that while azomethane decomposes by a free radical mechanism, it does not do

¹⁹⁶ H. W. Thompson and M. Meissner, *Trans. Faraday Soc.*, 34, 1222 (1938).

¹⁹⁶ H. J. Schumacher, *Chemische Gasreaktionen*, Leipzig, 1938.

¹⁹⁷ O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, 4, 242 (1936).

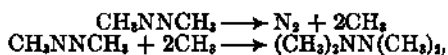
¹⁹⁸ D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, 4, 239, 608 (1936).

¹⁹⁹ J. A. Leermakers, *J. Am. Chem. Soc.*, 56, 3499 (1933).

²⁰⁰ F. O. Rice and B. L. Evering, *J. Am. Chem. Soc.*, 65, 3898 (1933).

so by a chain mechanism. (See references 201-204.) Thus Leermakers found that at 275° ethyl radicals did not react with azomethane. Also, up to 260° the quantum yield of the photodecomposition is approximately 2, and hence no long chains are set up by the methyl radicals produced in the primary process.

Taylor and Jahn²⁰⁵ have recently investigated the decomposition with emphasis on the analytical aspects of the problem. They conclude that the mechanism is



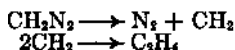
the ethane arising by secondary reactions. They find

$$k_{\infty} = 3.51 \times 10^{16} e^{-51100/RT} \text{ sec.}^{-1}$$

in good agreement with previous work. On the basis of their mechanism, the rate of decomposition of azomethane into methyl radicals will be only half this. The photolysis of azomethane has been investigated in considerable detail. It appears probable that the thermal reaction proceeds by a very similar mechanism. (See V-12.)

The thermal reactions of a number of other azo compounds have been investigated, and it appears probable that the mechanisms are similar to that of azomethane. In no case, however, is there any information which is relevant to the present discussion, except that in the case of the azo isopropane decomposition free radicals have been detected by the Paneth method.²⁰⁶

The decomposition of diazomethane has already been discussed (II-6) in connection with the detection of the methylene radical. There appears to be no doubt that the main reactions occurring are:



11. Alkyl Nitrites

Investigations have been made of the thermal decompositions of a series of alkyl nitrites²⁰⁷ including methyl, ethyl, n-propyl, iso-propyl, and

²⁰¹ G. S. Forbes, L. J. Heidt, and D. V. Sickman, *J. Am. Chem. Soc.*, 57, 1935 (1935).

²⁰² L. J. Heidt and G. S. Forbes, *J. Am. Chem. Soc.*, 67, 2331 (1935).

²⁰³ J. A. Leermakers, *J. Am. Chem. Soc.*, 65, 4508 (1933).

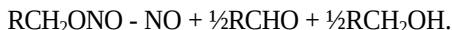
²⁰⁴ E. W. Riblett and L. C. Rubin, *J. Am. Chem. Soc.*, 69, 1537 (1937).

²⁰⁵ H. A. Taylor and F. P. Jahn, *J. Chem. Phys.*, 7, 470 (1939).

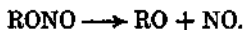
²⁰⁶ F. O. Rice and B. L. Evering, *J. Am. Chem. Soc.*, 66, 3898 (1933).

²⁰⁷ E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.*, 2, 345 (1934), 3, 344 (1935); *Proc. Roy. Soc. (London)*, A146, 388 (1934), A161, 685 (1935); E. W. R. Steacie and D. S. Calder, *J. Chem. Phys.*, 4, 96 (1936); E. W. R. Steacie and S. Rosenberg, *J. Chem. Phys.*, 4, 223 (1936); E. W. R. Steacie and W. McF. Smith, *J. Chem. Phys.*, 4, 504 (1936); E. W. R. Steacie, S. Katz, S. Rosenberg, and W. McF. Smith, *Can. J. Research*, B14, 268 (1936); E. W. R. Steacie and S. Katz, *J. Chem. Phys.*, 6, 125 (1937); A. G. Carter and M. W. Travers, *Proc. Roy. Soc. (London)*, A158, 495 (1937).

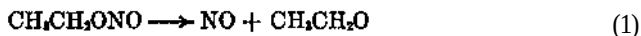
n-butyl nitrites. The major overall reaction is the same for all members of the series, viz.,



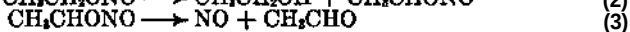
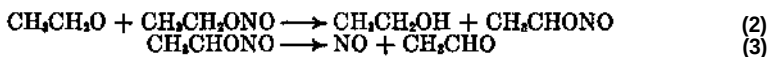
The reactions are all of the first order, and all have activation energies of 37 ± 1 kcal., as shown by Table X X I. It thus appears certain that the same type of reaction is occurring in every case, and that the primary step is almost certainly



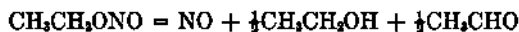
This conclusion is confirmed by an investigation of the decomposition of ethyl nitrite by the Paneth technique by Rice and Rodowskas.²⁰⁸ They suggest the primary reaction



should be followed by



The overall reaction would thus be



in agreement with the findings of Steacie and Shaw.

At low pressures we might expect

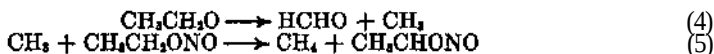


TABLE XXL DECOMPOSITION OF ALKYL NITRITES

Substance	A	E, kcal.
Methyl nitrite	1.84×10^{13}	36.4
Ethyl nitrite	1.39×10^{14}	37.7
Propyl nitrite	2.75×10^{14}	37.7
Iso-propyl nitrite	1.26×10^{14}	37.0
n-Butyl nitrite	3.02×10^{14}	37.0

followed by (3), leading to the overall reaction

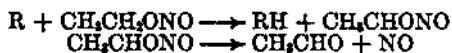


In Steacie and Katz's work the overall pressure increase at completion was the same at pressures down to 10^{-2} mm. as it was at high pressures. This Argues against Rice and Rodowskas' low pressure mechanism which requires a pressure increase at completion of 150 per cent at low pressures, as against 100 per cent at high pressures. There is, however, the possibility of the formaldehyde condensing out. In any case the change of mechanism at low pressures is not unreasonable.

Rice and Rodowskas point out that the above mechanism is unusual since the substrate itself acts as a chain breaker, and hence chain processes

²⁰⁸ F. O. Rice and E. L. Rodowskas, *J. Am. Chem. Soc.*, 67, 360 (1935).

cannot come into play. Thus if a free radical were introduced into ethyl nitrite it would disappear and be replaced by stable molecules by the reactions



They used the Paneth technique at 425° and found no mirror removal. However, this is not surprising if we assume that reactions (1) and (4) occur in the furnace, and are followed by (5) and (3) which remove the radicals before they can reach the mirror. To verify this they diluted the ethyl nitrite with various gases (CO_2 , C_2H_{10} , and ether) to cut down the rate of (5). With one per cent of ethyl nitrite mixed with the carrier gas mirrors were readily removed at temperatures as low as 400°. The product with tellurium mirrors was pure dimethyl ditelluride, so that only methyl radicals were formed.

From the rate of disappearance of standard mirrors at various temperatures they estimated that $E_i = 34.3 \pm 3$ kcal., in agreement with Steacie and Shaw's value for the overall reaction of 37 ± 1 kcal. They conclude that the failure to obtain mirror removal with pure ethyl nitrite means that E_h is less than 10 kcal. Reaction (7) is probably fairly strongly exothermic and has a small activation energy, so that the reverse reaction



would be expected to have too high an activation energy to be of importance. From the fact that reaction (4) apparently does not come into play until quite low pressures they conclude that $E_4 - E_2$ is about 16 kcal., and that plausible values are $E_2 = 12 - 18$ kcal., $E_4 = 28 - 34$ kcal.

The photolyses of a number of alkyl nitrites have also been investigated.²⁰⁹ The mechanism appears to be quite different from that of the thermal decompositions, however.

19. Ethyl Bromide

The thermal decomposition of ethyl bromide has been extensively investigated by Daniels and his co-workers.²¹⁰ The products are almost entirely those corresponding to the reaction

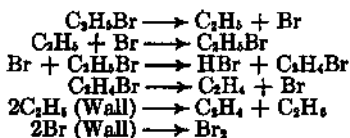


but there is the possibility of complications due to the back reaction. The reaction is accelerated by oxygen, and the rate is decreased by the addition of foreign gases. There is also an induction period under certain conditions. These facts point to the possible existence of reaction chains.

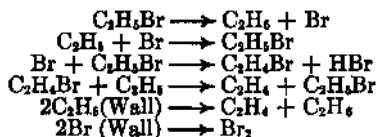
²⁰⁹ H. W. Thompson and C. H. Purkis, *Trans. Faraday Soc.*, 32, 674, 1466 (1936); H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, 33, 1546 (1937).

²¹⁰ E. T. Lessig, *J. Phys. Chem.*, 36, 2325 (1932); E. L. Vernon and F. Daniels, *J. Am. Chem. Soc.*, 54, 2563 (1932), 55, 922 (1933); P. Fugassi and F. Daniels, *J. Am. Chem. Soc.*, 60, 771 (1938); F. Daniels, *Chemical Kinetics*, Ithaca, 1938.

Daniels suggests that part of the reaction may go by the mechanism

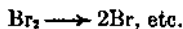


The reaction might also occur by a non-chain free radical mechanism, viz.



This is all speculative, however.

The decomposition is not inhibited by nitric oxide,²¹¹ which is evidence against the chain mechanism. It is, however, catalysed by bromine, undoubtedly by



Daniels and Veltman favor the non-chain free radical mechanism.

Daniels points out²¹² that an initial split of the C—Br bond would require 53 kcal.,* but that the activation energies of the decompositions of methyl, ethyl, and propyl bromides vary widely, viz., a very high *E* for methyl, 53.8 kcal. for ethyl, and 36 kcal. for propyl. The variation is much too great to arise from bond strength differences. However, if all the reactions occur by free radical mechanisms such differences are explainable on the basis of the subsequent secondary reactions.²¹³

Roof and Daniels²¹⁴ have shown that ethyl bromide can cause sensitized decomposition of acetaldehyde at temperatures from 357° to 400°, which is a definite indication of the presence of radicals in the decomposition of ethyl bromide. At 400° about 10 moles of CH₃CHO decomposed per mole of C₂H₅Br. The photolysis of acetone in the presence of ethyl bromide does not cause sensitized decomposition of the bromide, however, from which it appears that chain decomposition of ethyl bromide cannot be initiated by methyl radicals.

It thus appears that free radicals are definitely produced in the decomposition, but that free radical chain processes are not of importance.

²¹¹ F. Daniels and P. L. Veltman, *J. Chem. Phys.*, 7, 756 (1939).

²¹² F. Daniels, *J. Chem. Phys.*, 7, 766 (1939).

* More recent estimates of C—Br bond strengths (see Table V) put the values considerably higher, viz., CH₃—Br 68.5 kcal, C₂H₅—Br 67.0 kcal., C₃H₇—Br 64.5 kcal.

²¹³ See, for example, R. A. Ogg, *J. Chem. Phys.*, 7, 766 (1939).

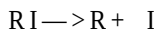
²¹⁴ J. G. Roof and F. Daniels, *J. Am. Chem. Soc.*, 62, 2912 (1940); J. G. Roof, *J. Am. Chem. Soc.*, 66, 358 (1944).

20. Alkyl Iodides

The thermal decompositions of a number of alkyl iodides have been investigated. The results are discussed in detail under the specific reactions in Chapter XI, and a brief general survey only will be given here. Using the values given in Table V, it will be seen that the strength of the R—I bond in alkyl iodides varies from about 54.0 kcal. for CH₃I to 49.0 for n-C₄H₉I. This is a low value for the strength of a bond in an organic molecule, and as a result free radical mechanisms appear to hold for all the alkyl iodides, the initial step being



Butler and Polanyi¹⁸ have investigated the pyrolysis of a number of iodides by a technique somewhat similar to the Paneth method. The iodide, at low pressure with a carrier gas, was flowed rapidly through a tube as in the experiments of Paneth and Rice. Instead of using mirrors, however, the reaction was followed by the iodine (and sometimes also by the hydrogen iodide) formed. On the assumption that the back reaction is negligible this is then directly analogous to Rice's work, and the activation energy of the primary split

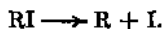


can be calculated from the temperature coefficient of iodine production. The results appear to be entirely consistent with this explanation, and the values of the activation energy calculated from the temperature coefficient are in good agreement with those calculated from the approximate relationship

$$k = 10^{12} e^{-E/RT}$$

They therefore conclude that while some error must exist on account of recombination, it cannot be serious.

In this way they arrived at the values given in Table X X I A for the activation energies of reactions of the type



These values are considerably higher than those found in earlier work. (See the discussion of specific cases in Chapter XI.)

The same primary step occurs in the photolysis of alkyl iodides. The photolyses have very low quantum yields, and the thermal reactions of methyl and ethyl iodides are much slower than would be expected from their low activation energies. This is undoubtedly due to the re-formation of the iodides in both the thermal and photochemical reactions by



and



since (3) and (4) appear to occur at practically every collision.

TABLE XXI A. ACTIVATION ENERGIES OF DECOMPOSITION OF IODIDES INTO FREE RADICALS

Iodide	<i>E</i> of primary split, kcal.	<i>k</i> _{500°} × 10 ⁴ , sec. ⁻¹
methyl	54	14
ethyl	52.2	50
<i>n</i> -propyl	50.0	250
<i>n</i> -butyl	49.0	560
iso-propyl	46.1	4,000
tert-butyl	45.1	9,000
allyl	39.0	630,000
vinyl	55.0	6.3
benzyl	43.7	23,000
phenyl	54.0	14
acetyl	50.7	160
benzoyl	43.9	18,000
acetylonyl	45.0	9,000

The actual products formed in the decompositions result from reactions such as



The back reactions (3) and (4) appear to be much less important in the case of the higher iodides, and this may be due to the fact that reaction (5) occurs more readily for propyl and butyl radicals than it does with methyl and ethyl where three-body restrictions may have some effect.

Considerable detailed information exists concerning the mechanisms of the reactions of the specific compounds, and these are discussed in connection with the relevant part reactions in Chapter XI.

Chapter IV

Free Radical Mechanisms in Polymerization Reactions

1. Introduction

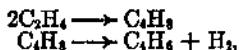
In a few cases, notably those of ethylene and acetylene, considerable information exists which has a bearing on the role of free radicals in polymerization processes. The information comes both from thermal and from photochemical sources. In the latter case, however, while the primary step may be photochemical, the polymerization processes are usually influenced by the secondary reactions of radicals produced in the primary step. Since the secondary reactions are independent of the source of the free radicals involved, it is convenient to consider the thermal and photochemical results together, and this will be done in the present chapter.

Very little information exists for reactions other than those of ethylene, propylene, and acetylene, and the present discussion will therefore be limited almost entirely to a discussion of these three substances.

2. The Thermal Reactions of Ethylene

If ethylene is heated to a moderately low temperature, the main reaction is polymerization. At higher temperatures it also undergoes decomposition. It is, in general, not possible to separate completely the two reactions, and hence the whole situation is complex.

Hague and Wheeler¹ on the basis of experiments complicated by a considerable amount of decomposition concluded that butadiene was the most important product in the polymerization of ethylene, the main reactions being



followed by further reactions of butadiene with ethylene to give benzene, etc. The same conclusion was reached by Wheeler and Wood.²

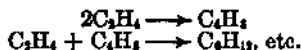
Pease³ in the first investigation of any kinetic significance found that by working at pressures of about 10 atmospheres it was possible to suppress the decomposition almost completely, and to obtain as products practically

¹ E. N. Hague and R. V. Wheeler, *J. Chem. Soc.*, **1929**, 378; *Fuel*, 8, 560 (1929).

² R. V. Wheeler and W. L. Wood *J. Chem. Soc.*, **1930**, 1819.

³ R. N. Pease, *J. Am. Chem. Soc.*, 62, 1158 (1930), 63, 613 (1931); R. N. Pease and P. R. Cheesebro; *Proc. Nat. Acad. Sci.* (Washington), 14, 472 (1928).

nothing but higher olefins. At lower pressures the reaction was complex, but at higher pressures it was definitely a second order association reaction with an activation energy of 35 kcal. The steric factor was low, about 1J2000. Pease suggested for the mechanism



It was found by Storch⁴ that the reaction is greatly accelerated by traces of oxygen. Storch obtained an activation energy of 42Jccal., a value somewhat higher than that of Pease. He suggests that this is due to the presence of oxygen in the ethylene used by Pease. In a later paper⁵ Storch attempted to purify ethylene sufficiently to enable really reproducible rates to be obtained. This was not successful, but he found that the addition of small amounts of ethyl mercaptan slowed down the average rate and made the results strictly reproducible. Further it was found that these rates were in agreement with the slowest rates obtained with "pure" ethylene. This suggests the presence of a catalyst of some sort under normal conditions, and he considers that the reaction is probably not a simple bimolecular change. The activation energy of the overall reaction was 43.5 kcal. in good agreement with his former estimate.

The reaction has also been investigated by Krauze, Nemtzov, and Soskina⁶ who also found it to be homogeneous and second-order. Their rates are given by

$$\log_{10} k = 10.85 - \frac{37,700}{2.3RT} \text{ liter mole}^{-1} \text{ sec.}^{-1}.$$

They calculate a collision efficiency of 1J400. The second order rate constants were found to fall off considerably as the reaction progressed.

TABLE XXII. PRODUCTS OF THE DECOMPOSITION AND POLYMERIZATION OF ETHYLENE AT 575°

Substance	Percent
N ₂	0.8
H ₂	0.8
CH ₄	2.6
C ₂ H ₄	84.4
C ₂ H ₆	3.2
C ₃ H ₈	0.0
C ₄ H ₈	1.2
C ₆ to C ₈	2.2
Higher	0.3

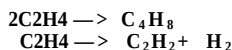
⁴ H. H. Storch, *J. Am. Chem. Soc.*, 56, 374 (1934); see also S. Lenher, *J. Am. Chem. Soc.*, 53, 3752 (1931).

⁵ H. H. Storch, *J. Am. Chem. Soc.*, 57, 2598 (1935).

⁶ M. V. Krauze, M. S. Nemtzov, and E. A. Soskina, *Compt. Rend. Acad. Sci. (U.R.S.S.)*, 2, 301 (1934); *J. Gen. Chem. (U.S.S.R.)*, 5, 343 (1935).

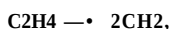
The reaction at higher temperatures is much more complex and consists of both decomposition and polymerization. It was shown by Frey and Smith⁷ to be homogeneous in silica vessels. The products included methane, ethane, hydrogen, and higher olefins. (See Table XXII.)

Burk, Baldwin, and Whitacre⁸ obtained similar results. At 625° the order of the reaction was slightly greater than unity. They suggest that the main reactions are

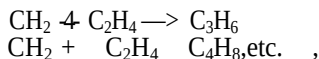


followed by further reactions of acetylene to give butadiene, etc.

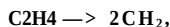
Egloff, Schad, and Lowry⁹ suggest that the primary reaction is



followed by



It should be pointed out, however, that Rice and his collaborators have been consistently unsuccessful in attempts to prepare radicals from decomposing ethylene, and Rice assigns an activation energy of 150 kcal. to the reaction



which would rule it out as the primary step. However, as pointed out in Chapter II, the Rice technique is perhaps not very successful in detecting methylene, and this estimate of the activation energy may be altogether too high. Kassel assigns a value of 77 kcal. to the reaction, which would perhaps make it a feasible primary process if the reaction proceeds by a chain mechanism.

The whole question as far as this mechanism is concerned really hinges on the state of the CH_2 formed in the postulated reaction. If the CH_2 is in the triplet state (*i.e.*, as the biradical $\text{—CH}_2\text{—}$), the process will be endothermic to the extent of the strength of the $\text{C}=\text{C}$ bond, and 125 to 150 kcal. is a reasonable estimate of the activation energy. If, however, the CH_2 reorganizes to the singlet state (*i.e.*, to molecules with bivalent carbon) in the process, the reaction will be much less endothermic and 77 kcal. is not an unreasonable value. There is evidence that such a reorganization may occur in some reactions, such as the photodecomposition of diazomethane and of ketene.

The ethylene-hydrogen-ethane equilibrium has been investigated by a number of workers, and Pease¹⁰ has investigated the rate of the hydrogenation

⁷ F. E. Frey and D. F. Smith, *Ind. Eng. Chem.*, 20, 948 (1928).

⁸ R. E. Burk, B. G. Baldwin, and C. H. Whitacre, *Ind. Eng. Chem.*, 29, 326 (1937).

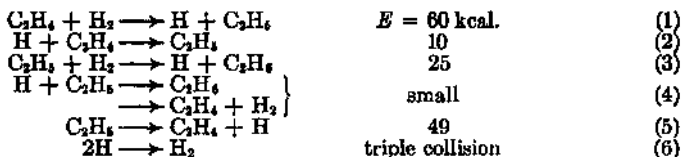
⁹ G. Egloff, R. E. Schad, and C. D. Lowry, *J. Phys. Chem.*, 35, 1825 (1931).

¹⁰ R. N. Pease, *J. Am. Chem. Soc.*, 52, 1158 (1930), 54, 1876 (1932).

tion of ethylene. He found that in the main the hydrogenation went smoothly to ethane, although a small amount of polymerization of ethylene occurred as well. The reaction was almost entirely homogeneous and of the second order. A steric factor of 0.1 was found, which is surprisingly high for an association reaction between comparatively simple molecules. The rate of the reaction was given by

$$\log_{10} k = 5.58 - \frac{43,150}{2.3RT} \text{ cm.}^3 \text{ mole}^{-1} \text{ sec}$$

Rice and Herzfeld¹¹ have suggested a free radical mechanism for the reaction, viz.,



or

This leads to good agreement with experiment, but in view of the criticisms which have already been raised against the Rice-Herzfeld mechanism for the reverse reaction (the ethane decomposition) it seems very unlikely that the above scheme is correct. In any case the assigned activation energies are by no means correct, especially those of reactions (2) and (3).

There is, however, a great deal of evidence that the rate of polymerization of ethylene is affected by the presence of free radicals. Rice and Sickman¹² found that ethylene was polymerized in the presence of decomposing azomethane at 300°. The mechanism is presumably



They found a peculiar concentration relationship, i.e.,

$$\frac{-dp}{dt} = [\text{CH}_3\text{NNCH}_3]^{\frac{1}{2}} [\text{C}_2\text{H}_4]^{\frac{3}{2}}.$$

Taylor and Jungers¹³ suggest that this is due to wall effects, since Rice and Sickman's work was carried out at low pressures (below 6 cm.). The reaction is also induced by radicals from the decomposition of ethylene oxide,¹⁴ and of vinyl ethyl ether.¹⁶

Considerable work has been done on the sensitization of the ethylene polymerization by radicals from the thermal decomposition of metal alkyls.

¹¹ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, 56, 284 (1934).

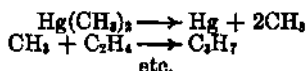
¹² O. K. Rice and D. V. Sickman, *J. Am. Chem. Soc.*, 57, 1384 (1935); D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, 4, 608 (1936).

¹³ H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, 33, 1353 (1937).

¹⁴ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2135 (1936).

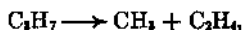
¹⁵ S. N. Wang and C. A. Winkler, *Can. J. Research*, B21, 97 (1943).

Taylor and Jones¹⁶ investigated the decomposition of mercury and lead alkyls in the presence of ethylene and hydrogen at temperatures from 250° to 300°. The main result was polymerization of ethylene, undoubtedly by the mechanism



Similar results with lead tetramethyl were obtained by Romm.¹⁷

Beeck and Rust¹⁸ investigated the polymerization sensitized by lead tetramethyl and lead tetraethyl, using mainly a flow method. With lead tetramethyl they found that 1.8 mole of olefin reacted per mole of methyl radicals when the mole per cent of the alkyl was 1.97, and 1.2 mole of olefin when the mole per cent was 4.06. The temperature was 450°. The products consisted of paraffins and olefins with carbon numbers from 3 to 6, together with very little methane. The products of low molecular weight contained more olefins than paraffins, which, together with the fact that the average carbon number is low, suggests that the formation of larger radicals is mainly interrupted by the decomposition of the radicals into olefins and smaller radicals, *i.e.*, by chain transfer through radical decomposition. The results with lead tetraethyl were very similar. Thus at 400° they found that when the concentration of lead alkyl was 0.5 and 1.5 mole per cent respectively, 1.6 and 1.2 moles of olefin reacted per mole of ethyl formed. The products were similar to those with lead tetramethyl. There appears to be no doubt that the mechanism with both compounds is that given above. No hydrogen was found in the products, and it may therefore be concluded that the higher radicals always decompose by a C—C split, *e.g.*,



rather than by splitting off a hydrogen atom



Cramer¹⁹ has investigated the sensitized polymerization of ethylene by lead tetraethyl in benzene solution at high pressures. The benzene was recovered unchanged and apparently did not take part in the reaction. The results were similar to those in the gas phase, but since increasing pressure favors association reactions the sensitizing action was more efficient. Thus 0.3 mole per cent of ethyl groups caused the polymerization of 90 per cent of the ethylene.

The radicals responsible for the sensitized polymerization of ethylene may obviously also be produced by photochemical means. Taylor and

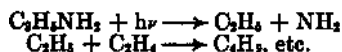
¹⁶ H. S. Taylor and W. H. Jones, *J. Am. Chem. Soc.*, 52, 1111 (1930).

¹⁷ F. S. Romm, *J. Gen. Chem. (U.S.S.R.)*, 10, 1784 (1940).

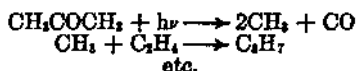
¹⁸ O. Beeck and F. F. Rust, *J. Chem. Phys.*, 9, 480 (1941).

¹⁹ P. L. Cramer, *J. Am. Chem. Soc.*, 56, 1234 (1934).

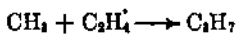
Emeleus²⁰ found that the reaction was photosensitized by ammonia, presumably owing to hydrogen atoms or to radicals from the ammonia decomposition. Methyl and ethyl amines show similar behaviour,²¹ the mechanism evidently being



Taylor and Jungers²² investigated the acetone photosensitized polymerization of ethylene over the temperature range 25° to 250°. There is no doubt that the primary step is the photodissociation of acetone to yield methyl radicals: these then induce the polymerization of ethylene, *i.e.*,



Taylor and Jungers found that the induced polymerization of ethylene occurs readily at room temperature, and the temperature coefficient of the reaction is very small. Thus the number of molecules of ethylene disappearing per acetone molecule decomposed rises from 1.4 for a mixture of 15 cm. of each constituent at 25° to only 3.4 for the same mixture and pressure at 250°. This appears to indicate an activation energy for the reaction

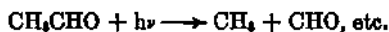


of only one or two kcal. The rate of polymerization was given by

$$-\frac{dp}{dt} = kI_0[\text{CH}_3\text{COCH}_3][\text{C}_2\text{H}_4],$$

and is thus proportional to $[\text{CH}_3][\text{C}_2\text{H}_4]$ as would be expected. They suggest that the relatively high activation energy of the thermal polymerization of ethylene (ca. 40 kcal.) is the activation energy of the primary step, probably involving the formation of a free radical. Once free radicals are produced it appears that subsequent polymerization reactions proceed with a low activation energy. Danby and Hinshelwood²³ have also shown that the reaction can be photosensitized by acetone and by diethyl ketone.

Roof and Daniels²⁴ showed that the reaction was photosensitized by acetaldehyde, undoubtedly by



Danby and Hinshelwood²³ investigated the acetaldehyde sensitized polymerization at 300° in some detail. It appears to be fairly well established

²⁰ H. S. Taylor and H. J. Emeleus, *J. Am. Chem. Soc.*, 52, 2150 (1930).

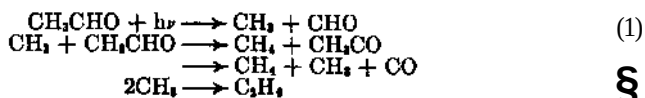
²¹ H. S. Taylor and H. J. Emeleus, *J. Am. Chem. Soc.*, 53, 3370 (1931).

²² H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, 33, 1353 (1937).

²³ C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A179, 169 (1941).

²⁴ J. G. Roof and F. Daniels, *J. Am. Chem. Soc.*, 62, 2912 (1940).

(Section V-3) that the acetaldehyde photolysis occurs principally by the mechanism:



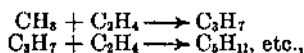
§

In the presence of ethylene the rate of photolysis of acetaldehyde is reduced. The photolysis normally has a considerable chain length at this temperature, and the reduction in rate is obviously to be ascribed to the removal of chain carriers by reaction with ethylene. Since the rate of polymerization is comparable with the rate of the acetaldehyde photolysis, it is evident that the polymerization must also have a considerable chain length, and Danby and Hinshelwood calculate values up to 48. (See Table XXIII.)

TABLE XXIII. POLYMERIZATION OF ETHYLENE INDUCED BY THE PHOTOLYSIS OF ACETALDEHYDE

Ethylene pressure mm.	Acetaldehyde Pressure 50 mm.			
	Rate, in arbitrary units of aldehyde photolysis	of ethylene polymerization	of aldehyde photolysis	Chain length of ethylene polymerization
0	17.0	—	28	—
100	12.5	14.0	20	23
200	10.8	19.5	18	32
300	9.8	24.0	16	39
400	8.9	28.3	14	48

The mechanism is presumably

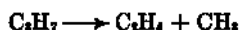


i.e., the successive addition of alkyl radicals to ethylene. However, in spite of the long chain length the product is of low molecular weight, *viz.*, not much greater than Co. Hence a reaction must occur which forms a low molecular weight olefin and regenerates a radical, *e.g.*,



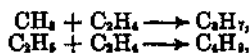
This is reasonable since it is well known that the higher alkyl radicals are unstable. Danby and Hinshelwood suggest that the inhibition of the photolysis by ethylene is due to an additional chain ending process such as chain termination by the decomposition of a chain carrier, rather than by the more obvious recombination of radicals.

They found that the polymerization of ethylene was also photosensitized by propionic and *n*-butyric aldehydes in a similar way. However, although the polymerization proceeded efficiently there was no inhibition of the photolysis of the aldehydes. They suggest that this might be due to the occurrence of reactions such as



so that the ethyl or propyl radicals which are normally produced in the photolysis are replaced by methyls, and that these react faster than ethyl or propyl and thus counterbalance the inhibiting effect.

From a comparison of the three aldehydes they conclude that there is little difference in the rates of the reactions

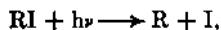


and

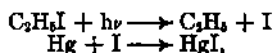


All this is somewhat speculative, but there appears to be no doubt that alkyl radicals from the photolysis of aldehydes can sensitize the ethylene polymerization, and that at 300° the sensitized polymerization is a chain reaction.

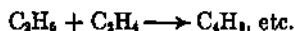
Further evidence along the same lines comes from work on the photo-sensitization of the polymerization by iodides.^{26,26,27} The primary step in the photolysis of alkyl iodides is



but the reverse reaction is very efficient and the net quantum yield is low. It is found that with ethyl iodide in the presence of ethylene the quantum yield is still very small, i.e., the reaction of radicals with iodine atoms to reform the alkyl iodide is much faster than their reaction with ethylene.²⁵ If mercury is added to the system, it fixes the iodine atoms formed in the primary step



and the ethyl radicals then cause an induced polymerization of ethylene,



Joris and Jungers found that the effect increased considerably with rising temperature in the range 108° to 260°: thus the time for the pressure to drop one half at a given light intensity decreased from ca. 220 min. at 108° to 46 min. at 269°. This fact together with the very slow reaction in the absence of mercury suggests that the reaction



has an appreciable activation energy, contrary to the previous conclusions of Taylor and Jungers for the analogous reaction with methyl radicals.

²⁸ G. G. Joris and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 47, 135 (1938).

²⁶ J. C. Jungers and L. M. Yeddapanalli, *Trans. Faraday Soc.*, 36, 483 (1940).

²⁷ R. v. Tassel, *Natuurw. Tijdschr.*, 20, 83 (1938).

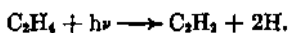
Sensitization by *n*- and iso-propyl iodides²⁶ is similar to that with **ethyl** iodide.

The ethyl iodide photosensitized polymerization of deuterio-ethylene proceeds at the same rate as that of normal ethylene.²⁸

From all the above work there is no doubt that free radicals can set up chain polymerization of ethylene. Evidence that free radical processes occur to at least some extent in the normal thermal polymerization comes from the work of Burnham and Pease,²⁹ on the inhibition of the polymerization by nitric oxide. They found that the rate of polymerization was reduced by a factor of 3 by the presence of a moderate amount of nitric oxide. This definitely indicates the occurrence of free radical processes of some sort, but it is difficult to construct a satisfactory mechanism, since the bond strengths involved are all so very much higher than the 40 kcal. activation energy of the thermal polymerization.

3. The Photoreactions of Ethylene

Early investigations did not distinguish very clearly between the direct photochemical reaction of ethylene and the mercury photosensitized reaction. The first definite information about the direct photoreaction was obtained by Mooney and Ludlam,³⁰ who found that ethylene did not absorb light of wave length greater than 2130A to any appreciable extent, and concluded that nothing was to be expected from investigations with a mercury arc source (provided that mercury vapor is kept out of the reaction vessel, since otherwise the mercury photosensitized reaction would come into play). Mooney and Ludlam used an aluminum spark with a high intensity at 1860A and found that acetylene was formed, perhaps by



Qualitative observations by Lind and Livingston³¹ are in agreement with these results. Taylor and Emeleus, however, showed that a mercury arc did cause appreciable polymerization of ethylene in the absence of mercury vapor,³² and they concluded that this was to be ascribed to absorption by ethylene of wave lengths near the limit of transmission of silica (probably mainly to $\lambda 1849$).

McDonald and Norrish³³ reinvestigated the reaction using a hydrogen lamp source and fluorite apparatus and were thus able to use shorter wave lengths. Hydrogen, a polymer and a condensable gas were formed under

²⁸ J. C. Jungers and G. G. Joris, *Bull. Soc. Chim. Belg.*, 50, 61 (1941).

²⁹ H. D. Burnham and R. N. Pease, *J. Am. Chem. Soc.*, 62, 453 (1940).

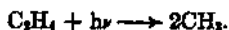
³⁰ R. B. Mooney and E. B. Ludlam, *Trans. Faraday. Soc.*, 25, 442 (1929).

³¹ S. C. Lind and R. Livingston, *J. Am. Chem. Soc.*, 55, 1036 (1933).

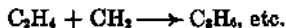
³² H. S. Taylor and H. J. Emeleus, *J. Am. Chem. Soc.*, 53, 562, 3370 (1931).

³³ R. D. McDonald and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, A157, 480 (1936).

these conditions. Spectroscopic observations suggest³⁴ that the primary process is



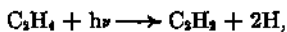
If this is so, the polymerization is easily explained as due to



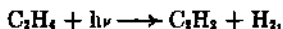
The formation of hydrogen is hard to explain, however, since on this basis it could only arise by



and this reaction seems very unlikely on account of the small concentration of methylene. As an alternative explanation they suggest



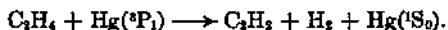
together with



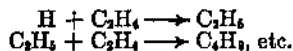
followed by secondary reactions of hydrogen atoms with ethylene to yield ethane and butane. This is all completely speculative.

4. The Photosensitized Reactions of Ethylene

The mercury photosensitized reaction has been investigated by a number of workers,⁸⁵ virtually all of whom adopt for the primary step the mechanism suggested by Taylor and Bates,



Taylor and Bates assumed that the subsequent reactions were the mercury photosensitized polymerization of acetylene, together with the reaction of hydrogen atoms and of radicals with ethylene,



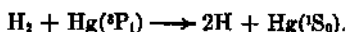
The main evidence for this mechanism was the detection of large amounts of acetylene in the products, and the fact that the pressure rises in the early stages of the reaction and then falls rapidly.

Melville did a few experiments on the polymerization of ethylene in connection with an investigation of the photosensitized polymerization of acetylene. He confirmed the well-known initial pressure rise, but in the absence of analytical data was led to assume that the acetylene produced

⁸⁴ H. J. Hilgendorf, *Z. Physik*, **95**, 781 (1935); W. C. Price, *Phys. Rev.*, **45**, 843 (1934), **47**, 444 (1935).

³⁶ D. Berthelot and H. Gaudechon, *Compt. Rend.*, **150**, 1169 (1910); M. Landau, *Compt. Rend.*, **155**, 402 (1912); H. S. Taylor and J. R. Bates, *J. Am. Chem. Soc.*, **49**, 2438 (1927); *Proc. Nat. Acad. Sci.* (Washington), **12**, 714 (1926); A. R. Olson and C. H. Meyers, *J. Am. Chem. Soc.*, **48**, 389 (1926); H. S. Taylor and D. G. Hill, *J. Am. Chem. Soc.*, **51**, 2922 (1929); H. W. Melville, *Trans. Faraday Soc.*, **32**, 258 (1936).

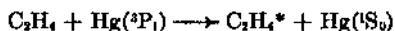
polymerized readily, and that the polymer was subsequently hydrogenated by hydrogen atoms produced in the reaction



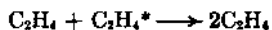
He assumed that after the maximum in total pressure was reached hydrogen and acetylene disappeared in equimolecular amounts. It must be emphasized, however, that in his work the only measurements actually made were of the overall pressure and of the pressure of non-condensable gas.

Recently a more detailed investigation of the mercury photosensitized reaction at 25° has been made by Le Roy and Steacie.³⁶ Their main findings were: (1) The initial pressure rise at low pressures corresponds exactly with the amounts of acetylene and hydrogen produced. (2) Hydrogen is the only non-condensable product. (3) At higher pressures there is evidence that the initial rate of production of acetylene is greater than the rate of pressure increase. (4) Butane and butene are important products of the reaction. (5) Acetylene is relatively inert up to high concentrations. The amount of acetylene increases regularly after the maximum pressure is reached. This is shown by Figure 13. Curve A shows the typical initial pressure rise, followed by a later decrease. Curve C gives the production of acetylene. It will be seen that the acetylene concentration continues to rise after the maximum pressure rise has been passed. Curve B represents a run which was stopped after the maximum pressure was passed, and all non-condensable gases were pumped off. On turning the lamp on again, the pressure again rose as shown in the figure. The decrease in pressure in the later stages of the reaction is thus due to the presence of hydrogen, and has nothing to do with the polymerization or other reactions of acetylene. (6) The rate of reaction decreases with increasing initial ethylene pressure. (7) The rate is directly proportional to the light intensity. (8) The quantum yield is less than unity.

The fact that the rate falls with increasing pressure suggests that some sort of deactivation process is occurring. They therefore suggest a reaction of the type



This is then followed by



or by



the first of these alternatives becoming more prominent as the pressure is increased. In view of the fact that butane is a product and that hydrogen is responsible for the decrease in pressure in the later stages, there seems to be no doubt that secondary reactions are

³⁶ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.*, 9, 829 (1941).

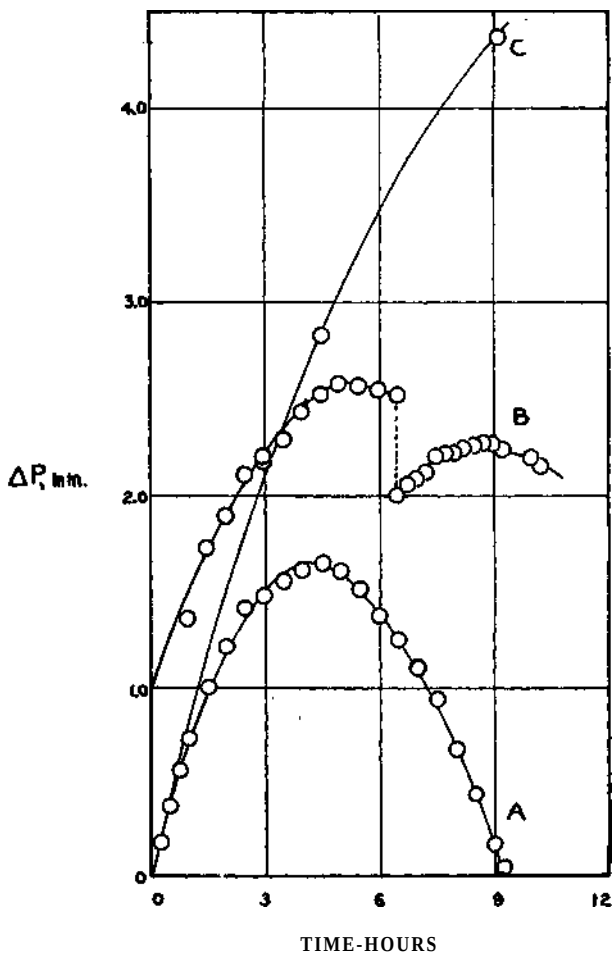
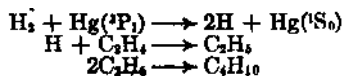


Figure 13. Mercury photosensitized reactions of ethylene.

A, Pressure change. B, Run interrupted at 6½ hrs. and non-condensable gases pumped off. C, Acetylene produced, mm.

In a further paper³⁷ the same authors investigated the reaction at higher temperatures. They found that the initial rate of pressure increase decreased as the temperature was raised until at 250° the initial pressure rise had disappeared altogether as shown by Figure 14. The effect of pressure was different at higher temperatures, the rate of ethylene disappearance increasing as the pressure was increased. The rate of formation of hydrogen

⁸⁷ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.*, 10, 676 (1942).

and acetylene did not change appreciably at higher temperatures, but the rate of ethylene disappearance increased considerably with increasing temperature. This suggests strongly that free radicals are being formed and

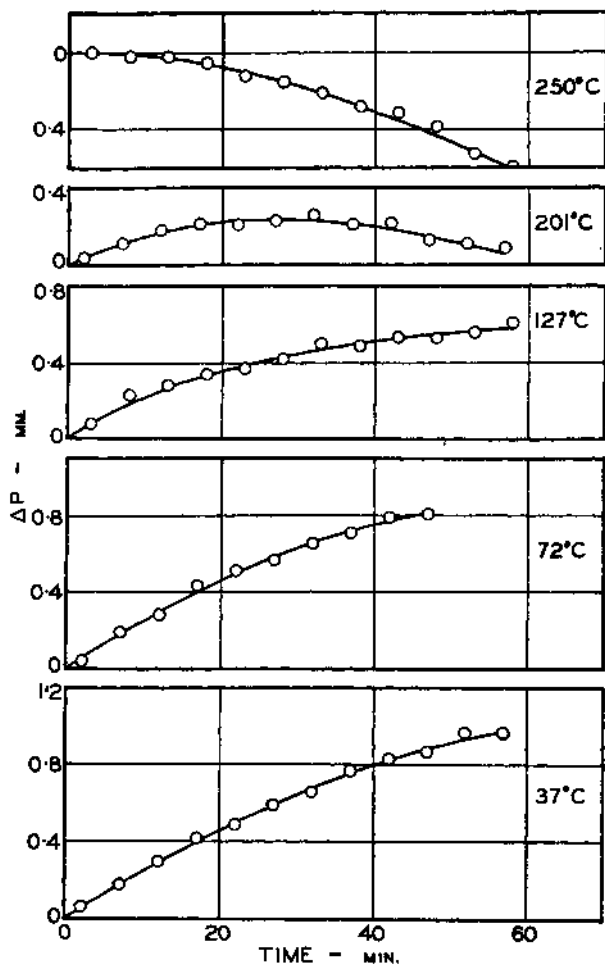


Figure 14. Rate of pressure change in mercury photosensitized reactions of ethylene. Initial ethylene pressure 15 mm.

that chains are being set up at the higher temperatures. This was proved by the addition of nitric oxide to the reaction system. It was found that in the presence of 10 per cent or more of nitric oxide the pressure *increased* initially at 300°, as at 25°. (See Figure 15.) Further, these rates were practically identical. Nitric oxide was shown to have little effect on the low temperature reaction. The main difference in the products of the high temperature reaction was the formation of propylene in relatively large

amounts, and an increase in products of higher molecular weight. The quantum yield at 300° was from 5 to 10 times greater than that at 25°.

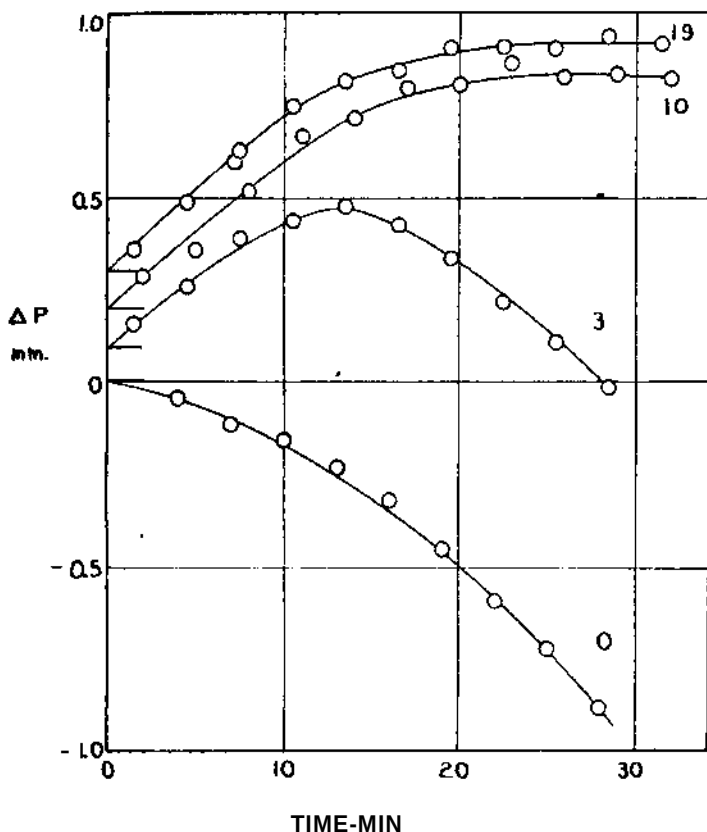
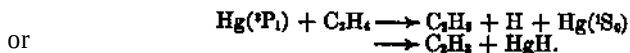


Figure 15. Pressure change in ethylene-nitric oxide mixtures. Temperature — 300° C, Ethylene pressure — 15 mm. NO pressure in mm as indicated on curves. Note: The ordinates of the successive curves have been shifted vertically by 0.1 mm. to avoid overlapping.

Since the formation of hydrogen and acetylene is not appreciably affected by raising the temperature, and since the inhibited high temperature reaction is very similar to the uninhibited low temperature reaction, there seems little doubt that the mechanism is that previously discussed, together with free radical processes which only become important at elevated temperatures. They suggest that in addition to the primary step previously given we also have to a limited extent

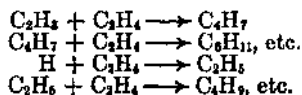


or

At 25° and higher pressures there was some evidence of polymerization occurring by other processes, and this could be well explained on the assumption that the above primary step occurs, followed by an H-atom and vinyl radical sensitized polymerization of ethylene. Such a process would be expected to become more apparent at higher pressures, as found experimentally.

There are two possible ways, on this basis, of explaining the increase in quantum yield and the absence of an initial pressure rise at high temperatures. (1) It may be assumed that the number of excited mercury atoms forming vinyl radicals increases at higher temperatures, and (2) we may assume that the quantum yield of the H-atom and vinyl radical sensitized ethylene polymerization increases with increasing temperature. The latter alternative is undoubtedly the correct one since the quantum yield of hydrogen and acetylene production is independent of temperature ($\phi_{H_2} \sim \phi_{C_2H_2} \sim 0.04$ at high and low temperatures). In either case it would be expected that the polymerization would be inhibited by nitric oxide.

The large quantum yield at higher temperatures would thus appear to be due to reactions of the type postulated previously to explain the sensitized polymerization, viz.,



together with chain transfer reactions, and the usual chain stopping steps of recombination and decomposition. The formation of propylene at high temperatures is probably the result of the decomposition of butyl radicals,



This would occur at 300°, and not at 25°.

Investigations have also been made of the ethylene polymerization photosensitized by a number of other metals. Jungers and Taylor³⁸ found that excited sodium atoms, (²P), were efficiently quenched by ethylene, but that no reaction occurred. The quenching was investigated by Norrish and Smith³⁹ and a very large cross-section was found. The lack of reaction is thus certainly not due to lack of quenching, but must be attributed to the small excitation energy of the ²P sodium atom (48.3 kcal.).

Bates and Taylor⁴⁰ made the first investigation of the cadmium sensitized reaction of ethylene-hydrogen mixtures, using the resonance line at 3261A, i.e. ⁵3P_i cadmium atoms. A more detailed investigation with an improved light source was made by Steacie and Potvin.⁴¹ The results are

³⁸ J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, 4, 94 (1936).

³⁹ R. G. W. Norrish and W. McF. Smith, *Proc. Roy. Soc. (London)*, **A176**, 295 (1940).

⁴⁰ J. R. Bates and H. S. Taylor, *J. Am. Chem. Soc.*, 60, 771 (1928).

⁴¹ E. W. R. Steacie and R. Potvin, *Can. J. Research*, **B16**, 337 (1938).

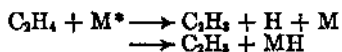
striking in that they indicate a quantum efficiency of about 0.5 for a 1:1 ethylene-hydrogen mixture, but a yield of only about 0.015 for pure ethylene. This is not due to lack of quenching by ethylene, since ethylene quenches $\lambda 3261$ very strongly.⁴²

Two possible explanations suggest themselves for the difference between the results with $\text{Cd}(^3\text{P}_1)$ and $\text{Hg}(^3\text{P}_1)$ atoms. The reaction



is endothermic to the extent of 42.9 kcal.⁴³ The activation energy of the reaction has not been determined but Taylor and van Hook⁴⁴ have found that of the reverse reaction to be roughly 42 kcal. Combining these results we obtain an activation energy of approximately 85 kcal. for reaction (1). It is therefore possible that the 112 kcal. associated with a $^3\text{P}_1$ mercury atom can cause reaction, while the 87 kcal. excitation energy of a $^3\text{P}_1$ cadmium atom cannot be used efficiently enough to do so. (For a discussion of this point and of the mechanism of quenching from the standpoint of potential energy surfaces see footnote 45.)

On the other hand, there is, as we have seen, a great deal of evidence that the polymerization of ethylene can be induced by free radicals, and this suggests the possibility of the photosensitized reactions involving a split into radicals,



or

If this is the case, the $\text{Cd}(^3\text{P}_1)$ photosensitized reaction would be ruled out if the strength of the C—H bond in ethylene is greater than 103 kcal. However, as we have seen, this type of mechanism plays only a minor role as far as the primary process in the mercury photosensitized reaction is concerned, although it probably does come into play to an appreciable extent. The lack of reaction in the case of $\text{Cd}(^3\text{P}_1)$ therefore seems to be due to both the above causes.

The reaction sensitized by $\text{Cd}(^5\text{P}_1)$ atoms, i.e., by the resonance line at 2288Å, has been investigated by Steacie and Le Roy.⁴⁶ The excitation energy of this state is 124.4 kcal. It was found that reaction occurred readily, the quantum yield being about 1. The products of the reaction were olefins, mainly butenes and hexenes, together with a small amount of hydrogen and acetylene. The concentration of acetylene was found to rise to a maximum and then remain sensibly constant. The initial rate of acetylene formation was independent of pressure. The ratio of pressure

⁴² E. W. R. Steacie and D. J. Le Roy, *J. Chem. Phys.*, 11, 164 (1943).

⁴³ F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of Chemical Substances*, New York, 1936.

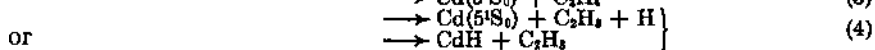
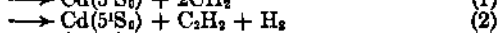
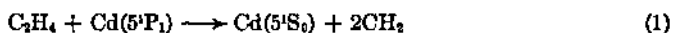
⁴⁴ H. A. Taylor and A. van Hook, *J. Phys. Chem.*, 39, 811 (1935).

⁴⁵ K. J. Laidler, *J. Chem. Phys.*, 10, 34 (1942).

⁴⁶ E. W. R. Steacie and D. J. Le Roy, *J. Chem. Phys.*, 10, 22 (1942).

decrease to acetylene formation was high at high pressures, and fell to about 2 at lower pressures, *i.e.*, the rate of pressure decrease rose rapidly with increasing pressure. There was no measurable pressure rise at the beginning of an experiment.

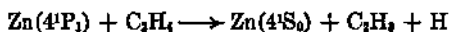
There are four possible primary steps which require consideration:



Reaction (1) appears to be unlikely on energetic grounds. In any case the predominance of C_4 and C_6 olefins in the products and the absence of propylene and methane seem to rule it out. Reaction (2) can certainly be ruled out as the principal primary step since acetylene is not a major product of the reaction, and acetylene appears to be surprisingly inert in the presence of ethylene. Reactions (3) and (4) are favored by analogy with the mercury photosensitized reaction.

As we have seen, (4) appears to occur to some extent in the case of mercury, but (3) is the principal primary process. In view of the relatively small production of acetylene here, it appears that the situation is reversed with 5^1P_1 cadmium atoms, and that (4) is the major primary process, with (3) occurring to a limited extent only. Subsequent to (4) polymerization will then occur by an atom and radical sensitized process, as with mercury.

The zinc photosensitized reaction has also been investigated, using both resonance lines, X2139 and X3076.⁴⁷ The results are very similar to those with cadmium, little reaction occurring with $\text{Zn}(4^3\text{P}_1)$ atoms, while reaction occurs readily with $\text{Zn}(4^1\text{P}_1)$ atoms. The products of the reaction are similar to those with cadmium, except that acetylene formation is negligible. It thus appears that in this case the primary step is exclusively

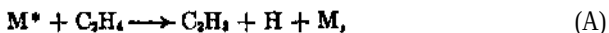


or

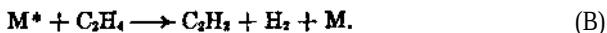


The results with the various sensitizers have been summarized and compared,⁴⁸ as shown in Table XXIV.

It will be seen that the reaction with $\text{Na}(2^2\text{P})$, $\text{Cd}(3^3\text{P}_1)$, and $\text{Zn}(3^3\text{P}_1)$ atoms is very slow, the energies apparently being too small. On the other hand, the reaction with $\text{Hg}(3^3\text{P}_1)$, $\text{Cd}(1^1\text{P}_1)$, and $\text{Zn}(1^1\text{P}_1)$ atoms is quite rapid. The mechanisms appear to be the same in all the latter cases, *i.e.*,



followed by an H-atom and vinyl radical sensitized polymerization, and



⁴⁷ H. Habeeb, D. J. Le Roy, and E. W. R. Steacie, *J. Chem. Phys.*, 10, 261 (1942).

⁴⁸ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.*, 10, 676 (1942).

The relative importance of (A) and (B) is different in the three cases, that of (B) diminishing in the order Hg, Cd, Zn.

TABLE XXIV. COMPARISON OF PHOTOSENSITIZED REACTIONS OF ETHYLENE

Sensitizer		Excitation energy kcal.	Heat of formation of hydride kcal.	Remarks
Na(² P)	5890	48.3	51.6	No reaction.
Cd(³ P ₁)	5896			
Cd(³ P ₁)	3261	87.3	15.5	Slow reaction.
Zn(³ P ₁)	3076	92.5	23.1	Slow reaction.
Hg(³ P ₁)	2537	112.2	8.5	Fast. C ₂ H ₂ an im- portant product.
Cd(¹ P ₁)	2288	124.4	15.5	Fast. C ₂ H ₂ rela- tively small.
Zn(¹ P ₁)	2139	133.4	23.1	Fast. No C₂H₂.

It should be emphasized that relating excitation energies to bond strengths is a drastic approximation. Any precise treatment of the transfer of energy from a sensitizer to a reactant must involve a detailed consideration of the transition states.⁴⁹ However, the fact that the reactions of Hg(³P₁) atoms fall in with those of the high energy group, in spite of the difference in multiplicity, indicates that the approximation of a simple transfer of energy is not inconsistent with the data on the photosensitized reactions of ethylene.

5. The Thermal Decomposition and Polymerization of Acetylene

There is an enormous literature on the effect of heat on acetylene. Most of the work, however, is inaccurate and purely pyrolytic. At low temperatures (below 600°) polymerization is almost the only reaction of acetylene, the products being either a yellow solid, probably cuprene, or a liquid of aromatic character. From 600° to 1000° polymerization and decomposition both occur, the decomposition products being carbon, hydrogen, and some methane. Above 1000° decomposition is the only reaction of importance, and the decomposition is complete at 1200° to 1300°. At still higher temperatures some acetylene exists in equilibrium with hydrogen, carbon, and methane.

Although a very large number of papers have been published on the **high** temperature decomposition of acetylene, very little is known about the kinetics of the process, and little can be added to the early work of Bone and his collaborators. Bone and Coward⁶⁰ found that at 800° and higher acetylene always "flashed" on being admitted to the reaction vessel

⁴⁹ K. J. Laidler, *J. Chem. Phys.*, 10, 34, 43 (1942).

⁵⁰ W. A. Bone and H. F. Coward, *J. Chem. Soc.*, 93, 1197 (1908); *Proc. Chem. Soc.* (London), 24, 167 (1908).

unless largely diluted with nitrogen or hydrogen. This explosive character* istic, which is due to the exothermic nature of the reaction, prevents any accurate determination of the rate of the reaction under isothermal conditions. It was found that a certain amount of polymerization accompanied the decomposition during "flashing." While a great deal of further pyrolytic work has been done, little is known about the mechanism of the process. The original mechanism proposed by Bone and Coward was a split into radicals



It is now known that such a primary step would be impossibly endothermic. (See III-1.)

Rather more information is available concerning the polymerization which occurs at lower temperatures. The first kinetic measurements of any significance were made by Pease⁶¹ who found that at low temperatures the reaction was almost purely polymerization. He suggested that the primary product was $(\text{C}_2\text{H}_2)_4$.

Zelinski,⁵² on the other hand, found diacetylene to be a product, and suggested that its formation was the primary process. The reaction was homogeneous and approximately bimolecular. A more thorough investigation was made by Taylor and van Hook.⁶³ Their results were admittedly only approximate, and led to a value of 40.5 kcal. for the activation energy of the polymerization. They also found the reaction to be bimolecular.

There is little information on the role of free radicals in the thermal decomposition of acetylene. The two possible modes of decomposition into radicals are



and



The first of these is so strongly endothermic that it is certainly of no importance. The second is probably endothermic to the extent of ca. 104 kcal. This makes it unlikely to be of major importance, but it is not impossible that radicals play some role in the reaction.

Paneth and Hofeditz⁵⁴ found that the products of the acetylene decomposition had no effect on metallic mirrors. Recently, however, Burnham and Pease^{54a} have found the reaction to be inhibited by nitric oxide.

A more detailed investigation of the nitric oxide inhibited reaction has been made by Frank-Kamenetzky^{54b} over the temperature range 400° to

⁵¹ R. N. Pease, *J. Am. Chem. Soc.*, 51, 3470 (1929).

⁵² N. D. Zelinski, *Ber.*, 67, 264 (1924); see also P. Schapfer and M. Brunner, *Helv. Chim. Acta*, 13, 1125 (1930).

⁵³ H. A. Taylor and A. van Hook, *J. Phys. Chem.*, 39, 811 (1935).

⁵⁴ F. Paneth and W. Hofeditz, *Ber.*, 62, 1335 (1929).

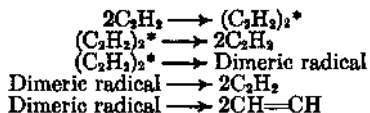
^{54a} H. D. Burnham and R. N. Pease, *J. Am. Chem. Soc.*, 64, 1404 (1942).

^{54b} D. A. Frank-Kamenetzky, *Acta Physicochimica* (U.R.S.S.), 18, 148 (1943).

700°. The thermal polymerization was found to have an induction period, which was greatly lengthened (by a factor of 100 or more) by the presence of one per cent of nitric oxide. "Nitric oxide was consumed during this process, but there was no volume change. The nitric oxide consumption was given by

$$-\frac{d}{dt}[\text{NO}] = k[\text{C}_2\text{H}_2]^2.$$

He suggests a mechanism involving the reactions



followed by the radical sensitized polymerization of acetylene. This is highly speculative. It appears certain, however, that radicals play some part in the thermal polymerization, but it seems doubtful that they play a predominant part.

Comparatively little work has been done on the action of free radicals on acetylene. Sickman and Rice⁵⁵ found that the polymerization could be induced by methyl radicals from the decomposition of azomethane at 300°. The initial step might be



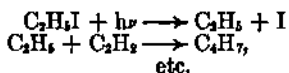
or



The former is, perhaps, the more likely.

Taylor and Jungers⁵⁶ found that the polymerization could be induced by methyl radicals from the photodecomposition of acetone at 25°. The number of molecules of ethylene polymerized per acetone decomposed increased slightly with rising temperature and considerably with increasing acetylene pressure. It was about 5 at 250° and 20 cm. pressure of acetylene.

Joris and Jungers⁵⁷ investigated the polymerization of acetylene photosensitized by ethyl iodide. The mechanism appears to be



The rate of polymerization was approximately one-half that of ethylene under comparable conditions. Jungers and Joris⁵⁸ irradiated mixtures of ethyl iodide with C_2H_2 or C_2D_2 in the temperature range of 80° to 245°.

⁵⁵ D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, 4, 608 (1936).

⁵⁶ H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, 33, 1353 (1937).

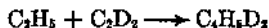
⁵⁷ G. G. Joris and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 47, 135 (1938).

⁵⁸ J. C. Jungers and G. G. Joris, *Bull. Soc. Chim. Belg.*, 50, 61 (1941).

The results showed no difference in the rate of the sensitized polymerization of C_2H_2 and C_2D_2 , *i.e.*, the reactions



and



apparently proceed at the same rate.

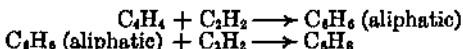
6. The photopolymerization of Acetylene

Early papers on the photopolymerization⁵⁹ were purely qualitative. Lind and Livingston⁶⁰ made the first investigation in which the photoreaction was properly separated from the mercury photosensitized reaction. A solid resembling cuprene was formed, with no gaseous products. The quantum yield for X2150 was about 9.2 at 25°.

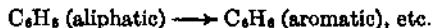
Kemula and Mrazek⁶¹ investigated the reaction for the purpose of proving the presence or absence of benzene and gaseous products. The reaction was followed by absorption spectroscopy so as to be able to detect transitory products. The results confirmed the work of Lind and Livingston in a general way, but showed that some benzene was formed in the reaction together with small amounts of saturated hydrocarbons, olefins, and naphthalene derivatives. Kato⁶² also found benzene to be a product. Kemula and Mrazek suggest that the primary reactions are



Various secondary changes are then postulated such as



or



Livingston and Schiflett⁶³ confirmed the results of Kemula and Mrazek, and found that benzene was formed in considerable quantities at temperatures above 270°. Since the solid polymer found by Kemula and Mrazek had the approximate composition $(C_2H_9)_n$, Lind and Livingston⁶⁴ suggest the following mechanism for the photopolymerization

⁵⁹ P. Thenard, *Compt. Rend.*, 78, 219 (1874); D. Berthelot and H. Gaudechon, *Compt. Rend.*, 160, 1169 (1910); H. Reinioke, *Z. angew. Chem.*, 41, 1144 (1928); J. R. Bates and H. S. Taylor, *J. Am. Chem. Soc.*, 49, 2438 (1927).

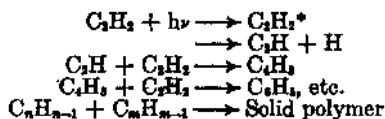
⁶⁰ S. C. Lind and R. Livingston, *J. Am. Chem. Soc.*, 52, 4613 (1930), 54, 94 (1932).

⁶¹ W. Kemula and S. Mrazek, *Z. physik. Chem.*, B23, 358 (1933).

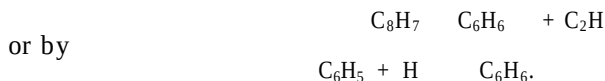
⁶² S. Kato, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 10, 343 (1931).

⁶³ R. Livingston and C. H. Schiflett, *J. Phys. Chem.*, 38, 377 (1934).

⁶⁴ S. C. Lind and R. Livingston, *J. Am. Chem. Soc.*, 56, 1550 (1934).



They suggest that benzene may arise by



All this is, of course, purely speculative.

Dunicz^{64a} has recently shown by absorption spectroscopy that vinyl acetylene is not formed in appreciable quantities during the photopolymerization of acetylene, although traces could be detected under certain conditions. He also showed that the irradiation of a mixture of vinyl acetylene and acetylene produced products which differed from those with acetylene alone, and he therefore concludes that the dimer which is the first step in the polymerization chain is not vinyl acetylene. He suggests that the initial product is cyclobutadiene. In a later paper^{64b} he discusses the mechanism in more detail. The discussion appears to be rather elaborate for the information available.

7. The Mercury Photosensitized Reactions of Acetylene

It was first shown that acetylene could be polymerized by mercury photosensitization by Bates and Taylor.⁶⁵ A more thorough investigation was made by Melville.⁶⁶ He found that the rate was high at the start but fell off rapidly owing to the removal of mercury atoms by the polymerization process, presumably by the formation of a complex of some sort. If precautions were taken to ensure the presence of sufficient mercury vapor, the rate no longer fell off with time. All Melville's measurements were made at initial pressures below 10 mm. to reduce the formation of an opaque film on the walls of the reaction vessel. At low pressures (below 0.5 mm.) the rate was proportional to the acetylene pressure, because under these circumstances there is so little acetylene present that most excited mercury atoms radiate instead of being quenched. The quenching, therefore, does not appreciably lower the concentration of excited mercury atoms, and hence the number of activated acetylene molecules produced is proportional to the acetylene pressure. At high pressures the quenching lowers

^{64a} B. L. Dunicz, *J. Am. Chem. Soc.*, 63, 2461 (1941).

^{64b} B. L. Dunicz, *J. Chem. Phys.*, 12, 37 (1944); see also R. Cherton, *Bull. Soc. Roy. Sci., Liege*, 11, 203 (1942).

⁶⁵ J. R. Bates and H. S. Taylor, *J. Am. Chem. Soc.*, 49, 2438 (1927).

⁶⁶ H. W. Melville, *Trans. Faraday Soc.*, 32, 258 (1936); E. K. Rideal, *Proc. Roy. Soc. (London)*, A146, 266 (1934).

the concentration of excited mercury atoms to an appreciable extent, **and** the rate is proportional to a power of the acetylene pressure which is less than one, and approaches zero at still higher pressures.

Temperature was found to have a marked effect on the rate as shown by Table XXV.

TABLE XXV. EFFECT OF TEMPERATURE ON MERCURY PHOTOSENSITIZED POLYMERIZATION OF ACETYLENE (Melville)

Temperature, ⁰	30	99	209	267	355	436	528
Relative rate	1	8.8	12.7	9.0	7.5	6.2	5.3

It will be seen that the rate is a maximum in the neighbourhood of 200° to 250°. This is associated with the fact that the chain length is about 10 at room temperature, rises to about 100 at 250°, and decreases at higher temperatures. The chain length was found to be independent of pressure, surface or light intensity.

Melville gives a kinetic analysis of the polymerization process in terms of ordinary energy chain reaction theory, and concludes that the termination of the chains is by the collision of the active polymer with an acetylene molecule, the collision for some reason not being of the right type for propagation. The kinetic analysis is rather complex, and in the light of present knowledge does not appear to be capable of test.

The polymerization was also investigated by Jungers and Taylor⁶⁷ for the principal purpose of comparing acetylene with deuterioacetylene. They found that at low pressures the rates for both were proportional to the pressure, and above 7 mm. became independent of it. Over the whole pressure range the rate was 30 per cent greater for C₂H₂ than for C₂D₂. The quantum yield was about 6.5 for ordinary acetylene and 5 for the deuterio compound. (In this connection it may be noted that in the polymerization by alpha-particles⁶⁸ the rates for the two acetylenes are identical.)

Jungers and Taylor compared the quantum yields and ion-pair yields for ordinary acetylene under different conditions, as shown in Table XXVI.

TABLE XXVI. QUANTUM YIELD OF ACETYLENE POLYMERIZATION

Method	Quantum or ion-pair yield	Reference
Beta-particles	26	69
Alpha-particles	18 to 20	70
Photo-reaction	9.2	60
Mercury photosensitized reaction	6.5	67

⁶⁷ J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, 3, 338 (1935).

⁶⁸ S. C. Lind, H. S. Taylor, and C. H. Schiflett, *Phys. Rev.*, 46, 825 (1934).

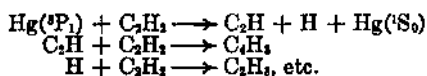
⁶⁹ W. Mund and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 40, 158 (1931).

TM S. C.-Lind and D. C. Bardwell, *J. Am. Chem. Soc.*, 48, 1556 (1926); W. Mund and W. Koch, *Bull Soc. Chim. Belg.*, 34, 125, 241 (1925).

It will be seen that the yield produced by each primary act falls off rapidly as the energy input in the primary act is diminished. Jungers and Taylor suggest, therefore, that the polymerization process must dissipate the initiation energy fairly rapidly as it progresses. However, in view of the scanty knowledge of the process it is by no means certain that the mechanism is the same in all four cases.

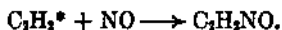
The mercury photosensitized reaction has recently been re-investigated by Le Roy and Steacie.⁷¹ In agreement with Melville and Jungers and Taylor, it was found that the rate was independent of pressure at higher pressures, but fell off rapidly at low pressures. This was shown to be entirely due to incomplete quenching. The quantum yield was 4.5 ± 1.2 at 25° and 40 mm. pressure. The chain length increased by a factor of about 3.7 on going from 25° to 300°, indicating a relatively small temperature coefficient. The reaction was found to be inhibited by nitric oxide, the rate decreasing by a factor of about 5 in the presence of 5 per cent NO at 25°, independent of the acetylene pressure. At 300°, about 10 per cent NO was required for maximum inhibition, and the rate was reduced by a factor of about 10.

The inhibition of the reaction by nitric oxide strongly suggests a free radical mechanism. This presumably would be



There seems to be no question that there is ample energy available to split the C—H bond in acetylene. (See III—1.) If such a mechanism holds a certain amount of hydrogen, C_2H_4 and C_2H_6 would be expected, and this was confirmed by analyses which showed the presence of appreciable amounts of hydrogen and of C_2 hydrocarbons other than acetylene.

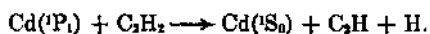
It should be emphasized that the evidence for a free radical mechanism is not entirely conclusive, and that it is not impossible that the reaction proceeds by an excited molecule mechanism, inhibition by nitric oxide being due to a reaction of the type



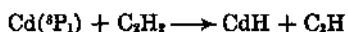
Le Roy and Steacie also made a few experiments on the inhibition of the cadmium photosensitized reaction, both cadmium resonance lines (XX3261 and 2288) being used. The results were approximate only owing to complications due to reaction of nitric oxide with traces of cadmium oxide. The indications were that with $\text{Cd}({}^3\text{P}_1)$ atoms (X3261) the rate was decreased by 20 per cent NO by a factor of 2.1 ± 0.5 (with 2.3 mm. of C_2H_2 at 270°). With $\text{Cd}({}^1\text{P}_1)$ atoms (X2288) under similar conditions the rate was

⁷¹ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.*, 12, 117 (1944).

decreased by a factor of 3.0 ± 1.0 . The results again suggest a free radical mechanism for the reaction. In the case of $\text{Cd}(^1\text{P}_1)$ ample energy is available for the primary split



With $\text{Cd}(^3\text{P}_1)$ atoms the excitation energy is 87.3 kcal. The heat of formation of CdH is 15.5 kcal. Hence the reaction



is possible if the C—H bond strength in acetylene is not over about 103 kcal. This is not an unreasonable value. As with the mercury photo-sensitized reaction, however, an excited molecule mechanism cannot be ruled out.

8. Higher Olefins

As with ethylene, the main reaction of the higher olefins is decomposition at high temperatures and polymerization at low. The decompositions are complex, and nothing very definite can be said about them.⁷² Most of our knowledge of the thermal polymerization reactions of the higher olefins comes from the work of Krauze, Nemtsov, and Soskina⁷³ who have investigated the polymerization at high pressures of ethylene, propylene, the butenes, and pentene in the temperature range 300° to 400°. The reactions were all of the second order, the products being mainly but not exclusively those corresponding to a straight association to give an olefin with twice the number of carbon atoms. The rate of polymerization falls off slightly with increasing molecular weight. The data are summarized in Table XXVII.

TABLE XXVII. THERMAL POLYMERIZATION OF OLEFINS

Reaction	<i>E</i> , kcal.	log ₁₀ <i>A</i>
$2\text{C}_2\text{H}_4 \longrightarrow \text{C}_4\text{H}_8$	38.4	10.8
$2\text{C}_3\text{H}_6 \longrightarrow \text{C}_6\text{H}_{12}$	38.0	10.2
$2\text{C}_4\text{H}_8 \longrightarrow \text{C}_8\text{H}_{16}$	38.0	10.0
$2\text{iso-C}_4\text{H}_8 \longrightarrow \text{C}_8\text{H}_{16}$	43.0	12.3
$2\text{C}_5\text{H}_{10} \longrightarrow \text{C}_{10}\text{H}_{20}$	38.0	9.8

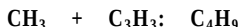
The high value of both *E* and *A* for iso-butene suggests errors in both which compensate one another, and it appears that the activation energies are all approximately 38 kcal.

⁷² See, e.g., F. E. Frey and D. F. Smith, *Ind. Eng. Chem.*, 20, 948 (1928); V. G. Moor, N. V. Strigaleva, and A. V. Frost, *J. Gen. Chem.* (U.S.S.R.), 7, 860 (1937); S. N. Mitsengendler, *J. Gen. Chem.* (U.S.S.R.), 7, 1848 (1937).

⁷³ M. V. Krauze, M. S. Nemtsov, and E. A. Soskina, *Compt. Rend. Acad. Sci.* (U.R.S.S.), 2, 301 (1934), 3, 262 (1934); *J. Gen. Chem.* (U.S.S.R.), 5, 343, 356, 382 (1935); see also G. Egloff and C. I. Parrish, *Chem. Rev.*, 19, 145 (1936).

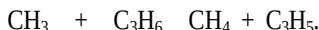
The polymerizations of isoprene⁷⁴ and of 1:3 butadiene^{74,75} are also homogeneous second order reactions, the activation energies being approximately 28.9 and 24.7 kcal. respectively.

There is considerable evidence that free radicals cause the induced polymerization of propylene and other olefins. Rice and Sickman⁷⁶ found that methyl radicals from the decomposition of azomethane caused some polymerization of propylene. This suggests that at temperatures in the neighbourhood of 300° the reaction



occurs to some extent. It appears, however, to be much slower than the corresponding reaction with ethylene.⁷⁷

Beeck and Rust⁷⁸ investigated the polymerization of propylene sensitized by methyl and ethyl radicals from the thermal decomposition of lead tetramethyl or lead tetraethyl. The reaction was also considerably slower than the corresponding reaction with ethylene. This is in agreement with the results of Taylor and Smith (see later) who found that methyl radicals reacted with propylene much more readily than with ethylene, the reaction evidently being



Apparently the polymerizing radical chain in propylene is thus easily broken by the formation of allyl radicals. These have a long life and are not highly reactive, and they thus disappear mainly by recombination.

Danby and Hinshelwood⁷⁹ investigated the polymerization of propylene photosensitized by acetaldehyde. (See Table XXVIII.) The results were similar to those with ethylene (q.v.) except that with propylene the rate of polymerization was smaller and there was much more marked inhibition of the photolysis.

Further, the rate of polymerization became independent of the olefin concentration at moderate propylene pressures. In other words the inhibition is so large that the radicals are practically all removed by the olefin. The aldehyde therefore acts merely as a source of radicals, the normal radical removing process being negligible by comparison with the new chain-ending step introduced by the olefin. If this is first order, the rate will become inde-

⁷⁴ W. E. Vaughan, *J. Am. Chem. Soc.*, **54**, 3863 (1932), **56**, 4109 (1933).

⁷⁵ V. G. Moor, N. V. Strigaleva, and L. Y. Shilyaeva, *J. Gen. Chem. (U.S.S.R.)*, **5**, 818 (1935).

⁷⁶ O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, **4**, 608 (1936).

⁷⁷ D. V. Sickman, unpublished work, quoted by F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

⁷⁸ O. Beeck and F. F. Rust, *J. Chem. Phys.*, **9**, 480 (1941).

⁷⁹ C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A179**, 169 (1941).

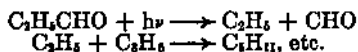
TABLE XXVIII. POLYMERIZATION OF PROPYLENE INDUCED BY THE PHOTOLYSIS OF ACETALDEHYDE

Propylene pressure mm.	Rate in arbitrary units of acetaldehyde photolysis	of propylene polymerisation
0	17.0	—
15	9.3	0.1
25	7.3	0.3
42	6.5	2.3
61	5.0	2.0
81	5.0	3.1
106	4.7	2.9
145	5.2	4.7
191	4.6	4.6
203	4.6	4.6
250	3.5	4.2
302	3.4	4.4
352	2.6	3.9
413	3.3	4.6

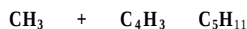
pendent of the olefin concentration. However the mechanism is too complex to allow definite conclusions to be drawn other than that the reaction



Similar results were obtained when the reaction was photosensitized by propionic aldehyde. The mechanism is presumably similar, viz.,

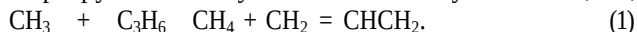


Danby and Hinshelwood also investigated the polymerization of butene-1 photosensitized by acetaldehyde. The results were similar to those with propylene and show that at 300° the reaction



occurs readily. They conclude that the alkyl radicals react about equally readily with ethylene, propylene, and butene, but that the chain length of the induced polymerization diminishes with the higher olefins.

Eltenton⁸⁰ investigated the reaction of methyl radicals with propylene by following the concentration of methyl and other radicals in the reaction system by means of a mass spectrometer. Methyl radicals were produced by the decomposition of lead tetramethyl. He concluded that (a) methyl radicals react readily with propylene, (b) at high temperatures methyl radicals can be detected in the decomposition of propylene itself, (c) in mixtures of methyl and propylene the allyl radical was easily detectable, *i.e.*,



The fact that propylene is an efficient inhibitor of free radical chain reactions is further evidence that free radicals react readily with propylene.

⁸⁰ G. C. Eltenton, *J. Chem. Phys.*, **10**, 403 (1942).

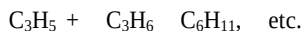
Taylor and Smith⁸¹ investigated the reaction of methyl radicals, produced by the photolysis of mercury dimethyl, with propylene. The activation energy of methane production was found to be 3.1 kcal., and this apparently corresponds to that of reaction (1). This is the lowest activation energy found by Taylor and his collaborators for any reaction of the type



and it appears certain that it is the hydrogens of the methyl group in propylene which are reacting. The pressure decrease which accompanied the reaction indicated that an efficient polymerization of propylene also occurs in the presence of methyl radicals, although this appears to be slower than the corresponding reaction with ethylene.⁸² It is difficult to say whether the polymerization occurs by



or by reaction (1) followed by



Taylor and Smith compare the reactions of methyl radicals with ethane, ethylene, and propylene, as follows: "This double bond influence is most marked in the reaction with propylene where the decrease in observed activation energy over the primary bond in saturated hydrocarbons amounts to 5 kcal. It is obvious that in any free radical mechanism involving saturated hydrocarbons reaction of the radical with propylene would be faster than that with either primary, secondary, or tertiary C—H bonds in the saturated molecule. Such interaction would yield, as Rice and Polly⁸⁵ have pointed out, the allyl radical. The weakness of the allyl—H bond here indicated as compared with the C—H bonds in the saturated molecules implies a correspondingly decreased efficiency as a chain link in such chain decomposition processes. The radical would have longer life and would have greater opportunity to disappear by collision with itself or another radical to produce diallyl or a substituted propylene respectively. The formation of this latter would have a net effect of breaking two radical chains and of producing an olefin of approximately equal efficiency with propylene as a chain breaking agent. The formation of diallyl would have the net effect of breaking one chain per propylene, the diallyl probably having a further efficiency as a chain breaker by reason of its C—H bonds on the carbon atoms in the beta position to the two double bonds.

"With ethylene such conditions do not immediately obtain. The strong C—H bonds in this compound imply a lesser reactivity with methyl radi-

⁸¹ H. S. Taylor and J. O. Smith, *J. Chem. Phys.*, 8, 543 (1940).

⁸² See, e.g., F. O. Rice and E. Teller, *J. Chem. Phys.*, 6, 489 (1938).

⁸³ F. O. Rice and O. L. Polly, *J. Chem. Phys.*, 6, 273 (1938).

cals to form methane than with the saturated hydrocarbons. Association of ethylene and alkyl radicals generates a higher alkyl radical. It is not surprising therefore that Echols and Pease^M found no inhibitory influence of ethylene and a marked influence of propylene on the thermal decomposition of *n*-butane."

Little information exists on the photopolymerization of the higher olefins, Lind and Livingston⁸⁵ have made a brief investigation of the photopolymerization of allene and of isoprene. Le Roy and Steacie⁸⁶ have shown that the quantum yield is low in the polymerization of propylene and the two butenes by Cd(³Pi) atoms.

Cramer⁸⁷ investigated the decomposition of tetraethyl lead dissolved in liquid olefins at 220° to 235° and high pressures. The results were similar to those with propylene and butene. The substances investigated included four of the hexenes, two heptenes, one of the octanes, and cyclohexene.

The polymerization of isoprene can be induced by methyl radicals from the photolysis of mercury dimethyl at 100°. ^{87o}

9. Butadiene

A number of papers have been published on the thermal and photochemical polymerization of butadiene.⁸⁸ There is, however, little information on its elementary reactions. Recently Gunning and Steacie⁸⁹ have investigated the mercury photosensitized polymerization and hydrogenation. In static runs with butadiene alone the pressure-time curve shows an initial induction period during which the pressure decrease is very small. This is followed by a linear period of pressure decrease. The length of the induction period is directly proportional to the butadiene pressure. The rate of pressure decrease in the linear region may be considered to be a measure of the reaction rate. This rate decreases with increasing pressure except at very low pressures (< 2 mm.), where quenching is incomplete.

A rapid photoreaction between butadiene and nitric oxide occurs, so that it is not possible to investigate the possible inhibition of the polymerization by nitric oxide.

In static runs the products of the reaction were a large amount of a dimer, a solid polymer which formed on the walls of the reaction vessel, and small amounts of hydrogen, ethane, and an acetylenic compound which

⁸⁴ L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, **61**, 1024 (1939).

⁸⁶ S. C. Lind and R. Livingston, *J. Am. Chem. Soc.*, **65**, 1036 (1933).

⁸⁶ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.*, **11**, 683 (1942).

⁸⁷ P. L. Cramer, *J. Am. Chem. Soc.*, **60**, 1406 (1938).

^{87a} H. E. Gunning and E. W. R. Steacie, unpublished work.

⁸⁸ See, for example, W. E. Vaughan, *J. Am. Chem. Soc.*, **54**, 3863 (1932); A. M. Kublitskii, *Sintet. Kauchuk*, p. 30 (1936); J. M. Bolland and H. W. Melville, *Proc Rubber Tech. Conf.*, 239 (1938).

⁸⁹ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **12**, 484 (1944).

was probably vinyl acetylene. In single pass flow runs much greater quantities of hydrogen and the acetylenic compound were found, as shown by the results of a typical run in Table XXVIII A.

TABLE XXVIII A. PRODUCTS OF MERCURY PHOTSENSITIZED BUTADIENE POLYMERIZATION

Product	Millimoles
H ₂	2.0
Acetylenic compound	0.5 (as C ₄ H ₄)
Dimer	0.37 (as C ₈ H ₁₂)
Solid polymer	Trace

The results indicate that hydrogen and the acetylenic compound are important products of the reaction, but that they are consumed in the later stages of static runs.

The rate of the reaction was found to be proportional to the light intensity, and the quantum yield to be approximately unity in agreement with the results of Gee.⁹⁰

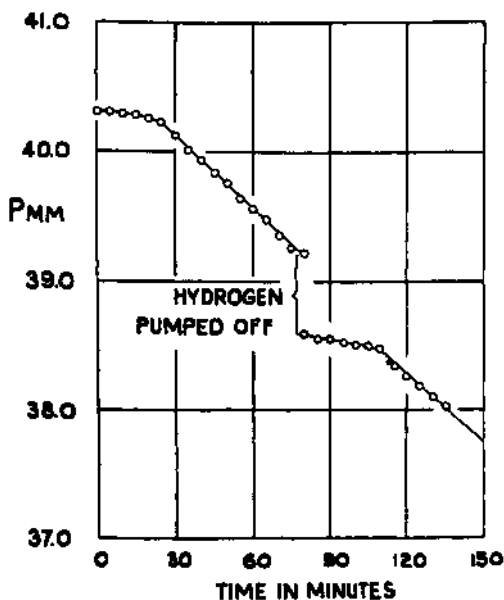
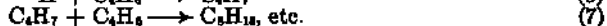
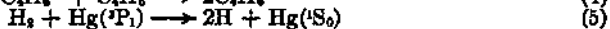
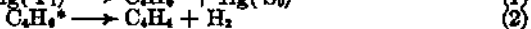
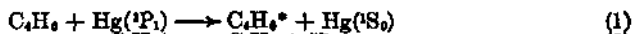


Figure 16. Mercury photosensitized polymerization of butadiene. The effect of pumping off hydrogen during a static run.

It was found that if a static run were stopped and the hydrogen pumped off a new period of induction was produced. (See Figure 16.) This seems to indicate definitely that the initial stage of the reaction leads to the formation of hydrogen and C₄H₄, and that the later pressure decrease is due to an H-atom sensitized polymerization.

⁹⁰ Unpublished, quoted by J. L. Bolland and H. W. Melville, *Proc. Rubber Tech. Conf.*, No. 90, p. 248.

By analogy with the results of Le Roy and Steacie on ethylene (see IV-4) they suggest the following mechanism:



Reactions (1), (2), (3), and (4) occur during the induction period. (4) is postulated, to account for the decrease in rate with increasing butadiene pressure. After sufficient hydrogen has been formed (5) becomes important and the subsequent reactions are sensitized by H-atoms.

Results with butadiene-hydrogen mixtures were compatible with this mechanism. The addition of hydrogen eliminated the induction period, and accelerated the rate of polymerization. As might be expected, the products were largely saturated under these conditions. The main product from runs with a 9 : 1 H_2 : C_4H_6 mixture was butane. This presumably arises by



The polymerization can also be sensitized by methyl radicals from the photolysis of mercury dimethyl.⁸⁷⁰

Chapter V

Free Radical Mechanisms in Photochemical Reactions

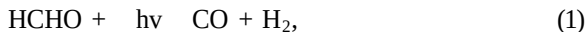
1. Introduction

The subject matter of this chapter should really include almost the whole of photochemistry, since atoms or radicals participate in most photochemical reactions. We will discuss here, however, only those reactions which in the first place throw some light on the kinetics of the elementary reactions involved, and in the second place involve several different part reactions in such a way that it is not possible to discuss them adequately in the subsequent chapters which deal with the specific elementary reactions.

It may be noted that in some cases the elementary steps in photochemical mechanisms are well established, and definite information is obtained about the elementary reactions involved. In other cases little is known about the mechanism other than the primary step, and any detailed reaction scheme which may be drawn up is almost purely speculative.

2. Formaldehyde

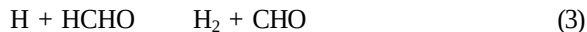
A considerable number of investigations of the photolysis of formaldehyde have been made.¹ Norrish and Kirkbride² found the quantum yield to be roughly unity at wave lengths from 2600A to 3500A at a temperature of 110°. They concluded that the primary process was a direct molecular split



since they argued that a primary split



would be followed by reactions such as



and would lead to a quantum yield greater than unity.

This, of course, is not a compelling argument since a quantum yield of approximately unity might result from a primary step of low efficiency followed by short chains.

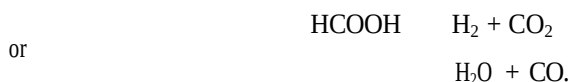
Patat³ investigated the reaction in the presence of added oxygen, which

¹ For references to earlier work see F. Patat, *Z. physik. Chem.*, **B26**, 208 (1934).

² R. G. W. Norrish and F. W. Kirkbride, *J. Chem. Soc.*, **1932**, 1518.

³ F. Patat, *Z. physik. Chem.*, **B25**, 208 (1934); T. Locker and F. Patat, *Z. physik. Chem.*, **B27**, 431 (1934).

would act as a detector for hydrogen atoms by reacting ultimately to form water. His results at 80° indicated that at wave lengths shorter than 2750Å H-atoms were present, but that none were formed at longer wave lengths. He therefore concluded that in the region of fine structure an excited molecule mechanism holds, but that at shorter wave lengths, in the region of predissociation or the continuum, the primary process is reaction (2). However, in later work Carruthers and Norrish⁴ found that the photooxidation of formaldehyde to formic acid proceeded readily in the light of a full mercury arc, the quantum yield being about 12.6 at 100°. The formic acid produced is then partially decomposed, and it follows that in Patat's work the fact that the CO/H₂ ratio was greater than unity may be due not to the loss of hydrogen to form water as he assumed, but rather to



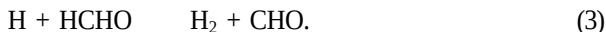
It may therefore be concluded that Patat's work is unreliable, and does not constitute definite evidence either for or against the presence of H-atoms in the formaldehyde photolysis.

Akeroyd and Norrish⁵ investigated the photolysis of formaldehyde at higher temperatures, using light from a full mercury arc. The quantum yield was found to increase strongly with increasing temperature, as shown by Table XXIX.

TABLE XXIX. QUANTUM YIELD OF FORMALDEHYDE PHOTOLYSIS

Temperature	100	200	250	300	325	350
Quantum yield	1.9	2.9	8.0	35.0	53.9	100.0

Since the reaction thus has chain characteristics it seems almost certain that reaction (2) occurs at least to some extent. The temperature coefficient of the reaction corresponds to an activation energy of 16.2 kcal., which they suggest is the activation energy of the reaction



Geib⁶ has investigated reaction (3) directly by the discharge-tube method. The reaction was complete at room temperature in a contact time of 0.3 sec. with a partial pressure of H-atoms of about 0.1 mm. The activation energy must therefore be no greater than 5 kcal. Geib suggests that there are two primary steps in the hydrogen atom reaction, viz., (3) and



⁴ J. E. Carruthers and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 1036.

⁵ E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 890.

⁶ K. H. Geib, *Ergeb. exakt. Naturwiss.*, **15**, 44 (1936).

It seems more likely that the results can be explained by reaction (3), together with



Style and Summers⁷ found that the photolysis of formaldehyde at temperatures above 100° is accelerated by hydrogen and nitrogen. The temperature coefficient of the rate corresponds to an activation energy of 12 kcal. They suggest that this is the activation energy of the reaction



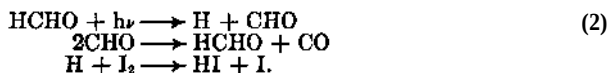
Gorin⁸ has investigated the photolysis of formaldehyde in the presence of iodine. In a similar investigation with acetaldehyde, as discussed later, he concluded that the formyl radical is stable at temperatures up to 100°, and that the activation energy of reaction (5) is at least 26 kcal.



This reaction is discussed in detail in (VII-27), and it appears to be rather well established that the formyl radical is stable up to 100°.

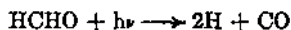
In the case of formaldehyde in the presence of iodine, Gorin determined the amounts of HI, CO, and H₂ formed at various pressures, using radiation of wave lengths 2537A, 3130A, and 3650A.

At 3130A and 2537A the permanent gases were almost exclusively CO, and the HI/CO ratio was almost exactly 2. It thus appears that the mechanism is



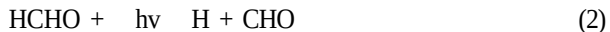
This agrees with the fact that the quantum yield of HI formation is approximately 1.

At 2537A the process



becomes energetically possible, but since the quantum yield of HI formation remains equal to unity, and the other features of the reaction do not differ significantly from those at 3130A, it appears probable that (2) is still the primary process at 2537A.

At 3650A a considerable amount of hydrogen is formed, and Gorin suggests that there are now two primary processes



and

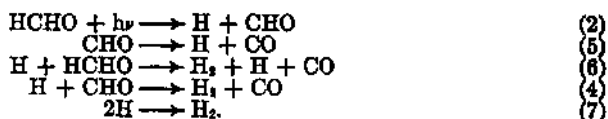


Since HI is formed at this wave length also, (2) must still be an important primary process. The energy available at X3650 is 78 kcal, and hence the

⁷ D. W. G. Style and Summers, *Trans. Faraday Soc.*, 35, 899 (1939).

⁸ E. Gorin, *J. Chem. Phys.*, 7, 256 (1939).

strength of the H—CHO bond cannot be higher than this. This is a much lower value than earlier estimates.⁹ Gorin suggests that at higher temperatures chains occur by a modification of the mechanism of Akeroyd and Norrish:



By a steady-state treatment of the results he arrives at the expression

$$k_3 - \frac{k_7}{2} [\text{H}]^2 - \frac{k_4 k_7}{2k_5} [\text{H}]^3 = 0 \quad (\text{A})$$

Since *E_b* has the high value of 26 kcal., the third term will be dominant at low temperatures, and the second will be dominant at high temperatures. (Gorin reverses these terms and thus arrives at an erroneous estimate of *E_S* = 9.2 kcal.*) Hence for the rate of disappearance of formaldehyde at high temperatures we obtain

$$\frac{d}{dt} [\text{HCHO}] = k_3 + k_4 \left(\frac{k_7}{k_5} \right)^{\frac{1}{2}} [\text{HCHO}].$$

If *E_i* is assumed to be zero, the overall activation energy of 16.2 kcal. becomes that of reaction (6), as assumed by Akeroyd and Norrish. It should be noted that the neglect of the third term of equation (A) at high temperatures is equivalent to the assumption that reaction (4) is negligible. All CHO radicals will thus decompose eventually to CO + H, and it is immaterial whether reaction (6) is written



as assumed by Gorin, or as



as assumed by Akeroyd and Norrish.

Norrish and Noyes¹⁰ have investigated the photolysis in the Schumann region. The products are still mainly hydrogen and carbon monoxide, but little can be said about the mechanism.

3. Acetaldehyde

As we have seen in Chapter III, the thermal decomposition of acetaldehyde appears to occur by a mixed free radical-molecular rearrangement mechanism, and the free radical chain part of the reaction almost certainly involves a mechanism very similar to that proposed by Rice and Herzfeld. Much work has been done on the photolysis, and while the mechanism is

* I am indebted to Dr. O. K. Rice for pointing out this error.

⁹ R. Mecke, *Z. Elektrochem.*, 36, 589 (1930).

¹⁰ R. G. W. Norrish and W. A. Noyes, *Proc. Roy. Soc. (London)*, **A163**, 221 (1937).

still a matter of considerable controversy, it undoubtedly bears a close similarity to that of the thermal reaction.

Absorption of light by acetaldehyde begins at about 3400A and extends to about 2400A,^{11,12} and a second absorption region starts around 2000A. Structure exists from 3400A down to about 2800A, but the whole banded region is underlaid by a continuum. (This may be a true continuum, or so much structure may be superimposed as to simulate one.) It is impossible to say at what point predissociation commences.

Following on considerable early work which had shown that the main products of the photolysis were methane and carbon monoxide, Leighton and Blacetⁿ made the first detailed study of the reaction. They found quantum yields at room temperature ranging from about 0.2 up to practically unity. The quantum yield of CO formation increased with decreasing wave length, but was not largely affected by pressure or intensity. A polymerization reaction was also present, the amount of which decreased with decreasing wave length.

Leighton and Blacet suggested that the decomposition occurred by an excited molecule mechanism in the banded region and by a free radical mechanism in the continuum. Norrish,¹³ however, considered that no free radicals were involved. His argument was based mainly on the absence of hydrogen as a product, since almost any conceivable free radical mechanism involves the production of some hydrogen. However, it was later shown¹⁴ that hydrogen is one of the products, the H₂JCO ratio increasing at short wave lengths from 0.05 at 3130A to 1.6 at 2537A.

The Products of the Reaction

In addition to CO, CH₄, and H₂ it has been shown by many workers that a variety of other products are formed. Recently Blacet and Volman¹⁵ investigated the products of the reaction and their variation with pressure, wave length, intensity, and temperature. The only gaseous products found were CO, CH₄, and H₂. The H₂JCO ratio had values up to 0.2, and varied in the following way: (a) It increased slightly with decreasing pressure, (b) It varied strongly with wave length, from almost zero at longer wave lengths to values as high as 0.22 at 2380A, (c) It also varied with intensity. Thus at 2654A, 25° and 205 mm., the ratio had the values:

Relative intensity	H ₂ JCO
100	0.103
52	0.082
16	0.061

¹¹ P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, 65, 1766 (1933).

¹² V. Henri, *Trans. Faraday Soc.*, 25, 765 (1929).

¹³ R. G. W. Norrish, *Trans. Faraday Soc.*, 30, 103 (1934).

¹⁴ F. E. Blacet and J. G. Roof, *J. Am. Chem. Soc.*, 58, 278 (1936).

¹⁵ F. E. Blacet and D. Volman, *J. Am. Chem. Soc.*, 60, 1243 (1938).

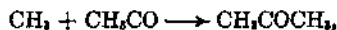
(d) With varying temperature the ratio increased from **0.057** at 0° to **0.128** at 25°, and then decreased strongly to 0.035 at 92°. These values were obtained at 2654Å and a concentration of 0.018 mole per liter.

Blacet and Blaedel¹⁶ have confirmed and extended the results of Blacet and Volman, and in addition have investigated the condensable products of the reaction. Acetone and methyl glyoxal were found to be absent, and formaldehyde, glyoxal, and diacetyl were present, in the relative quantities indicated in Table XXX. (In these experiments the full radiation from a mercury arc was used.)

TABLE XXX. PRODUCTS OF THE ACETALDEHYDE PHOTOLYSIS
(Blacet and Blaedel)

Temperature	Relative amounts in moles					
	CO	H ₂	CH ₄	(CH ₃ CO) ₂	(CHO) ₂	HCHO
25	1.00	0.063	0.87	0.084	0.014	0.018
60	1.00	0.049	0.92	0.012	0.0076	0.0022
102	1.00	0.033	0.94	0.007	0.000	0.0015

They suggest that the considerably higher quantities of formaldehyde found by Gorin¹⁷ were due to interference by diacetyl in his analyses. Woolgar and Allmand,¹⁸ however, consider that the polymer is probably paraldehyde, and conclude also that some acetone is formed, probably by the reaction

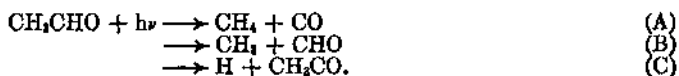


or by



The Primary Process

On the basis of the observed products, the following primary processes are obvious possibilities:



From the variety of products other than CO and CH₄, it is obvious that (A) cannot be the sole primary process. (C) has been suggested as a possibility.¹⁹ However, there are two arguments against this: (a) In an investigation of the photolysis of acetaldehyde-iodine mixtures to be described later Blacet and his collaborators failed to detect acetyl iodide as a product. This argues strongly against the production of acetyl in the primary step. (b) There is evidence that hydrogen atoms are not present in detectable

¹⁶ F. E. Blacet and W. J. Blaedel, *J. Am. Chem. Soc.*, **62**, 3374 (1940).

¹⁷ E. Gorin, *Acta Physicochimica* (U.R.S.S.), **9**, 681 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

¹⁸ C. W. Woolgar and A. J. Allmand, *Trans. Faraday Soc.*, **39**, 219 (1943).

¹⁹ W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases*, New York, 1941.

amounts. (See VII-27.) All evidence thus favors as the primary step either (B) alone, or (B) and (A) together. The main evidence for the occurrence of (B) as an important primary step is that free radicals appear to be undoubtedly involved. The evidence for the occurrence of radicals in the photolysis is discussed in the next section.

The Occurrence of Free Radicals

Striking proof that radicals are involved in the reaction, at least to some extent, comes from the work of Leermakers²⁰ who investigated the photolysis at temperatures from 80° to 310°. Quantum yields as high as 310 were found at high temperatures and low light intensities. At 117° the quantum yield was 15, while at 25° under similar conditions the calculated value was 0.03. In other words the chain reaction is absent at low temperatures. He found that his results could be expressed by the equation

$$\frac{d}{dt}[\text{CO}] = 0.3I_{\text{abs.}} + k\sqrt{I_{\text{abs.}}}[\text{CH}_3\text{CHO}].$$

The first term represents the non-chain part of the reaction, and can be interpreted as meaning that at low temperatures the quantum yield is 0.3, the remainder of the energy input being dissipated as fluorescence, etc. If the values of k calculated in this way are used for a $\log k - 1/T$ plot, it is found that an excellent straight line is obtained, corresponding to an activation energy of 10 kcal.

Leermakers discusses his results in terms of a mechanism of the Rice-Herzfeld type. We will return to a discussion of the mechanism later. From Leermakers' work it may thus be definitely concluded that: (a) At high temperatures the photolysis of acetaldehyde is a chain reaction. (b) A free radical mechanism is involved, (c) Free radicals introduced into acetaldehyde will cause its induced decomposition. Other work on the high-temperature photolysis, to be discussed later, amply confirms these conclusions.

Further proof that radicals are formed in the photolysis comes from the work of Pearson and Purcell²¹ who investigated the reaction by the Paneth method using heated tellurium mirrors. The previous failure of Pearson²² to detect radicals in the photolysis was shown to be due to the use of cold mirrors which were inactivated by traces of polymer. Pearson and Purcell proved the presence of methyl radicals by identifying dimethyl ditelluride. By means of a very rough calculation they concluded that more radicals are formed from acetone than from acetaldehyde under similar conditions at 100°, and from this result they inferred that at 100° part of the acetalde-

²⁰ J. A. Leermakers, *J. Am. Chem. Soc.*, 56, 1537 (1934).

²¹ T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, 1935, 1151.

²² T. G. Pearson, *J. Chem. Soc.*, 1984, 1718.

hyde photolysis proceeds by a direct molecular split without the intervention of radicals.

Rollefson²³ has discussed the relative occurrence of the free radical split and the direct molecular rearrangement in the primary process on the basis of the results of a number of workers. In this way he arrives at the values given in Table XXXI.

TABLE XXXI. PRIMARY PROCESS IN ACETALDEHYDE PHOTOLYSIS AT ROOM TEMPERATURE

Wave length, Å	Fraction of acetaldehyde molecules which			Polymerize
	Are deactivated or fluoresce	Split into radicals	Rearrange directly to CO + CH ₄	
3130	0.56	0.02	0.18	0.24
2804	0.37	0.094	0.43	0.11
2537	0.05	0.18	0.72	0.05

It should be emphasized that these estimates are dependent on assumptions regarding the mechanism. (See later.)

Further experiments by the Paneth technique have been made by Volman and Leighton.²⁴ Using tellurium mirrors, and adjusting the rates so as to give equal rates of formation of non-condensable products, they found the relative rates of mirror removal at room temperature given in Table XXXII.

TABLE XXXII. RELATIVE RATES OF MIRROR REMOVAL BY ACETONE AND ACETALDEHYDE

Wave length, Å	Acetone	Acetaldehyde
3160-80	1.06	1.0
2800	3.6	1.5
2537	10.8	nil

The lack of radical formation at 2537Å is remarkable and unexplained. Pending the detailed publication of the results, their findings must be accepted with considerable reserve.

Further significant information on the question of radical formation in the photolysis of acetaldehyde comes from the work of Rollefson and Grahame,²⁵ who investigated the quantum yield of carbon monoxide formation at 3132Å and 2652Å at temperatures up to 350°. Since radicals set up a sensitized chain decomposition of acetaldehyde at higher temperatures, and since the chains are very long, they account for practically all the decomposition. Hence at high temperatures a determination of the ratio of the quantum yields for the two wave lengths should give the ratio of the concentrations of radicals formed at the two wave lengths. If the measure-

rs G. K. Rollefson, *J. Phys. Chem.*, 41, 259 (1937).

²⁴ D. Volman and P. A. Leighton, *J. Chem. Phys.*, 7, 781 (1939).

²⁵ G. K. Rollefson and D. C. Grahame, *J. Chem. Phys.*, 7, 775 (1939).

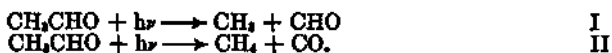
ments are made over a range of temperatures, the ratio of the quantum yields should remain constant provided that (a) the chain process is the main reaction, and (6) there is no change in the efficiency of radical production in the primary process. However, if thermal energy contributes to the dissociation at the longer wave length but not at the shorter, there should be a variation in the ratio of the quantum yields with temperature. They found the values in Table XXXIII.

TABLE XXXIII. QUANTUM YIELDS OF CO FORMATION IN ACETALDEHYDE PHOTOLYSIS (ROLLEFSON AND GRAHAME)

Temperature	Iabs ca. 300 ergs per sec.		
	ϕ_{212}	ϕ_{222}	$\frac{\phi_{212}}{\phi_{222}}$
22	0.92	0.38	0.41
60	—	1.66	—
100	7.10	6.90	0.97
200	69.0, 74.2	89.9	1.25
300	312, 321	450	1.42
350	584	770	1.32

It appears from these results that at high temperatures the quantum yield is about 30 per cent greater at 3132A than at 2652A, and since conditions are otherwise identical it may be concluded that more radicals are produced at high temperatures by 3132A. At low temperatures the effect is reversed, and they conclude that this is due to a contribution to the dissociation from thermal energy at the longer wave length but not at the shorter. They suggest that the reason for this is that the two wave lengths excite acetaldehyde to different electronic states. This explanation does not seem likely, and since processes other than those involving free radicals may be important at low temperatures, their argument is by no means strong.

In an attempt to obtain further information on the production of free radicals in the primary step Gorin¹⁷ investigated the photolysis of acetaldehyde in the presence of iodine. The basis of the method is that hydrogen atoms and alkyl radicals will react readily with iodine to form HI and RI, and that these will be stable under the conditions of the experiment. The results showed that the ratio of methane to methyl iodide was constant at any one wave length, and independent of temperature, pressure or intensity. Gorin therefore assumes that the ratio gives a true measure of the relative efficiencies of the two primary processes



By fixing the methyl radicals as methyl iodide secondary reactions which would normally occur are inhibited.

Gorin found:



at both 3130A and 2537A. He suggests, therefore, that the lower value of Θ_{total} usually obtained at 3130A is due to recombination of CH_3 and CHO .

(6) The ratio $\text{I/II} = 2.6\text{J1 at 3130A}$
 $\quad \quad \quad - 1\text{J2.9 at 2537A.}$

(c) Since $\Theta_{\text{total}} = 1$ at all wave lengths, the formyl radical appears to be stable with respect to the reactions



and



This is substantiated by the fact that Θ_{HI} is very small at temperatures below 100. At higher temperatures the yield of HI increases rapidly. From the temperature coefficient of the ratio $\text{HI/CH}_3\text{I}$ he calculates an activation energy of 26 ± 2 kcal. for the decomposition of the formyl radical.

(d) In the presence of iodine considerably more CO is formed than CH_4 . The extra amount of CO is approximately equal to one-half the methyl iodide formed. This is attributed to the reaction

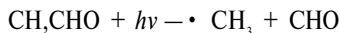


and is substantiated by analyses for formaldehyde. (But note that these analyses are questioned by Blacet and Blaedel.)

Blacet and his co-workers²⁸ have repeated Gorki's work, using a number of different wave lengths and varying the iodine pressure and the temperature. Their results differ from those of Gorin in a number of particulars.

At 3130A and an acetaldehyde concentration of 10^{-2} mole/liter, Θ_{CO} was 0.34 at 60° and increased to 2.29 at 135° in the absence of iodine. At iodine pressures greater than 1 mm. Θ_{CO} was 0.21. Θ_{CH_4} decreased from 0.32 in the absence of iodine to 0.013 or less. For iodine pressures over 1 mm. $\Theta_{\text{CH}_3\text{I}}$ was 0.20. The values of Θ_{CO} and $\Theta_{\text{CH}_3\text{I}}$ for iodine pressures over 1 mm. remained practically constant at 0.20 over the range from 60° to 170° .

No more than a trace of hydrogen was formed, and no acetyl iodide, while HI was produced in considerable quantity. They therefore conclude, contrary to Gorin, that at 3130A Θ_{CO} is much less than unity, and



appears to be the only important primary process.

Iodine apparently reacts readily with both CH_3 and CHO radicals, thus stopping all secondary reactions. The reaction with formyl presumably leads to CO and HI, viz.



Since Θ_{CO} without iodine is greater than Θ_{total} in the presence of iodine, it is evident that recombination of CH_3 and CHO in the ordinary photolysis

²⁶ F. E. Blacet and D. E. Loeffler, *J. Am. Chem. Soc.*, **64**, 893 (1942); F. E. Blacet and J. D. Heldman, *J. Am. Chem. Soc.*, **64**, 889 (1942).

cannot be of importance. It can presumably be concluded that the primary dissociation quantum yield, Θ , in the normal photolysis is given by

$$\phi = \phi_{CO} = \phi_{CH_3I} = 0.2,$$

and hence collisional deactivation must account for a large part of the absorbed radiation.

At other wave lengths somewhat different results were obtained. Thus at 60° for iodine pressures over 1 mm. the results in Table XXXIV were obtained.

TABLE XXXIV. PHOTOLYSIS OF ACETALDEHYDE-IODINE MIXTURES

Wave length Å	Θ_{CO}	Θ_{CH_3I}	Θ_{CH_3I}
3130	0.21	0.01	0.20
2804	0.50	0.15	0.44
2654	0.63	0.28	0.35
2380	0.62	0.37	0.39

The relative importance of methane thus increases at shorter wave lengths. A detailed investigation of the effect of temperature was carried out at 2654Å. The results are illustrated by Figure 17. With sufficient iodine

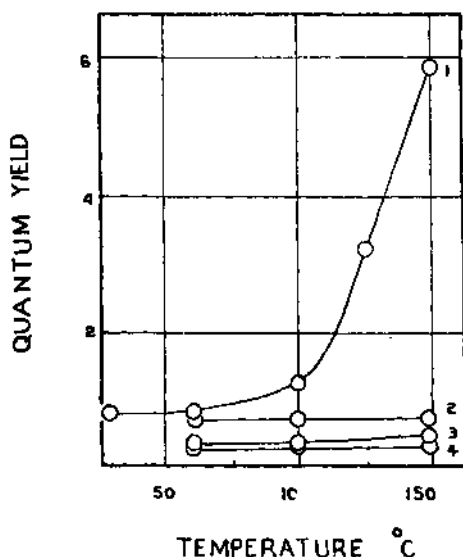
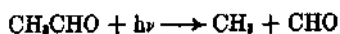


Figure 17. Quantum yield of acetaldehyde photolysis with λ 2654 (Blacet and Loeffler).

(1) Θ_{CO} without iodine. (2) Θ_{CO} in presence of iodine. (3) Θ_{CH_3I} . (4) $\Theta_{CH_3I^-}$.

present Θ_{CO} , Θ_{CH_3I} , and $\Theta_{CH_3I^-}$ are all independent of temperature, and iodine thus inhibits all chains completely.

The fact that Θ_{CH_3I} does not fall below about 0.3 in the presence of iodine indicates that at 2654Å the two primary processes



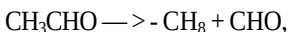
and



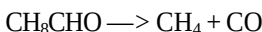
are both coming into play, II accounting for about 28 per cent of the absorbed energy, and I for about 35 per cent. As before



Summed up, the whole investigation of Blacet and his collaborators means that at 3130A the only primary process is



while at shorter wave lengths



is equally important.

As discussed above, Goring results lead also to the conclusion that the molecular rearrangement is of greater importance at shorter wave lengths. Quantitatively however the two investigations differ sharply, since Blacet suggests that all of the molecules reacting do so by an initial free radical split at 3130A, while Gorin arrives at the value of 72 per cent free radical split and 28 per cent rearrangement at the same wave length.

It is difficult to explain the discrepancy, since other evidence is ambiguous, and some of it certainly supports Gorin's conclusions qualitatively. In view *pi* the more detailed nature of the work of Blacet and his collaborators, however, the writer feels that his results should be given the most weight.

Experiments on the inhibition of the photolysis by nitric oxide furnish further evidence of the importance of free radicals in the reaction at high temperatures. Thus Mitchell and Hinshelwood²⁷ found that with 300 mm of acetaldehyde at 300°, 10 mm. of nitric oxide reduced the quantum yield from 186 to 1.14. Larger amounts of nitric oxide resulted in a photochemical oxidation. The nitric oxide was consumed in the reaction, and the quantum yield of its disappearance was approximately 1, so that whenever a chain is broken a nitric oxide molecule disappears. They assume that inhibition occurs by the reaction



The Rate Law and Temperature Coefficient

There is substantial agreement among various workers as to the form of the rate equation, and the temperature coefficient of the photolysis.

As we have seen Leermakers²⁰ found that the rate was given by an equation of the form

$$\frac{d}{dt}[\text{CO}] = k_1 I_{\text{abs.}} + k_2 I_{\text{abs.}}^{\frac{1}{2}} [\text{CH}_3\text{CHO}]. \quad (\text{A})$$

²⁷ J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A169, 32 (1937).

At high temperatures, where the quantum yield is large (i.e., the chain length is considerable), the first term becomes negligible and the rate is given by

$$\frac{d}{dt}[\text{CO}] = k_2 I_{\text{abs}} \frac{1}{2} [\text{CH}_3\text{CHO}].$$

This rate law has been confirmed for the high temperature photolysis by Akeroyd and Norrish,⁶ Mitchell and Hinshelwood,²⁷ and Grahame and Rollefson.²⁸ Blacet and Volman¹⁵ suggest that quite good agreement with the facts can be obtained even at room temperature by leaving out the constant term in equation (A).

For the temperature coefficient of the high-temperature reaction the following values have been obtained:

Investigator	Temperature range	Overall activation energy
Leermakers ²⁰	80-310	10kcal.
Mitchell and Hinshelwood ²⁷	300-450	9.7
Akeroyd and Norrish ⁵	100-350	9.8
Blacet and Loeffler ²⁶	100-150	9.6
Grahame and Rollefson ²⁸	100-350	8.3-8.6

The Mechanism of the Reaction

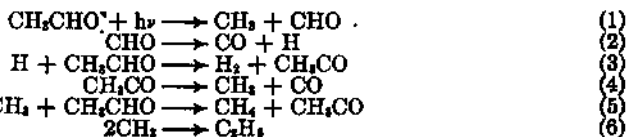
For the low temperature reaction the main doubtful point is the extent to which a direct molecular rearrangement may accompany a split into radicals in the primary process.

For the high temperature reaction only the free radical primary process is of importance. There is general agreement that the reaction involves free radical chains, and that the primary process is

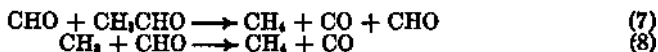


There is, however, a considerable divergence of opinion regarding the chain-propagating and chain-ending processes. It will be convenient to discuss the high-temperature mechanism first.

Leermakers²⁰ discussed his results in terms of the Rice-Herzfeld mechanism:



This yields a rate expression in agreement with that found experimentally. Leermakers also considers two other possible part reactions



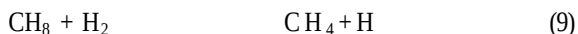
²⁸ D. C. Grahame and G. K. Rollefson, *J. Chem. Phys.*, 8, 98 (1940).

A mechanism based on 1, 4, 5, 7, 8 will also yield the correct rate law, and it is thus not possible to decide from the data whether CHs alone or both CH₈ and QHO are the chain carriers.

Patat²⁹ attempted to verify the Leermakers mechanism by investigating the stationary hydrogen atom concentration during the photolysis of acetaldehyde by the para-ortho hydrogen conversion method. He adopts as a mechanism reactions (1) to (6) above, except that (6) is written as a three body process



In addition, in the presence of added hydrogen the reaction



comes into play. From this mechanism he obtains for the stationary H-atom concentration

$$[\text{H}] = \frac{I_{\text{abs.}}}{k_4[\text{CH}_3\text{CHO}]} + \frac{k_2}{k_4} \sqrt{\frac{2I_{\text{abs.}}}{k_4[\text{M}]}} \frac{[\text{H}_2]}{[\text{CH}_3\text{CHO}]} \quad (\text{B})$$

By measuring the rate of the para-ortho conversion he calculated the stationary H-atom concentration in the photolysis over the temperature range from room temperature to 425°. The catalysis of the conversion was negligible up to about 200°, and hence at lower temperatures only the upper limit to the H-atom concentration could be estimated. The results were accurately represented by the equation

$$[\text{H}] = k' \sqrt{I_{\text{abs.}}} \frac{\sqrt{[\text{H}_2]}}{[\text{CH}_3\text{CHO}]} \quad (\text{C})$$

Now in equation (B) the first term represents the non-chain part of the photolysis and is negligible. In Patat's experiments the concentration of hydrogen was much higher than that of acetaldehyde, roughly in the ratio 10J1, and [M] is therefore approximately equal to [H₂]. Equations (B) and (C) are thus identical, and

$$k' = \frac{k_2}{k_4 k_5^{\frac{1}{2}}}$$

The activation energy of k' was found experimentally to be about 1.9 kcal. Hence, assuming $E_6 = 0$,

$$E_1 - E_2 = 1.9 \text{ kcal.}$$

By calculating the absolute rate of the conversion from collision theory Patat concludes that the ratio of the frequency factors

$$p_2/p_1 \sim 1/4000.$$

This calculation is, of course, open to some question, especially since possible wall effects are neglected throughout.

²⁹ F. Patat, *Z. physik. Chem.*, B32, 274 (1936).

Patat then attempted to evaluate E_9 and E_z separately. This was done by invoking the first term of equation (B) for the reaction at room temperature. At room temperature no catalysis of the conversion was observed, and $[H]$ is thus $\leq 10^{-11.6}$ mole/liter. Now at room temperature

$$[H] = \frac{I_{\text{abs.}}}{k_3[\text{CH}_3\text{CHO}]}$$

whence, assuming a steric factor of 1 for reaction (3),

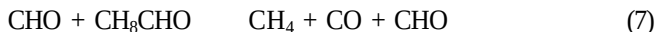
$$E_3 \leq 8.5 \text{ kcal.}, \quad E_9 \leq 10 \text{ kcal.}$$

If p_3 is assumed to be equal to 0.1, then

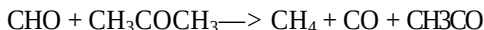
$$E_2 \leq 7.2 \text{ kcal.}, \quad E_9 \leq 9 \text{ kcal.}, \quad \text{and} \quad p_9 \sim 1/10000.$$

These values are not in good agreement with other estimates, and it appears that Patat's calculations are too detailed for the information at his disposal. It should be emphasized that Patat's investigation is not a measurement of the H-atom concentration, but rather is a calculation of it from a detailed kinetic mechanism. One definite conclusion can, however, be drawn, and this is that Patat's work constitutes direct evidence for the presence of hydrogen atoms and/or free radicals in the photolysis.

The photolysis was also investigated at high temperatures by Akeroyd and Norrish,⁵ the main object of their work being an explanation of the fact that the acetaldehyde photolysis leads to long chains at higher temperatures, while that of acetone does not. Their results were in excellent agreement with those of Leermakers. They also found that in mixtures of acetone and acetaldehyde there was no inhibition by acetone of the chain propagation in acetaldehyde, and on the other hand acetaldehyde did not sensitize the decomposition of acetone. They suggest that this is evidence against reaction (7) of Leermakers' scheme, since if (7) occurs



it would be expected that in the presence of acetone the analogous reaction



would also occur. They therefore consider that Leermakers⁷ mechanism is essentially correct, but that reaction (7) should be omitted. The argument for the omission, however, is not particularly strong.

Akeroyd and Norrish obtained a value of 9.8 kcal. for the overall activation energy of the photolysis, in excellent agreement with the value of 10 kcal. found by Leermakers. They conclude that this is the activation energy of the reaction



Actually the rate expression is

$$\frac{d}{dt} [\text{CH}_3\text{CHO}] = \frac{k_2}{k_3} [\text{CH}_3\text{CHO}] I_{\text{abs.}}^{\frac{1}{2}},$$

so that really

$$E_{\text{photo}} = E_i - E_s.$$

They are thus tacitly assuming $E_s = 0$.

Grahame and Rollefson²⁸ have recently made a very thorough investigation of the high temperature photolysis. They obtained a rate law similar to that of Leermakers, viz.,

$$\phi_{\text{decomp.}} = k_1 + k_2 [\text{CH}_3\text{CHO}] I_{\text{abs.}}^{-\frac{1}{2}}.$$

The values of k_2 are given in Table XXXV.

TABLE XXXV. ACETALDEHYDE PHOTOLYSIS AT HIGH TEMPERATURES
(GRAHAME AND ROLLEFSON)

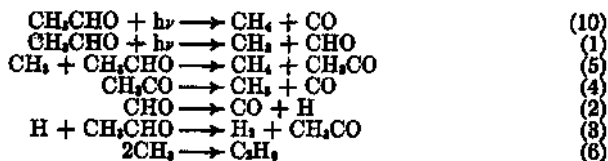
Temp.	3130A labs. quanta $\times 10^{-16}$	kt	Temp.	2652A labs. quanta $\times 10^{-16}$	fa	Temp.	3303A labs. quanta $\times 10^{-16}$	
350	2.67	324	350	2.45	248	300	0.117	142
300	3.61	186.5	300	2.64	127	200	0.239	30
200	1.65	41.9	300	1.69	131	100	0.750	2.0
200	11.05	38.7	300	2.41	111	60	5.73	
200	3.48	40.2	300	2.96	102			
200	8.02	39.4	300	2.43	131			
200	7.94	42.8	300	1.40	129			
200	9.30	45.8	300	1.01	110			
100	32.3	3.1	252	3.80	73.4			
			212	5.23	39.2			
			200	9.43	30.0			
			100	28.0	2.7			
			96	26.4	2.1			
			96	18.4	2.5			
			96	17.7	3.2			

k_1 had the value 0.63, and was thus negligible except at low temperatures where Θ was small. A plot of $\log k_2$ against $\sqrt{I}$ gave a straight line with a slope corresponding to an activation energy of 8.6 kcal. for X3130, and to 8.3 kcal. for XX2652 and 3303. This is somewhat lower than Leermakers' value.

Since the rate is accurately proportional to the first power of the acetaldehyde concentration, the chain terminating step must be second order (or it could be third order if the primary step were second order). Grahame and Rollefson point out that the chain carriers CH_3CO and CHO are unstable and hence must either react or decompose. The concentration of methyl must thus be much greater than that of acetyl or formyl, and the chain terminating step at high temperatures must therefore be the reaction



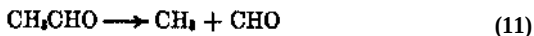
Hence for the mechanism they write:



This is the same as the Rice-Herzfeld mechanism except for the inclusion of the non-free radical primary process in addition to (1). The usual steady-state method gives

$$E_{\text{photo}} = E_1 - \frac{1}{2}E_4 = 8.6 \pm 0.3 \text{ kcal.}$$

If the same mechanism is adopted for the thermal reaction, substituting for the primary step



and if Letort's value of the activation energy of the thermal reaction is used, then we get

$$\begin{aligned}
 E_{\text{thermal}} &= E_1 - \frac{1}{2}E_4 + \frac{1}{2}E_{11} \\
 &\approx 46.0 \pm 0.5 \text{ kcal.}
 \end{aligned}$$

Whence, independent of all assumptions other than that the mechanisms are the same in both cases,

$$\begin{aligned}
 E_{11} &= 2(E_{\text{thermal}} - E_{\text{photo}}) \\
 &= 74.8 \pm 1.6 \text{ kcal.}
 \end{aligned}$$

This result is in good agreement with Rice and Johnston's estimate by the Paneth method of 69.4 kcal. for the activation energy of the thermal split into radicals. In the opinion of the writer, however, the limits of error given above are far too narrow and should be at least ± 5 kcal.

Grahame and Rollefson point out that Allen and Sickman's investigation of the azomethane sensitized decomposition (see III—10) leads to

$$E_1 - \frac{1}{2}E_4 = 13.8 \pm 2 \text{ kcal.,}$$

but they consider that the discrepancy is due to erroneous assumptions regarding the pyrolysis of azomethane. In any case the limits of error are probably wide enough to cover the discrepancy.

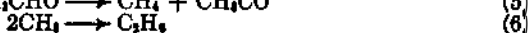
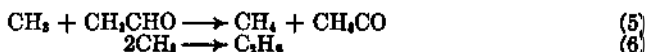
Haden, Meibohm, and Rice³⁰ investigated the photolysis using intermittent light from a rotating sector. Since the rate is proportional to the square root of the light intensity, the reaction will be faster for a rapidly moving sector than it is for a slow one, or for continuous illumination of the same average intensity. They found that the increased rate first became noticeable for a rotation speed of two revolutions per second, so that a reaction chain lasts about 0.5 sec. under their experimental conditions.

In a later paper³¹ Haden and Rice extended the investigation with inter-

³⁰ W. L. Haden, E. P. H. Meibohm, and O. K. Rice, *J. Chem. Phys.*, 8, 998 (1940).

³¹ W. L. Haden and O. K. Rice, *J. Chem. Phys.*, 10, 445 (1942).

mittent light and gave a more detailed discussion of their results. It is apparent from the preceding discussion that there is general agreement that a mechanism of the Rice-Herzfeld type is operative, although there is some difference of opinion regarding the chain-terminating step. Haden and Rice question this conclusion on the following grounds: they accept the Rice-Herzfeld mechanism for the azomethane induced reaction, but consider that the acceptance of the mechanism for the induced reaction makes it untenable for the photo-reaction. They arrive at this result by accepting Gorin's estimate that 0.7 of the absorbed quanta give rise to radicals. They then take Ramsperger's value of the rate constant of the azomethane decomposition and combine it with Allen and Sickman's data to get the absolute rate of the induced reaction. From this they conclude that $k_5 J k_6$ is 3 times as great for the photo-reaction as it is for the induced reaction, where f_a and f_{c_6} refer to

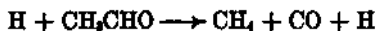


In the opinion of the writer the agreement of calculations involving data taken from 4 different sources to within a factor of 3 is all that can be expected. (It should, however, be noted that Haden and Rice's estimate of a factor of 3 is a conservative one, since the use of Blacet's data instead of that of Gorin or of Grahame and Rollefson's instead of Leermakers would increase the factor.) However, the partial pressures of azomethane used by Allen and Sickman were low, from about 1 to 10 mm. At these pressures, in the absence of acetaldehyde the rate of the azomethane decomposition would have fallen off by a factor of from 2 to 5. The presence of acetaldehyde will certainly compensate this to some extent, but it appears fairly certain that the azomethane decomposition will be still below the high pressure rate in Allen and Sickman's experiments. In any case agreement between different observers for the absolute values of thermal reactions is rarely very good, in view of the uncertainties of temperature measurement, control, and uniformity at elevated temperatures.

On the basis of the above discrepancy between the photo-reaction and the induced reaction Haden and Rice conclude that the chain-carrying steps must be different and hence suggest for the photo-reaction a mechanism based on the chain-carrying step



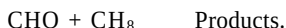
If one discounts the discrepancy between the two sets of results, the argument for CHO as a chain carrier loses its weight, but the possibility of CHO being a chain carrier is still not ruled out. It is also possible that a chain involving



might occur at elevated temperatures.

Haden and Rice's results with intermittent light lead by a somewhat complex analysis to an activation energy of < 2.6 kcal. for the chain-breaking step and to the conclusion that this reaction occurs at virtually every collision, and to 11.3 kcal. for the chain-carrying step as an upper limit. If the activation energy of the chain-breaking step is put equal to zero, then that of the chain-carrying step becomes 10 kcal.

If Haden and Rice's mechanism is accepted then it is E_7 which has the value of 10 — 11.3 kcal., and the activation energy of 2.6 kcal. refers to the chain-ending step



If we reject their mechanism then the above activation energies apply to (5) and (6) respectively instead of (7) and (12), and are thus in agreement with the usual estimates. Haden and Rice's results are thus in line with those of other workers.

They also conclude that there is an additional first order chain-ending process which occurs at the wall with an activation energy of roughly 7.6 kcal. They attribute this to the reaction



It thus appears that the main doubtful point in the high-temperature photolysis is the question of the participation of CHO in the chain-carrying step. It is of course possible that the chains are carried by both methyl and formyl radicals. The simplest assumption is that the chain is carried by methyls as in the thermal reaction. While this cannot be said to be established, in the opinion of the writer all the existing data can be explained on this basis.

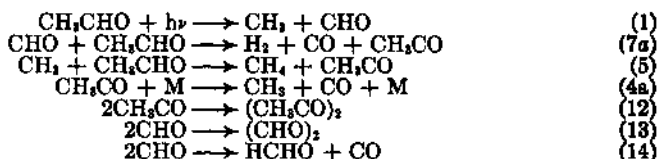
For the low-temperature reaction (i.e., from room temperature to 60 or 70°), as we have seen, the rate-law is of the form

$$I [\text{CO}] = k_1 [\text{abs.}] + k_2 [\text{abs.}]^{1/2} [\text{CH}_2\text{CHO}].$$

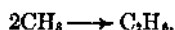
It has usually been considered that the second term on the right corresponds to the free-radical chain process. The temperature coefficient of k_2 is considerable (roughly equivalent to an activation energy of 10 kcal.) and hence at low temperatures the second term will become negligible. The experimentally determined quantum yield of 0.2 or 0.3 at room temperature is then attributed to the first term. This might correspond to a direct molecular rearrangement or to a free radical process which does not involve chains.

The results of Blacet and his collaborators^{15, 16, 26} indicate that at X3130 the primary process is entirely a free-radical one, while at lower wave lengths a direct molecular rearrangement also comes into play. Blacet and Volman suggest that the low-temperature reaction can also be explained on

the basis of a Rice-Herzfeld type of mechanism. Blacet and Volman's work antedates that of Blacet and Loeffler, which indicates that the free radical process is not the only one at $\lambda 2654$. The mechanism of Blacet and Volman is thus applicable to the entire process at X3130, but only to about one-half of the total reaction at $\lambda 2654$. Their proposed mechanism is:



In other words they are proposing a mechanism similar to that of Leermakers at room temperature also. The only essential difference is in the chain-ending step. Since they found no ethane or ethylene in the products at room temperature they rule out the normally accepted step



or the possible step



It is, of course, in every way possible for the chain-ending process to vary with temperature since the acetyl and formyl radicals will be unstable at high temperatures. They consider reaction (12) to be the main chain-ending step at room temperature. The chain-carrying step does not differ essentially from that proposed by Leermakers. They suggest that good agreement with the facts can be obtained by leaving out the constant term in Leermakers' rate expression, and merely assuming that the chain mechanism holds over the entire temperature range. If this is done, the mechanism yields a value of Θ of 0.2 to 0.3 at room temperature in agreement with experiment. This assumes a much lower efficiency for the primary step than had previously been estimated.

Since on this mechanism

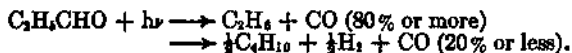
$$\begin{aligned}
 \phi_{\text{CO}} &= \frac{d}{dt} [\text{CO}] \times \frac{1}{I_{\text{abs.}}} \\
 &= k[\text{CH}_3\text{CHO}]I_{\text{abs.}}^{-1/2},
 \end{aligned}$$

the variation of rate with intensity is explained. The formation of hydrogen without ethane or ethylene is also explained. Increased intensity favors chain-breaking, and hence diminishes the chain-length and increases the H_2/CO ratio. The maximum in the ratio at 30° or so is perhaps due to the fact that the acetyl radical is stable at room temperature and unstable at higher temperatures. The increase in the ratio with decreasing wave length might be due to the simultaneous occurrence of a molecular split at longer wave lengths. This, however, is very unlikely in view of the work of Blacet and Heldman.

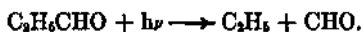
Mignolet³² investigated the acetaldehyde photolysis in the presence of small amounts of oxygen. A photo-oxidation occurred, and the primary product was diacetyl peroxide. Unlike the thermal reaction, however, oxygen had no catalytic effect on the photolysis.

4. Propionaldehyde

The photolysis of propionaldehyde has been investigated by several workers. Leighton and Blacet³³ found that decomposition and polymerization both occurred at room temperature. The quantum yield of decomposition increased with decreasing wave length from 0.51 at 3130Å to 1.02 at 2537Å, and was independent of pressure. The quantum yield of polymerization, on the other hand, decreased to zero as zero pressure was approached, suggesting a bimolecular process. The overall decomposition was



They conclude that the primary step is



The following steps would then be expected to be analogous to those occurring with acetaldehyde.

A number of free radical investigations of the photolysis have been made. West³⁴ was unable to detect radicals or hydrogen atoms by the para-ortho hydrogen method. Pearson⁸⁶ obtained negative results by the Paneth method. However, later work by Pearson and Purcell³⁶ showed that the former negative results in the case of acetaldehyde were due to the inactivation of the mirrors by the formation on them of polymers, and the same explanation would presumably also invalidate Pearson's negative results with propionaldehyde.

The question has recently been re-investigated by May, Taylor, and Burton.⁸⁷ A mercury lamp giving mainly X2537 was used, and the lead mirrors employed were heated to 100° to avoid the deposition of polymers. The results were very variable because of trouble with the desensitizing of the mirrors, but alkyl radicals were definitely detected in a qualitative way. Tests for atomic hydrogen were also made by the guard mirror technique. The results indicated that not over 2 per cent of the mirror-active particles were H-atoms, and that even this 2 per cent was probably due to alkyl radicals passing the guard mirror.

⁸² J. Mignolet, *Bull. Soc. Roy. Liege*, 10,343 (1941); *Chem. Abstracts*, 37, 2660 (1943) (seen in abstract only).

³⁸ P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, **54**, 3165 (1932).

⁸⁴ W. West, *J. Am. Chem. Soc.*, 57,1931(1935).

⁸⁶ T. G. Pearson, *J. Chem. Soc.*, **1934**, 1718.

⁸⁸ T. G. Pearson and R. H. Pin-cell, *J. Chem. Soc.*, **1935**,1151.

⁸⁷ L. May, H. A. Taylor, and M. Burton, *J. Am. Chem. Soc.*, 63, **249** (1941).

It was thus safe to use antimony mirrors to detect alkyl radicals, and these gave much more reproducible results and permitted the unequivocal detection of alkyl radicals. Half-life measurements with these mirrors gave a value of 3.8×10^{-3} sec, in agreement with Paneth and Lautsch's value of 3.9×10^{-8} sec. for ethyl radicals. However, the conditions were distinctly different in the two investigations, and hence the agreement between the values is probably fortuitous. It does appear probable, however, that the radicals were at least partly ethyl. Their results also indicated that approximately equal concentrations of radicals were obtained from acetone and from propionaldehyde under the same conditions of illumination. Since the absorption by the two substances is not very different, they suggest that practically all of the propionaldehyde photolysis proceeds by a primary free radical split.

A more detailed investigation of the propionaldehyde photolysis, especially from a free radical point of view has been made by Garrison and Burton,³⁸ using $\lambda\lambda 2537, \sim 2900$, and ~ 3200 . By the Paneth method, in a manner similar to that of May, Taylor, and Burton, it was found that the radicals produced were exclusively ethyl, and that no appreciable amount of hydrogen atoms were formed. The primary process is thus certainly in part



and the process

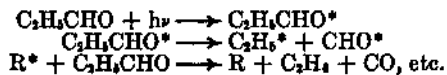


does not occur.

The ratio of C_2H_5 (as determined from the lead transported from the mirror) to CO was approximately 0.33 at $\lambda 3200$, 0.45 at $\lambda 2900$, and 0.37 at $\lambda 2537$, all measurements being made at 30° . The excess of CO over ethyl radicals is most simply explained in terms of the partial occurrence of the primary step



They suggest, however, that the results can also be explained by assuming a primary act which involves free radicals exclusively, *i.e.*,



All this is highly speculative. Their investigation shows definitely, however, that a free radical decomposition occurs at all wave lengths.

Mitchell and Hinshelwood³⁹ have investigated the inhibition of the propionaldehyde photolysis at high temperatures by nitric oxide, and incidentally have done some work on the photolysis itself. The rate at 300° was found to be proportional to the square root of the light intensity. The

³⁸ W. M. Garrison and M. Burton, *J. Chem. Phys.*, **10**, 730 (1942).

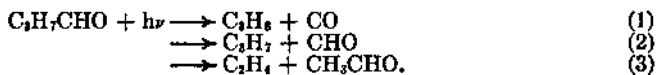
³⁹ J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A159**, 32 (1937).

quantum yield varied with pressure in a manner similar to that of acetaldehyde, i.e., it increased considerably with increasing pressure. It had a **value** of about 10 at low intensities and 300 mm. pressure at 300°, and of about 30 under similar conditions at 450°. These values are much less than those for acetaldehyde. The activation energy of the overall reaction was about 6.5 kcal.

The reaction is inhibited by nitric oxide, but larger amounts are required for inhibition than with acetaldehyde. The quantum efficiency of nitric oxide consumption is about 0.22, roughly 5 times less than with acetaldehyde. They conclude that either recombination of radicals occurs more efficiently than with acetaldehyde, or else the efficiency of radical production in the primary step is less.

6. Butyraldehydes

The photolyses of n- and iso-butyraldehyde are similar to those of the lower aldehydes⁴⁰ at room temperature. At high temperatures the quantum yield rises to 9 for iso- and 14 for n-butyraldehyde at 600°K. In order to account for the products three primary processes have been postulated:



In the case of (2) Leighton *et al.* assume a free radical mechanism similar to that for acetaldehyde. For the high temperature reaction of n-butyraldehyde the rate can be expressed by an equation similar to that of Leermakers for acetaldehyde:

$$\frac{d}{dt}[\text{CO}] = 0.45I_{\text{abs.}} + kI_{\text{abs.}}^{1/2}[\text{RCHO}].$$

The temperature dependence of J_c corresponds to an activation energy of 5.6 kcal. The behaviour of iso-butyraldehyde is more complex.

6. Acetone

A great many investigations of the photodecomposition of acetone have been made. (For reviews see references 41-45.) One of the first of the more accurate investigations was that of Damon and Daniels,⁴⁶ who found a quantum yield of 0.2 to 0.4 at atmospheric pressure which increased with

⁴⁰ P. A. Leighton, L. D. Levanas, F. E. Blacet, and R. D. Rowe, *J. Am. Chem. Soc.*, 69, 1843 (1937).

⁴¹ G. K. Rollefson and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions*, New York, 1939.

⁴² W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases*, New York, 1941.

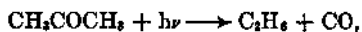
⁴³ P. A. Leighton, *J. Phys. Chem.*, 42, 749 (1938).

⁴⁴ W. A. Noyes, *Rev. Mod. Phys.*, 6, 280 (1933).

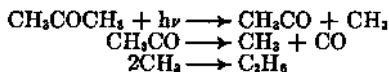
⁴⁵ R. G. W. Norrish, *Trans. Faraday Soc.*, 27, 407 (1931).

⁴⁶ G. H. Damon and F. Daniels, *J. Am. Chem. Soc.*, 66, 2363 (1933).

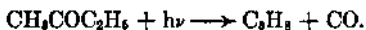
decreasing intensity and decreased with decreasing pressure. The yield was roughly independent of wave length at 3130A and 2650A. The products did not altogether correspond to the simple process



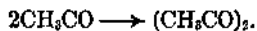
but were 47% CO, 27.9% C₂H₆, 13.2% CH₄, 4.2% H₂, and 7.6% unaccounted for. Norrish^{47,48} concluded that the primary process is a split into radicals



The evidence for this is very strong by analogy. In the case of methyl ethyl ketone he found amounts of ethane, propane, and butane of the same order of magnitude. This is strong evidence for the split into radicals, since otherwise only propane would have been expected, viz.,



Further evidence that the primary step involves a split into methyl and acetyl radicals comes from the work of Barak and Style⁴⁹ who identified diacetyl in the products of the photolysis at room temperature, obviously owing to the reaction



There is also plenty of evidence from experiments by the Paneth method that free radicals are formed in the photolysis. Pearson and Purcell⁶⁰ found that antimony, tellurium, and lead mirrors were removed by the products of the reaction, and the half-life of the radicals was in good agreement with values obtained by Paneth for methyl.⁶¹ The identification of the radicals as methyl was further confirmed by the identification of the products formed with tellurium, mercury, and arsenic mirrors as methyl tellurides, dimethyl mercury, and trimethyl arsine respectively.

By means of rough estimates of light absorption they concluded that about 6 times as many radicals are produced per quantum absorbed from acetone as from acetaldehyde. This is only a rough estimate because (a) the light absorption measurements were very approximate, (b) the full mercury arc was used, but the assumed quantum yields were those for X3130, (c) the quantum yields used in the calculation were for much higher pressures than those employed by Pearson and Purcell. However, the results probably do indicate a more efficient production of radicals from acetone in the primary step.

⁴⁷ R. G. W. Norrish, *J. Chem. Soc.*, 1934, 874, 1456.

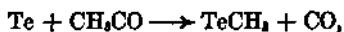
⁴⁸ R. G. W. Norrish, *Trans. Faraday Soc.*, 30, 103 (1934).

⁴⁹ M. Barak and D. W. G. Style, *Nature*, **135**, 307 (1935).

⁵⁰ T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, **1934**, 1718, **1935**, 1151.

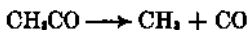
⁶¹ F. Paneth and W. Hofeditz, *Ber.*, 62, 1335 (1929); F. Paneth, W. Hofeditz, and A. Wunsch, *J. Chem. Soc.*, **1935**, 375.

Radicals were also detected by the Paneth technique by Prileshajeva and Terenin⁵² and by Glazebrook and Pearson.⁶⁸ The latter authors also detected diacetyl in the products in agreement with Barak and Style. They found no diacetyl at temperatures above 60°, however, indicating decomposition of the acetyl radical. In the presence of tellurium at room temperature diacetyl formation was also prevented, possibly by the reaction



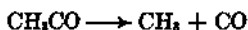
or else by the formation of a very unstable acetyl telluride which subsequently splits off CO. By comparing the rates of mirror removal and diacetyl formation they concluded that methyl and acetyl radicals are formed in the photolysis in substantially equal amounts.

They estimate that in the presence of quartz the acetyl radical has a life much shorter than that of alkyl radicals (10^{-4} sec. or less under their experimental conditions). The absence of diacetyl when the walls of the vessel were coated with tellurium suggests that diacetyl formation is a wall reaction. If this is so, the average acetyl radical at room temperature survives about 100 collisions with other molecules before reaching the walls. In this connection Bawn⁵⁴ concludes from calculations by the transition state method that the activation energy of the reaction



is about 16 kcal.

Further evidence for the formation of diacetyl at the wall comes from the work of Iredale and Lyons^{64a} who photolysed acetone in the presence of inert gases. It was found that at room temperature with 150 mm. of acetone 500 to 600 mm. of added carbon dioxide or nitrogen completely inhibited the formation of diacetyl. At the same time the production of carbon monoxide increased relative to that of ethane. Both facts are readily explainable on the assumption that diacetyl formation is a wall reaction, and that the inert gas prevents diffusion of acetyl to the walls and thus permits the reaction



to predominate.

Leighton and Volman⁶⁵ investigated the effect of wave length on the rate of removal of tellurium mirrors at room temperature and 1.5 mm. pressure. The relative rates were

λ	Relative rate of mirror removal
3160-80	1.06
2800	3.6
2537	10.8

⁸² N. Prileshajeva and A. Terenin, *Trans. Faraday Soc.*, **31**, 1483 (1935).

^M H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1937**, 567.

^M C. E. H. Bawn, *Trans. Faraday Soc.*, **34**, 598 (1938).

^{64b} T. Iredale and L. E. Lyons, *J. Chem. Soc.*, **1944**, 588.

^w P. A. Leighton and D. Volman, *J. Chem. Phys.*, **7**, 781 (1939).

In each case the light intensities were adjusted so as to give the same rate of formation of non-condensable gaseous products.

Feldman, Ricci, and Burton⁵⁶ have investigated the production of free radicals in the acetone photolysis at 45° by the following method. A long heavy lead mirror was deposited in a tube. Radicals reacting with it formed lead alkyls, and the lead in these was estimated by a micro-method. They found that if a second mirror were deposited farther down the tube more lead alkyl was formed. This is due to the fact that while all the methyl radicals are picked up by the first mirror, acetyl radicals are not. These decompose on their way down the tube, and the methyls formed in the decomposition are caught by the second mirror.

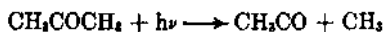
If the photolysis is carried out at 100°, however, no additional pick-up of lead occurs at the second mirror. This furnishes proof of the previously accepted conclusion that the acetyl radical is relatively stable at 45°, but is almost completely decomposed at 100°.

Another investigation with a bearing on the question of free radical production in the primary process is that of Gorin,⁶⁷ who photolysed acetone in the presence of iodine, which served to "fix" the radicals present as methyl iodide, acetyl iodide, hydrogen iodide, etc. The full radiation from a mercury arc was used. At lower temperatures the results in Table XXXVI were obtained:

TABLE XXXVI. THE PHOTOLYSIS OF ACETONE IN THE PRESENCE OF IODINE (GORIN)

Acetone pressure, mm.	I ₂ , mm.	Temp- erature	Moles CH ₃ I × 10 ⁴	Moles CO × 10 ⁴	φ _{CH₃I}	Moles CH ₃ COI × 10 ⁴
652	4	80	21.4	0.40	1.00	—
652	0	60	—	3.63	—	—
365	2	80	17.6	0.39	0.91	—
365	0	60	—	3.29	—	—
616	1	80	18.7	0.36	0.93	2.5
616	0	60	—	3.42	—	—
561	1	60	19.4	0.10	0.94	2.2
561	0	60	—	3.51	—	—

The quantum yield of methyl iodide formation is thus approximately unity, which points strongly to the primary process



as the exclusive one. It also appears that very little CO is formed in the presence of iodine, which suggests that the acetyl radical is quite stable. The production of acetyl iodide is much smaller than that of methyl iodide,

⁶⁶ M. H. Feldman, J. E. Ricci, and M. Burton, *J. Chem. Phys.*, **10**, 618 (1942).

⁶⁷ E. Gorin, *Acta Physicochimica* (U.S.S.R.), **8**, 513 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

however, and Gorin concludes that this is due to the establishment of an equilibrium

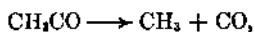


Further experiments on the photolysis in the presence of iodine were carried out at higher temperatures, with the results given in Table XXXVII.

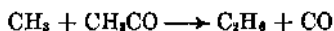
TABLE XXXVII. THE PHOTOLYSIS OF ACETONE-IODINE MIXTURES AT HIGHER TEMPERATURES (GORIN)

Acetone, mm.	I ₂ , mm.	Moles CH ₃ I × 10 ⁴	Moles CH ₃ COI × 10 ⁴	Moles CO × 10 ⁴ *	Tempera- ture
165	4	21.7	9.3	1.62	100
487	2	43.0	4.0	2.67	100
430	4	29.4	8.8	5.28	115
156	2	36.8	4.6	5.82	115
517	4	14.6	7.0	4.96	128
169	2	41.6	3.4	15.02	130

The increase in carbon monoxide as the temperature is raised is what would be expected if there is a competition between decomposition of the acetyl radical and the formation of acetyl iodide. The amount of acetyl iodide formed at higher temperatures, however, is surprisingly large and indicates a greater stability of the acetyl radical than was previously supposed. Gorin estimates a minimum value of 17 kcal. for the activation energy of the decomposition



and concludes that the disappearance of diacetyl as a product in the normal photolysis at higher temperatures must be largely due to the reaction



rather than to the decomposition of the acetyl radical.

In filtered light of wave length 3130A Gorin found a quantum yield of methyl iodide production of about 0.8. It thus appears that even at this wave length the predominant primary process is still a free radical split.

Further work on the photolysis of acetone-iodine mixtures was done by Benson and Forbes,⁶⁸ using $\lambda 2537$. Their results were somewhat erratic, but the following points were established:

(a) They were unable to separate methyl and acetyl iodides by Gorki's method. They conclude that acetyl iodide is probably small compared with methyl iodide, and that Gorin's analyses for acetyl iodide were unreliable.

(6) Appreciable amounts of CO were formed in the presence of iodine at all temperatures, contrary to Gorin. No diacetyl was formed in the presence of iodine at any temperature.

(c) The lamp used was aging rapidly and it is thus difficult to compare

⁶⁸ S. W. Benson and G. S. Forbes, *J. Am. Chem. Soc.*, 65, 1399 (1943).

the results of different experiments. The results of successive pairs of runs given in Table XXXVIII are fairly reliable, however.

From their results Benson and Forbes draw the following conclusions. The absence of ethane in the presence of iodine means that the primary process is a free radical split, and that ethane in the normal reaction arises by

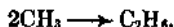


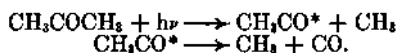
TABLE XXXVIII. PHOTOLYSIS OF ACETONE-IODINE MIXTURES
(BENSON AND FORBES)

Temperature	Iodine present	$\frac{(\text{CH}_3)_2\text{CO}}{(\text{CO})}$	$\frac{\text{C}_2\text{H}_6}{(\text{CO})}$	$\frac{(\text{CH}_3\text{CO})_2}{(\text{CO})}$
00	No	0.083	1.23	0.29
00	Yes	0.017	1.23	0.29
100	No	0.067	1.01	0.29
100	Yes	0.015	1.01	0.29
142	No	0.100	0.91	0.00
	Yes	0.014	0.91	0.00

$$P_{\text{acetone}} = 12.0 \text{ mm.}$$

$$\frac{P_{\text{acetone}}}{P_{\text{iodine}}} = 54$$

The large yield of CO in the presence of iodine supports Herr and Noyes' conclusion (see later) that at least part of the acetyl radicals formed decompose spontaneously



This is supported by the fact that with the smaller quantum at X3130 Gorin found only slight amounts of CO.

Gorin reported diacetyl in the presence of iodine at X3130, in contrast to its absence in Benson and Forbes investigation. They conclude from their work that a plot of

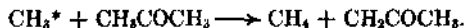
$$\log \frac{\text{diacetyl}}{\text{CO}} \text{ against } 1/T$$

corresponds to an activation energy of 15 ± 2 kcal. Correcting this for the small increase in CO with increasing temperature they get $E = 16$ kcal., which they ascribe to the reaction



They suggest that this reaction is heterogeneous.

Methane formation is not reduced to zero in the presence of iodine. They suggest that this is due to the carrying over of energy from the primary step by methyl radicals, followed by



By an indirect and rather roundabout method they estimate an overall quantum efficiency of about unity, in agreement with Herr and Noyes.

Acetyl iodide was not determined. If its presence is assumed, and its amount calculated by difference from a material balance, then $\log [\text{CH}_3\text{CO}]$ plotted against $1/T$ gives an apparent activation energy of 6 kcal. If, as assumed by Gorin, there is a rapidly established equilibrium



then 6 kcal. is the difference between the activation energies of the reactions

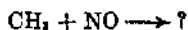


and

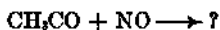


On this assumption the latter reaction has an activation energy of 9 kcal. This estimate is of rather dubious validity, however.

Mitchell and Hinshelwood⁵⁹ investigated the effect of nitric oxide on the photolysis of acetone at 300°, and found that no effect was produced by small amounts of nitric oxide, indicating the absence of reaction chains. This is in agreement with the fact that the quantum yield is about unity. (They found $\phi = 1.10$ at 300°.) Larger amounts of nitric oxide caused oxidation. The photolysis in the presence of large amounts of nitric oxide was investigated in more detail by Anderson and Rollefson,⁶⁰ who found that CO production was decreased strongly. A similar effect was found in the photolysis of diacetyl and acetyl bromide. A four-fold excess of nitric oxide also completely eliminated ethane production at room temperature. Since carbon monoxide production is not completely eliminated under the same circumstances, it appears that the reaction



is faster than



The complete absence of hydrocarbons in the presence of excess nitric oxide indicates that a purely free radical mechanism is operative.

Further evidence for the free radical nature of the reaction comes from work on the photolysis of acetaldehyde-acetone mixtures. Akeroyd and Norrish⁶¹ found that acetone had no inhibitory effect on the photolysis of acetaldehyde. On the other hand acetone was able to photosensitize the chain decomposition of acetaldehyde. This is further definite proof of the presence of free radicals in the photolysis of acetone. These results were confirmed by Grahame and Rollefson.⁶² Since at high temperatures the photolysis of acetaldehyde is a chain reaction, and the chains may be started by radicals from either acetone or acetaldehyde, a comparison of the rate

⁵⁹ J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A159**, 32 (1937).

⁶⁰ H. W. Anderson and G. K. Rollefson, *J. Am. Chem. Soc.*, **68**, 816 (1941).

⁶¹ E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 890.

⁶² D. C. Grahame and G. K. Rollefson, *J. Chem. Phys.*, **8**, 98 (1940).

with an acetone-acetaldehyde mixture with that for pure acetaldehyde provides a measure of the relative efficiencies of radical production in the primary processes of the two substances. They thus obtained the values

λ	Relative rates	
	CH_3CHO	CH_3COCH_3
3130	1.00	0.70
2652	0.55	0.92

The relative acetone values are in good agreement with Gorin's estimate.

In an investigation of a somewhat similar sort Danby and Hinshelwood⁶³ studied the polymerization of ethylene photosensitized by acetone and acetaldehyde. Since in both cases the polymerization is induced by radicals, it is possible to estimate the relative radical production from the relative rates of polymerization. They conclude that the efficiency of radical production in acetone is only 70 per cent that in acetaldehyde. Danby and Hinshelwood used the full radiation from a mercury arc in their investigation, so that their results are in general agreement with those of Gorin given above.

The above discussion indicates that there is no doubt that radicals are produced in the photolysis of acetone, and that they play a major role in the reaction. As with the thermal reaction, however, there is much evidence to show that chains are not set up at high temperatures as occurs with acetaldehyde. Thus Leermakers⁶⁴ found that the quantum yield of the photolysis did not rise appreciably at temperatures up to 400°.

Winkler⁶⁶ made a somewhat more thorough investigation of the high temperature photolysis. Quantum yields were not determined, the results being reported in terms of the relative rate of pressure increase. The rate was found to increase by a factor of about 5 from 60° to 200°, and then increase further quite rapidly up to 400°. The following results were obtained:

Wave length	Rate at 400°
	Rate at 60°
2200-2800A	18
2800-3300A	50
3135A	40

If a quantum yield of 0.3 is assumed at 60°, then the value is 1.5 at 100° in agreement with Leermakers. Winkler assumes that the quantum yield does not rise above this value and that the further increase in rate at high temperatures is caused by increased light absorption. This is plausible in view of the short light path which was probably used. He suggests that in view of the formation of unsaturates and tarry material at high temperatures

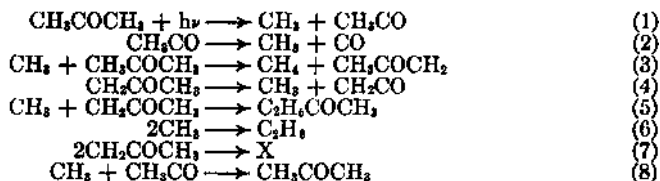
⁶³ C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A179, 169 (1941).

⁶⁴ J. A. Leermakers, *J. Am. Chem. Soc.*, 66, 1899 (1934).

⁶⁶ C. A. Winkler, *Trans. Faraday Soc.*, 31, 761 (1935).

ketene is formed in the primary process. There seems to be no evidence for this, although it might be a secondary product.

In explaining his high temperature results Leermakers adopted the Rice-Herzfeld mechanism in principle, viz.,



This will explain the products found experimentally. The essential feature of the mechanism is that (4) must have a high activation energy, since otherwise chains would be set up. If this is so, and if (3) has a moderate activation energy, then ethane will be the main hydrocarbon product at low temperatures and methane at high temperatures, and no chains will occur since acetyl radicals will disappear by (7) without regenerating radicals.

The high temperature photolysis has also been investigated by Akeroyd and Norrish,⁶¹ using the full radiation from a mercury arc. The relative rates given in Table XXXIX were obtained:

TABLE XXXIX. HIGH TEMPERATURE PHOTOLYSIS OF ACETONE
(AKEROYD AND NORRISH)

Temperature	63	99	199	300	396
Rate in arbitrary units	3.95	6.15	6.52	8.5	9.91

The increase from 60° to 100°, and again above 200° is in general agreement with Winkler's results, but the ratio of the rate at 400° to that at 60° is only about 2.5 as compared with Winkler's value of 20 to 50. This is probably due to a much longer light path, so that Akeroyd and Norrish's results were only slightly affected by increasing light absorption.

TABLE XL. PHOTOLYSIS OF ACETONE IN THE PRESENCE OF HYDROGEN

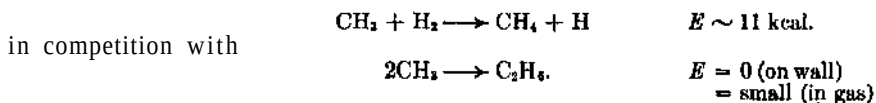
Temp.	$\frac{\text{C}_2\text{H}_6}{\text{CO}}$		$\frac{\text{CH}_4}{\text{CO}}$		$\frac{\text{C}_2\text{H}_6 + 4\text{CH}_4}{\text{CO}}$	
	H ₂ present	H ₂ absent	H ₂ present	H ₂ absent	H ₂ present	H ₂ absent
71	1.09	1.17	0.073	0.083	1.13	1.21
160	0.855	0.982	0.268	0.057	0.99	1.01
200	0.595	0.86	0.585	0.11	0.89	0.91
250	0.319	0.692	1.04	0.264	0.84	0.82
300	0.219	0.570	1.35	0.530	0.89	0.83

The photolysis of acetone in the presence of hydrogen has been investigated by Taylor and Rosenblum⁶⁶ over the temperature range 70° to 300°.

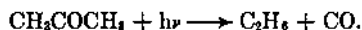
⁶⁶ H. S. Taylor and C. Rosenblum, *J. Chem. Phys.*, 6, 119 (1938).

The carbon monoxide production did not vary greatly in the presence or absence of hydrogen, *i.e.*, the quantum yield remained sensibly constant. In the absence of hydrogen ethane decreased with rise in temperature and methane increased. In the presence of hydrogen these effects were much more pronounced (Table XLI).

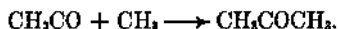
The last column really amounts to a carbon-oxygen balance, and the results show that at low temperatures there is a CO deficiency, obviously owing to diacetyl formation. At high temperatures there is a CO excess, evidently owing to the formation of hydrocarbon polymers. They conclude that the drop in ethane with rise in temperature is caused by the reaction



The above data show that at 300° in the presence of hydrogen 75 per cent of the decomposed acetone appears as methane, and must therefore have been in the form of methyl. Hence practically all the primary process must involve radical formation, and virtually none the reaction



Taylor and Rosenblum suggest that the lower quantum yield at low temperatures is probably caused by the participation of the acetyl radical in recombination,



The high temperature photolysis has also been investigated by Allen,⁶⁷ using the full radiation from a mercury arc. His results are in general agreement with those of previous workers. In addition, he made an accurate determination of the amount of methane produced in the reaction (Table XLI).

TABLE XLI. METHANE PRODUCTION IN HIGH TEMPERATURE
PHOTOLYSIS OF ACETONE

Temperature, °K	$\frac{\text{CH}_4}{\text{CO}}$
520	0.164
550	0.243
567	0.277
619	0.529

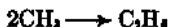
Methane is thus becoming a major product at higher temperatures. The activation energy of methane production from these figures is 7.1 kcal., in satisfactory agreement with Taylor and Rosenblum's value of 8.6 kcal. Since methane is produced, a material balance requires the presence of some

⁶⁷ A. O. Allen, *J. Am. Chem. Soc.*, 63, 708 (1941).

oxygen-containing compound, and Allen showed that methyl ethyl ketone was present. Distillation analyses showed that small amounts of propane and butane were also formed. These can obviously be accounted for by radical recombination reactions. Allen suggests a mechanism similar to that proposed by Leermakers, except that he assumes that the only important recombination reaction is

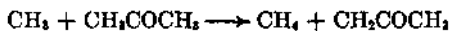


He omits the reaction



since this would make the formation of methane pressure dependent, contrary to his results. However, the results in this connection are confined to too limited a range of pressures to be convincing.

Allen also found a slight deposit on the walls of the vessel and some lack of reproducibility. This points to wall effects, and he suggests that the formation of acetonyl by



and its disappearance by reaction with methyl to form methyl ethyl ketone are both wall reactions. As evidence for the heterogeneous nature of reaction (5) is cited the fact that Rice, Rodowskas, and Lewis⁶⁸ found that methyl radicals from the pyrolysis of dimethyl mercury gave diacetyl on reaction with acetone, in contrast to the methyl ethyl ketone found here.

Saunders and Taylor⁶⁹ have also investigated the reaction at high temperatures. They were primarily concerned with the effect of mercury on the reaction, but they also obtained results on the photolysis of acetone alone, and they discuss the mechanism in some detail. Their work was done in the range 100° to 250°. As products they found CH₄, CO, and C₂H₆, and also traces of hydrogen, ethylene, and propane at higher temperatures. There were also indications of complex compounds at higher temperatures, since there was a considerable carbon deficiency, up to 20 per cent, in the gaseous products. They adopt a mechanism which is in the main the same as that previously proposed. The main difference is that, in line with the general views of Taylor and Burton (see Section VI-28), they rule out the reaction



and hence assume ethane to be formed solely by



Also in view of the detection of acetonyl acetone by Rice, Rodowskas, and Lewis in the thermal decomposition of acetone they suggest

⁶⁸ F. O. Rice, E. L. Rodowskas, and W. R. Lewis, *J. Am. Chem. Soc.*, **56**, 2497 (1934).

⁶⁹ K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).



as an important process.

From the above discussion it is apparent that there is fairly good agreement in a general way as to the mechanism of the acetone photolysis at high temperatures. At lower temperatures there have been a number of much more comprehensive investigations. These agree in a general way with the mechanisms proposed at high temperatures, but much more information is available on which to base detailed mechanisms.

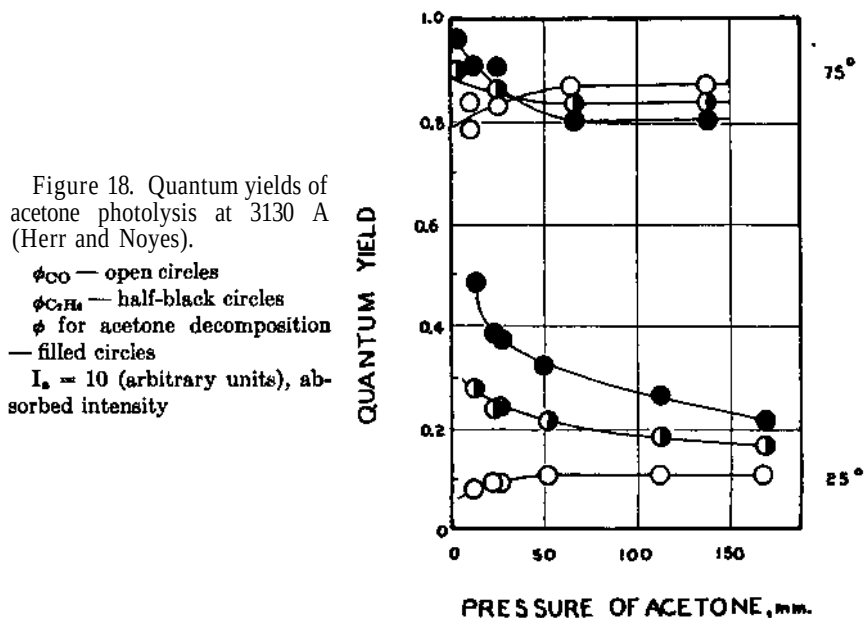


Figure 18. Quantum yields of acetone photolysis at 3130 Å (Herr and Noyes).

ϕ_{CO} — open circles
 $\phi_{\text{C}_2\text{H}_4}$ — half-black circles
 ϕ for acetone decomposition — filled circles
 $I_a = 10$ (arbitrary units), absorbed intensity

Spence and Wild⁷⁰ investigated the photolysis with special reference to the variation of products with wave length. The production of diacetyl at low temperatures, but not at 60° and above was confirmed, and it was shown to be an important product. Spence and Wild found the quantum yield, within somewhat wide limits of error, to be independent of pressure and of light intensity, as would be expected if no chain processes are involved and recombination is not important.

They paid particular attention to the ratio $\text{C}_2\text{H}_6\text{JCO}$ in the products under various conditions, and contrary to the results of Norrish, Crone, and Saltmarsh⁷¹ they did not find a value of unity with a full mercury arc, but rather about 1.5. With filtered light in the continuum (2200 to 2900Å) at very low intensities the value of the ratio was not far from 1.5. At higher

⁷⁰ R. Spence and W. Wild, *J. Chem. Soc.*, **1937**, 352; *Nature*, **138**, 206 (1936).

⁷¹ R. G. W. Norrish, H. G. Crone, and O. D. Saltmarsh, *J. Chem. Soc.*, **1934**, 1456.

intensities, however, it approached 2.5, and it also increased with increasing acetone pressure. In the banded region the ratio was much lower, being about unity. In the continuous region the ratio decreased with increasing temperature to about 1 at 60°.

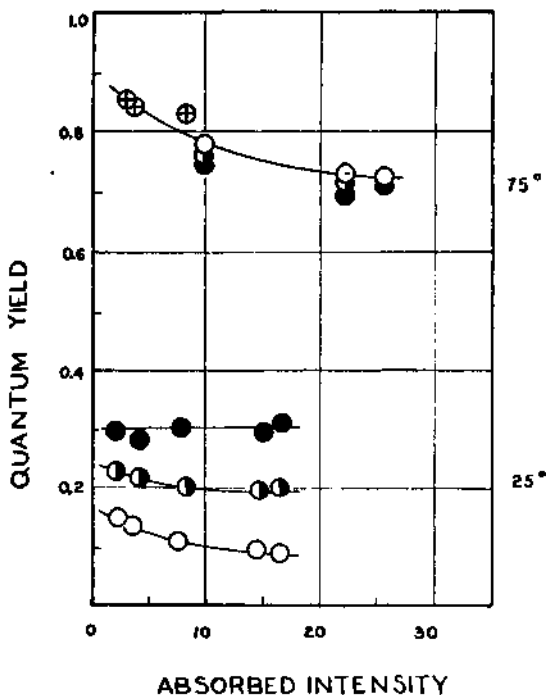
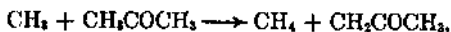


Figure 19. Quantum yields of acetone photolysis at 3130 Å and 50 mm. (Herr and Noyes).

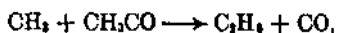
⊕ — points for which $\phi_{\text{CO}} = \phi_{\text{C}_2\text{H}_6} = \phi_{\text{decomposition}}$. Other symbols as in Figure 18.

Their work is definitely contrary to that of Norrish in that even at 60° they found that much methane was formed, although the $\text{C}_2\text{H}_6/\text{CO}$ ratio was approximately unity. Thus they found 46.6 per cent CO, 44.2 per cent C_2H_6 , and 9.4 per cent methane. At 60° the quantity of methane increased with increasing pressure and decreasing intensity. They concluded that methane arose by

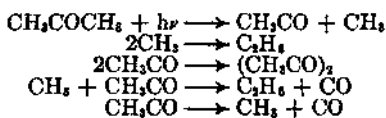


in agreement with investigations at higher temperatures.

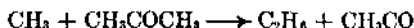
The decrease in the ratio $\text{C}_2\text{H}_6/\text{CO}$ with increasing temperature is obviously to be ascribed to the absence of diacetyl at the higher temperatures. They explain the increase with increasing light intensity as due to the occurrence of the reaction



i.e., for the mechanism they write:



They rule out the reaction



since it would impart chain characteristics to the photolysis.

Herr and Noyes⁷² have determined the ratio of ethane to carbon mon-

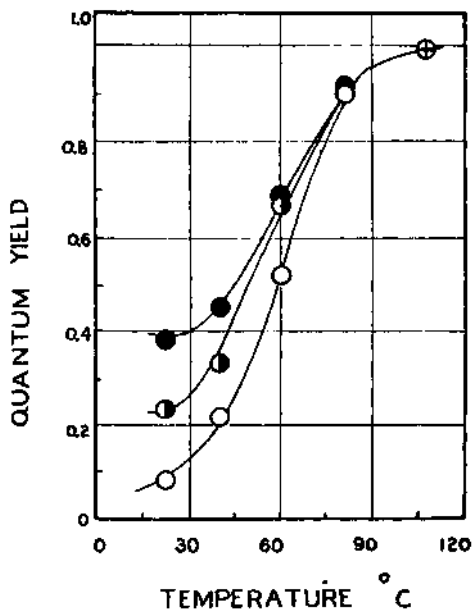
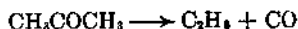


Figure 20. Quantum yields of acetone photolysis at 3130 Å and 25 mm. (Herr and Noyes).

$I_a = 10$. Symbols as in Figures 18 and 19.

oxide and the quantum yield under a wide variety of conditions at 3130 Å and 2537 Å. Up to the highest temperature at which they worked, about 110°, they conclude that methane formation is negligible, and that the entire reaction at these temperatures is to be ascribed to the overall reactions



and



They point out that in order to vary the intensity without the simultaneous variation of other variables, it is necessary to consider the absorbed not the incident intensity. Thus in dealing with the effect of pressure at constant

⁷² D. S. Herr and W. A. Noyes, *J. Am. Chem. Soc.*, 62, 2052 (1940).

intensity it is necessary at lower pressures to use a higher incident intensity in order to keep the absorbed intensity constant. In the subsequent discussion "intensity" means absorbed intensity.

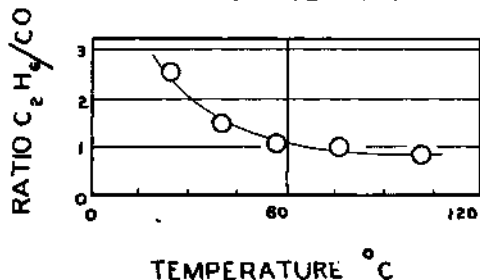
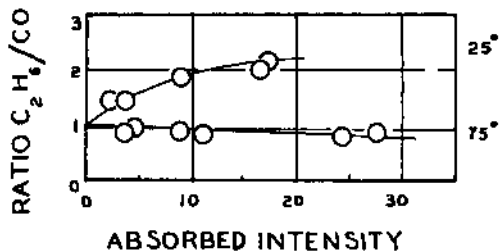
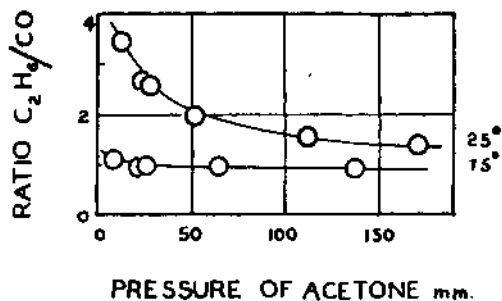


Figure 21. Ratios C_2H_6/CO for acetone photolysis (Herr and Noyes).

(above curve) 3130A, $I_a = 10$

(center) 3130A, 50 mm.

(below) 3130A, 25 mm., $I_a = 10$.

In a general way their results were:

At 5150A

The quantum yield of acetone decomposition varies from 0.1 to 0.5 at 25°, and from 0.7 to 1 at 75°.

- (a) It decreases with increasing pressure. (See Figure 18.)
- (b) It is independent of intensity at 25°, and decreases somewhat with increasing intensity at 75°. (See Figure 19.)
- (c) It increases rapidly with temperature between 30° and 90°. (See Figure 20.)

At 75° ϕ_{CO} , $\phi_{\text{C}_2\text{H}_4}$, and $\phi_{\text{decomp.}}$ are not greatly different. At 25°, however, $\phi_{\text{decomp.}}$ is greater than the others, and ϕ_{CO} less on account of diacetyl production. This is shown clearly by the values of the $\text{C}_2\text{H}_6\text{JCO}$ ratio given in Figure 21. At 75° the ratio is equal to 1 and is independent of pressure and of intensity. At 25° it decreases from 4 or so to nearly 1.5 with increasing pressure at moderate intensities, and decreases to nearly 1 at very low light intensities. Obviously, from the above, the ratio decreases to 1 as the temperature is raised, and becomes independent of other factors.

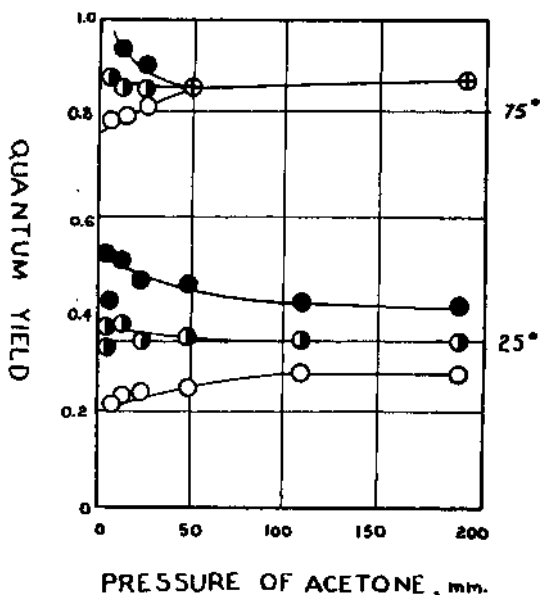


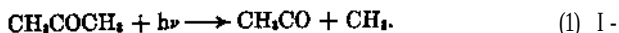
Figure 22. Quantum yields of acetone photolysis at 2537 Å (Herr and Noyes).

$I_a = 10$. Symbols as in Figures 18 and 19.

At 2537 Å

At 2537 Å the behaviour is qualitatively the same, but in general the quantum yields at low temperatures are rather higher, and the $\text{C}_2\text{H}_6\text{JCO}$ ratio lower. (See Figures 22-24.)

Herr and Noyes give a detailed discussion of the mechanism. In view of their work, and especially of that of Gorin, they conclude that the primary process at both wave lengths is



They consider that the quantum yield of the primary process (1) is probably not far from 1. They suggest as secondary processes:

(a) The decomposition of the acetyl radical



Owing to the excess energy of the products they suggest that a fraction, a , of the primarily formed acetyl radicals decompose spontaneously. This is

necessary since the quantum yield of CO formation at low temperatures increases with decreasing wave length from ca. 0.1 at 3130A to 0.25 at 2537A. It will be noted that Gorin found some CO formation even in the presence of iodine.

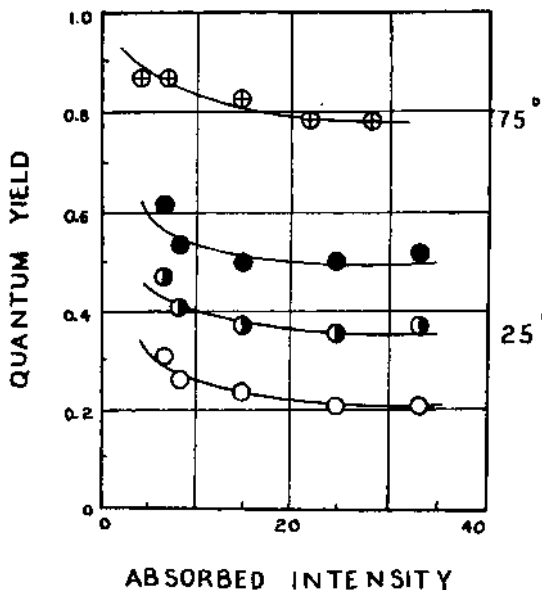


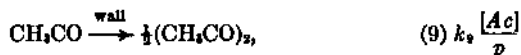
Figure 23. Quantum yields of acetone photolysis at 2537A (Herr and Noyes). Pressure = 50 mm. Symbols as in Figures 18 and 19.

(6) A first order decomposition of acetyl must also be postulated, to explain the increase in $\phi_{\text{decomp.}}$ and in ϕ_{CO} with increasing temperature,



where $[\text{Ac}]$ is the concentration of acetyl radicals. In view of the rapid rise in ϕ_{CO} with temperature, and the rapid fading out of diacetyl, E_i must be high. They conclude that E_2 is approximately 18 kcal., in agreement with Gorki's value of 17 kcal. At high temperatures (2) becomes more important than (2') and hence ϕ_{CO} varies less with wave length.

(c) They postulate diacetyl formation by diffusion of acetyl to the walls, i.e.,



where p is the total (i.e., CH_3COCH_3) pressure, f_a will be proportional to V_y . Evidence for this as a wall process is the fact that $\text{C}_2\text{H}_6\text{JCO}$ increases as the pressure is lowered at constant intensity. However, since there is some increase in $\text{C}_2\text{H}_6\text{JCO}$ with intensity at constant pressure, there must be some homogeneous recombination of acetyl also. As a first approximation they neglect this.

(d) They explain the low value of $\phi_{\text{decomp.}}$ by

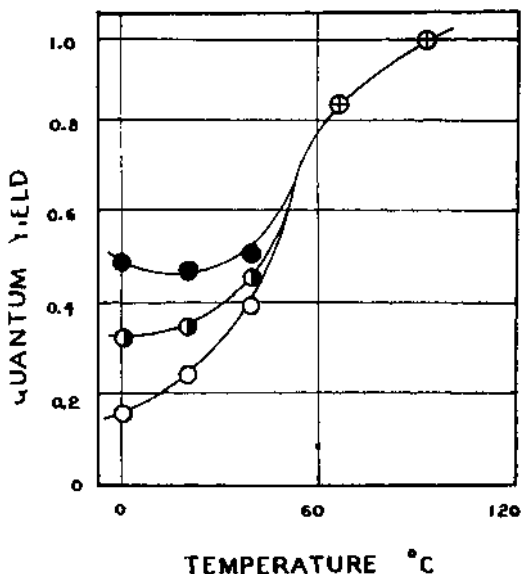


Figure 24. Quantum yields of acetone photolysis at 2537 Å (Herr and Noyes).

Pressure = 25 mm. $I_a = 10$. Symbols as in Figures 18 and 19.

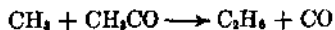
(e) Ethane production is assumed to take place mainly on the walls,



From this by the usual steady state treatment they obtain

$$\frac{\phi_{\text{CO}} - a\phi}{2(\phi_{\text{C}_2\text{H}_6} - \phi_{\text{CO}})p} = \frac{k_2}{k_9}$$

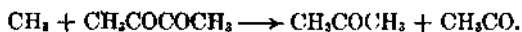
This expression is shown to be in reasonable agreement with the facts. They conclude that the reaction



suggested by Gorin is not important, since its inclusion, along with (9) and (60) would make the quantum yields and the $\text{C}_2\text{H}_6/\text{CO}$ ratios independent of intensity and pressure. However, these reactions may play some part at higher pressures where wall effects are relatively unimportant.

The main conclusion from their work is that homogeneous recombination reactions do not occur to a large extent. However, they may be more important in the case of other workers who used higher pressures and intensities, and if so this would explain some of the discrepancies encountered.

It has also been suggested⁷³ that the low quantum yield in the acetone photolysis might be ascribed to the occurrence of the reaction



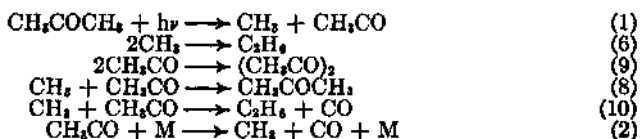
This, however, is ruled out by the work of Herr, Matheson, and Walters⁷⁴ who investigated the photodecomposition of acetone in the presence of deuterio-diacetyl. If the above reaction occurred readily, it would be expected that some of the ethane formed would be deuterized. This was not found to be the case at temperatures at which diacetyl is important in the acetone photolysis. (This work is discussed in more detail under diacetyl in section V-7.)

In a further paper Spence and Wild⁷⁶ give additional data and discuss the mechanism, particularly in the light of the conclusions of Herr and Noyes, as follows:

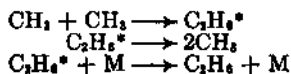
(a) *In the continuum* {2587A}

Spence and Wild's data indicate that Herr and Noyes' findings need extension. Their results agree with Herr and Noyes in that at 25° C₂H₆JCO increases with increasing intensity. As far as pressure is concerned, however, they find in agreement with Herr and Noyes that C₂H₆JCO decreases with increasing pressure *at low intensities*. At intensities higher than those used by Herr and Noyes, however, the situation is reversed and the ratio rises to values of 2.3 or so.

As the mechanism in the continuum they suggest



It will be seen that this is, in general, the same as Herr and Noyes' mechanism, so long as we do not specify the way in which (2), (6), and (9) occur. Herr and Noyes put (6) and (9) as wall reactions and assume that (2) occurs partially on account of excess energy carried over from the primary step. Spence and Wild assume that (6) occurs homogeneously by



and that (8) and (9) occur by a similar mechanism. This is, of course, merely suggesting that the reactions are bimolecular, with a low frequency factor due to three-body restrictions.

⁷³ H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, 33, 1353 (1938); H. S. Taylor and C. Rosenblum, *J. Chem. Phys.*, 6, 119 (1938).

⁷⁴ D. S. Herr, M. S. Matheson, and W. D. Walters, *J. Am. Chem. Soc.*, 63, 1464 (1941).

⁷⁵ R. Spence and W. Wild, *J. Chem. Soc.*, 1941, 590.

A steady state treatment on this basis yields results in agreement with Spence and Wild's experiments, in that it predicts that

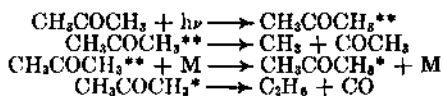
(a) ϕ decreases slowly with increasing pressure.

(6) At high intensities ϕ is independent of I_{abs} . At very low intensities it increases somewhat with increase in I_{abs} .

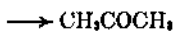
The main feature of Spence and Wild's work is thus to cast doubt on Herr and Noyes' explanation of wall recombination, and, especially at higher intensities, to substitute homogeneous recombination reactions.

(b) *In the banded region (3130A)*

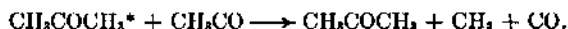
The results of Spence and Wild are here in general agreement with those of Herr and Noyes. However, they find that in "mixed" light that C_2H_6J CO value for the continuum is reduced much more than would be expected on an additive basis, and they consider that this effect can only be explained by an active molecule mechanism, such as



or



The peculiar effects in mixed light are then accounted for by



This does not seem very plausible. At higher temperatures they concede the possibility of a direct split into radicals in the banded region also.

Supplementary experiments are described by Howland and Noyes⁷⁶ in which acetone was photolysed in the presence of an inert gas (carbon dioxide). In the paper by Herr and Noyes it was concluded that the reaction



occurred on the wall. In work on diacetyl discussed below Anderson and Rollefson⁷⁷ concluded that (9) and (2),



were either both homogeneous or both heterogeneous. Howland and Noyes, on the basis of Herr and Noyes' mechanism, conclude that in the presence of a high pressure of a foreign gas we might expect:

(a) Since diffusion will be hindered, (2) will be favoured and less diacetyl and more CO will be formed, provided that all reactions of CH_3CO other than (2) are wall reactions.

⁷⁶ J. J. Howland and W. A. Noyes, *J. Am. Chem. Soc.*, 63, 3404 (1941).

⁷⁷ H. W. Anderson and G. K. Rollefson, *J. Am. Chem. Soc.*, 63, 816 (1941).

(6) Since $\text{CH}_3 + \text{CH}_3\text{CO} \rightarrow \text{CH}_3\text{COCH}_3$ is supposed to be homogeneous with a small E , it will be only slightly affected, and if anything will decrease slightly at a given concentration of radicals.

(c) Since a considerable amount of CO is produced directly in the primary process, the effect of a foreign gas on ϕ_{CO} will be small, at least at room temperature. What effect there is will be an increase.

(d) On the basis of the above the presence of a foreign gas should decrease the ratio $\text{C}_2\text{H}_6/\text{CO}$.

Howland and Noyes found that ϕ_{CO} was increased considerably at low intensities, but only slightly at high. This they conclude means that (2) is homogeneous and (9) heterogeneous, but at high intensities (9) proceeds homogeneously as well. At the intensities used by Anderson and Rollefson, which were several hundred times higher, (9) will be almost entirely homogeneous. Hence both (9) and (2) are homogeneous under their conditions. They therefore conclude that the scheme of Herr and Noyes is confirmed, *'provided that low intensities are used'*. It may be noted that this explains the discrepancies between the work of Herr and Noyes and of Spence and Wild, since the latter used much higher intensities.

Howland and Noyes^{77a} carried out some further experiments for the specific purpose of comparing the mechanism of Herr and Noyes with that of Spence and Wild. In the first place it was shown that the reaction at X3130 was similar in all essential respects to that at X2537. There thus* appears to be no reason to take seriously the excited molecule mechanism proposed by Spence and Wild. In the second place the increase in the $\text{C}_2\text{H}_6/\text{CO}$ ratio with increasing pressure at high intensities found by Spence and Wild was not confirmed. The ratio was found to rise with decreasing cell size under all conditions. They conclude that Spence and Wild's results at high intensities are complicated by effects due to the heterochromatic nature of the light used, and are thus unreliable. Howland and Noyes' results thus furnish strong confirmation of the mechanism of Herr and Noyes.

Some work on the photolysis of acetone with X2537 has also been done by Anderson and Rollefson.⁷⁷ In a general way their results agree with previous work, especially that of Herr and Noyes. The CO yield was found to rise rapidly with increasing temperature to a value of unity at temperatures above 110° . The rise was very similar to that with diacetyl and acetyl bromide, indicating definitely that the acetyl radical is responsible. Direct analyses for diacetyl showed that it fell off with increasing temperature and was absent above 115° .

The fact that the CO yield at low temperatures approaches a value of ca. 0.15 rather than zero indicates that, in agreement with Herr and Noyes,

^{77a} J. J. Howland and W. A. Noyes, *J. Am. Chem. Soc.*, 66, 974 (1944).

some of the acetyl must decompose on account of the excess energy carried over from the primary step, rather than by an ordinary unimolecular decomposition.

The fact that in the case of acetyl bromide the CO yield, while it rises with temperature, becomes asymptotic at higher temperatures to a value of much less than 1 (ca. 0.56) leads them to suggest that the acetyl radicals do not disappear by a homogeneous first order reaction, but rather by wall recombination. On this basis the limit of CO production is reached when every acetyl radical which reaches the wall decomposes. If, as in the case of acetone, no other very fast reaction is competing, then at high temperatures the CO yield will become equal to 1. Further evidence along these lines is discussed under diacetyl and acetyl bromide (*q.v.*).

The photolysis of acetone has also been investigated with light of short wave length, corresponding to the second absorption region.⁷⁸ The main feature of the reaction is a greatly increased production of hydrogen as compared with investigations at longer wave lengths. Little can be said about the mechanism, but it appears possible that it involves both radicals and excited molecules.

7. Diacetyl

It appears probable that the fluorescence of acetone is due mainly to the presence of excited diacetyl molecules.⁷⁹ On this account there have been many investigations of diacetyl fluorescence⁸⁰ and of its photolysis. It will be convenient to consider the thermal decomposition of diacetyl here as well.

Hurd and Tallyn⁸¹ showed that ketene is formed in the thermal decomposition. The kinetics of the decomposition were investigated by Rice and Walters⁸² in the range 424° to 470°. They followed the reaction by the pressure change and concluded that the main overall reaction was



together with some secondary decomposition and polymerization of ketene. The reaction was of the first order with an activation energy of 66.5 kcal. They suggested a typical Rice chain mechanism:

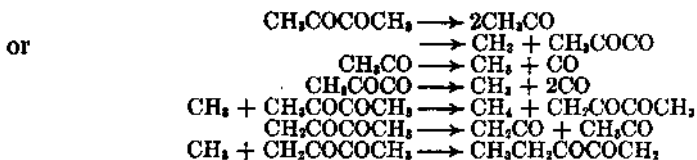
⁷⁸ W. M. Manning, *J. Am. Chem. Soc.*, 56, 2589 (1934); W. A. Noyes, A. B. F. Duncan, and W. M. Manning, *J. Chem. Phys.*, 2, 717 (1934); J. P. Howe and W. A. Noyes, *J. Am. Chem. Soc.*, 58, 1404 (1936).

⁷⁹ M. S. Matheson and W. A. Noyes, *J. Am. Chem. Soc.*, 60, 1857 (1938); W. A. Noyes and F. C. Henriques, *J. Chem. Phys.*, 7, 767 (1939).

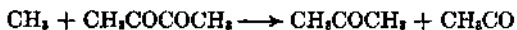
⁸⁰ H. Q. Fuller, L. W. Phillips, and G. M. Almy, *J. Chem. Phys.*, 7, 973 (1939); G. M. Almy, H. Q. Fuller, and G. D. Kinzer, *Phys. Rev.*, 56, 238 (1939); F. C. Henriques and W. A. Noyes, *J. Am. Chem. Soc.*, 62, 1038 (1940); G. M. Almy and S. Anderson, *J. Chem. Phys.*, 8, 805 (1940); R. D. Rawcliffe, *Rev. Sci. Inst.*, 13, 413 (1942); G. M. Almy and P. R. Gillette, *J. Chfm. Phys.*, 11, 188 (1943).

⁸¹ C. D. Hurd and W. H. Tallyn, *J. Am. Chem. Soc.*, 47, 1779 (1925).

⁸² F. O. Rice and W. D. Walters, *J. Chem. Phys.*, 7, 1015 (1939).



They ruled out the possible reaction



for the reasons given by Rice and Teller for many analogous cases. The reaction was further investigated by Walters⁸³ who followed it by analysis and obtained the more reliable value of 63.2 kcal. for the activation energy. The decomposition was found to be inhibited to some extent by propylene. Rice and Walters⁸⁴ found that in the neighbourhood of 500° diacetyl can induce the decomposition of a number of substances. This is further evidence for the free-radical nature of its decomposition. The decomposition is catalysed by iodine,⁸⁵ which also points to a free-radical mechanism.

Klute and Walters^{85a} found that the thermal decomposition of diacetyl at 437° is not inhibited by small amounts of nitric oxide. Large amounts caused some acceleration. It is possible that the lack of inhibition is due to the masking effect of the accompanying catalysis. This effect appears to be a general one for carbonyl compounds, since the diacetyl sensitized decompositions of acetone and acetaldehyde (III—10 and III—14) are also not inhibited by nitric oxide.

Early experiments on the photolysis⁸⁶ indicated that ethane and carbon monoxide were the main products. Anderson and Rollefson⁸⁷ investigated the photolysis with X2537, and found a small amount of methane as a product in addition to ethane and carbon monoxide. The $\text{CO}/\text{C}_2\text{H}_6$ ratio was always greater than 2, and condensable products must therefore have been formed as well. The quantum yield, ϕ_{CO} rose from about 0.34 at room temperature to 0.85 at 120°, and then remained constant up to 140°, the highest temperature investigated.

In the presence of a large excess of nitric oxide the carbon monoxide yield fell off to about one-tenth of its normal value, and no hydrocarbons were formed. This proves the free-radical nature of the photolysis. Since carbon monoxide formation is not entirely eliminated by nitric oxide, while hydrocarbon formation is, they suggest that the acetyl radical reacts less readily with nitric oxide than does methyl. It should be noted, however, that if a

⁸⁸ W. D. Walters, *J. Am. Chem. Soc.*, 62, 880 (1940).

⁸⁴ F. O. Rice and W. D. Walters, *J. Am. Chem. Soc.*, 63, 1701 (1941).

⁸⁸ G. M. Gantz and W. D. Walters, *J. Am. Chem. Soc.*, 63, 3412 (1941).

^{85a} C. H. Klute and W. D. Walters, *J. Am. Chem. Soc.*, 67, 550 (1945).

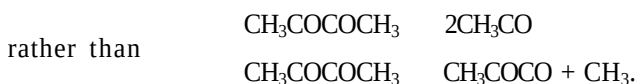
⁸⁶ C. W. Porter, H. C. Ramsperger, and C. Steel, *J. Am. Chem. Soc.*, 45, 1827 (1923);

R. G. W. Norrish and F. W. Kirkbride, *Trans. Faraday Soc.*, 27, 404 (1931).

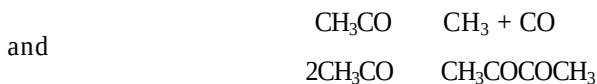
⁸⁷ H. W. Anderson and G. K. Rollefson, *J. Am. Chem. Soc.*, 63, 816 (1941).

fraction of the acetyl radicals decompose immediately on account of excess energy carried over from the primary step, then some carbon monoxide would be formed even in the presence of nitric oxide.

Since the decrease in ϕ_{CO} with temperature is very similar for acetone, diacetyl and acetyl bromide, they conclude that the primary step is

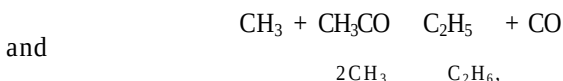


In some of their experiments an excess of nitrogen was added, but this produced no appreciable effect, and they conclude, therefore, that



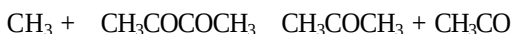
must both occur homogeneously, or both heterogeneously. However, the nitrogen pressure employed was only of the order of 25 mm., and the data are few, so that this conclusion does not rest on very convincing evidence, although it is in every way plausible.

The photolysis was also investigated by Roof and Blacet,⁸⁸ who found ϕ_{CO} for several wave lengths from 2380A to 3660A to be less than unity at room temperature, and to rise rapidly with increasing temperature to about 9 at 262°. ϕ_{CO} also increased somewhat with decreasing wave length and decreased with increasing intensity. At higher temperatures the products were very similar to those of the thermal decomposition, and there thus appears to be the same chain process, no matter how it is initiated. They accept Rice and Walters' mechanism with the addition of the reactions

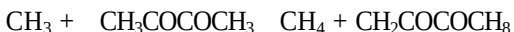


to account for ethane formation.

Herr, Matheson, and Walters⁸⁹ have investigated the photolysis of acetone-deutero-diacetyl mixtures. (See V-6.) As pointed out previously, they conclude that the reaction



is not of importance at low temperatures. They suggest that



is a more probable reaction, and that it has an activation energy of about 13 kcal.

⁸⁸ J. G. Roof and F. E. Blacet, *J. Am. Chem. Soc.*, 63, 1126 (1941).

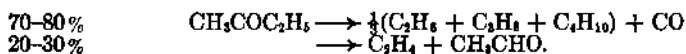
⁸⁹ D. S. Herr, M. S. Matheson, and W. D. Walters, *J. Am. Chem. Soc.* 63, 1464 (1941).

8. Methyl Ethyl Ketone

On the basis of mirror experiments there is no doubt that free radicals are produced in the photolysis of methyl ethyl ketone.⁹⁰ With the same apparatus and illumination 80 per cent as many radicals were obtained as from acetone. Glazebrook and Pearson suggest that this indicates less free radicals in the primary step, but since no correction was made for possible differences in light absorption, the evidence is rather flimsy.

Further evidence that the primary process involves radicals is furnished by the work of Barak and Style⁹¹ who found diacetyl in the products of the photolysis at room temperature, thus suggesting a mechanism analogous to that for acetone.

The photolysis was investigated at temperatures slightly above room temperature by Norrish and Appleyard,⁹² who found that the overall process could be represented by



This is evidence for radical production since otherwise only propane and carbon monoxide would be expected. A peculiar feature of their results was the fact that ethane, propane, and butane were formed approximately in the ratio 1:1:1, contrary to what would be expected from probability considerations. The result, however, is not reliable since it was obtained by simple bulb-to-bulb distillation of the mixture of hydrocarbons, followed by combustion. (See later.)

Ells and Noyes⁹³ showed that diketones are formed in the photolysis with wave lengths around 3130A, so that acetyl and probably propionyl are formed in the low temperature photolysis. At higher temperatures some methane was formed in addition to ethane, propane, and butane. The quantum yield rose only slightly with increasing temperature indicating the absence of chain processes as with acetone. (See Table XLII.)

TABLE XLII. PHOTOLYSIS OF METHYL ETHYL KETONE (ELLS AND NOYES)

Pressure, mm.	Temperature	ϕ_{CO}	$\frac{\text{CO}}{\text{CH}_4}$	ϕ_{CH_4}
43	105-110	0.79	4.2	0.19
4.8	160-165	0.79	4.0	0.20
45	160-165	0.85	2.2	0.38
43	195-200	0.71	1.5	0.47

Diketones were also formed at short wave lengths (1850A to 2000A). The quantum yield in this region was about 1 at low pressures and decreased as the pressure was raised.

⁹⁰ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1937**, 567.

⁹¹ M. Barak and D. W. G. Style, *Nature*, **135**, 307 (1935).

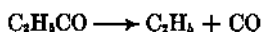
⁹² R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, **1934**, 874.

⁹³ V. R. Ells and W. A. Noyes, *J. Am. Chem. Soc.*, **60**, 2031 (1938).

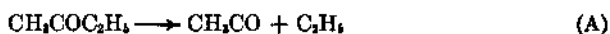
In a later paper they found⁹⁴ the quantum yield of CO formation at 3130Å to be about 0.1 for acetone and methyl ethyl ketone, and about 0.7 for diethyl ketone. Since the low CO yield for acetone is mainly due to the formation of diacetyl predominating over the reaction



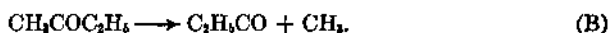
this points to



occurring more readily than the decomposition of acetyl. This is reasonable, since the higher radical would be expected to be less stable. The low value of ϕ_{CO} for methyl ethyl ketone thus points to the primary step being mainly



rather than



At short wave lengths, however, the excess energy is high enough so that small differences in bond strengths are unimportant and they conclude that (A) and (B) become almost equally probable. At these wave lengths it is also probable that energy carried over from the primary step causes a considerable fraction of both acetyl and propionyl radicals to decompose spontaneously.

Gorin⁹⁵ has investigated the photolysis of methyl ethyl ketone in the presence of iodine at 70°. The investigation was much less thorough than that with acetone, but the results show that the quantum yield of alkyl iodide formation is close to unity, pointing to an exclusively free radical primary process. His results did not distinguish between methyl and ethyl iodides.

Moore and Taylor⁹⁶ reinvestigated the photolysis at temperatures from 90° to 200° for the principal purpose of checking the ratio of ethane, propane, and butane in the products. At low temperatures diketones were identified, but not at high. The products of the reaction were those given in Table XLIII.

TABLE XLIII. PRODUCTS OF THE METHYL ETHYL KETONE PHOTOLYSIS
(MOORE AND TAYLOR)

	90°	110°	155°	200°
H ₂	0.4	0.1	0.3	0.0
CO	47.5	49.0	47.0	48.5
CH ₄	3.4	4.4	9.0	18.0
C ₂ H ₆	2.2	0.5	1.7	3.0
C ₃ H ₈	11.5	13.0	14.5	12.5
C ₄ H ₁₀	19.1	20.0	18.6	11.0
C ₄ H ₈	13.2	13.0	9.0	7.0
C ₄ H ₆	1.5	—	0.0	—

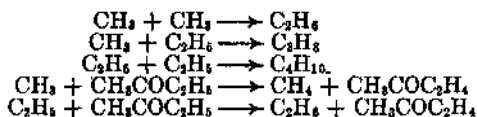
⁹⁴ V. R. Ells and W. A. Noyes, *J. Am. Chem. Soc.*, 61, 2492 (1939).

⁹⁵ E. Gorin, *Acta Physicochimica* (U.R.S.S.), 8, 513 (1938); *J. Chem. Phys.*, 7, 256 (1939).

⁹⁶ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 466 (1940).

It is evident that methane formation rises decidedly with increasing temperature, and that the ethane-propane-butane ratio is at low temperatures, approximately the 1:2:1 ratio demanded by probability (or, taking the collision frequency into account the theoretical ratio becomes 1:1.74:0.83) rather than 1:1:1 as found by Norrish and Appleyard. It may also be noted that while propane and butane fall off decidedly at high temperatures, ethane does not.

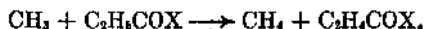
Neglecting the acetyl and propionyl radicals, which will be unimportant at higher temperatures, they give as the main secondary reactions



The hydrocarbons are thus accounted for. They point out that methane is more readily produced than in the case of acetone, and suggest that



occurs less readily than



Also, since more ethylene survives in the photolysis of diethyl ketone than here, they conclude that methyl radicals sensitize the ethylene polymerization more efficiently than ethyl. This is contrary to the conclusions of Danby and Hinshelwood.⁹⁷ (See IV-2.)

9. Diethyl Ketone

The ethyl radical has been detected in the photolysis of diethyl ketone by the Paneth method by Pearson and Purcell,⁹⁸ who used arsenic mirrors, and identified triethyl arsine dimercurichloride.

The main part of the fluorescence of diethyl ketone, excited by light in the near ultra violet, is the same as that of propionaldehyde⁹⁹ and the propionyl radical is thus undoubtedly involved. The photolysis has been investigated by Ells and Noyes.⁹⁴ With wave lengths from 1850 to 2000Å the gaseous products at room temperature were carbon monoxide, butane, and smaller amounts of ethane and ethylene. ϕ_{CO} was about 1, and is thus higher than is the case with acetone and methyl ethyl ketone. This effect is even more pronounced with $\lambda 3000$. Thus at 36 mm. pressure, the values of ϕ_{CO} were

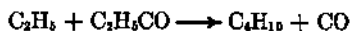
CH_3COCH_3	0.095
$\text{CH}_3\text{COC}_2\text{H}_5$	0.12
$\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$	1.04

⁹⁷ C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A179**, 169 (1941).

⁹⁸ T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, **1935**, 1151.

⁹⁹ M. S. Matheson and J. W. Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

This must indicate that $\text{C}_2\text{H}_5\text{CO}$ is much less stable than CH_3CO , or else that some reaction such as



has a very low activation energy. The former alternative seems much more plausible.

Danby and Hinshelwood⁹⁷ found that the polymerization of ethylene at 300° could be photosensitized by diethyl ketone. This furnishes further evidence for the formation of free radicals in the photolysis. The results also indicated that no chain decomposition of the ketone occurred.

10. Higher Ketones

Methyl Propyl Ketone

Glazebrook and Pearson¹⁰⁰ have detected radicals by the Paneth technique in the photolysis of methyl propyl ketone. By comparing rates of mirror removal with the same light source they conclude that only 62 per cent as many radicals are produced as from acetone, and they therefore suggest that part of the primary process does not involve free radicals. As pointed out previously, this conclusion is open to considerable doubt since the effect may be due merely to differences in light absorption.

Methyl Butyl Ketone

Radicals have been detected in the photolysis at room temperature,¹⁰⁰ but under comparable conditions only about 28 per cent as many radicals are produced as with acetone. This may be due merely to decreased light absorption, but Norrish's results, described below, seem to indicate that the effect is real.

Norrish and Appleyard¹⁰¹ found that the major part of the photolysis could be represented by the overall equation



and they therefore concluded that this part of the reaction does not involve radicals. However, the analyses are rather indefinite, and methane, ethane, and hydrogen are also formed.

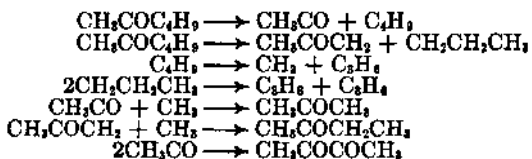
In later papers Noyes and his collaborators¹⁰² made a somewhat more detailed investigation of the photolysis, and found as products ethane, propylene, acetone, methyl ethyl ketone, and diacetyl. The carbon monoxide production was very small and increased slightly with temperature. It thus seems unlikely that the straight split into CH_3CO and C_4H_9 or $\text{C}_4\text{H}_5\text{CO}$

¹⁰⁰ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1937**, 567.

¹⁰¹ R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, **1934**, 874; B. M. Bloch and R. G. W. Norrish, *J. Chem. Soc.*, **1935**, 1638.

¹⁰² W. Davis and W. A. Noyes, *J. Am. Chem. Soc.*, **64**, 2676 (1942); J. E. Wilson and W. A. Noyes, *J. Am. Chem. Soc.*, **65**, 1547 (1943).

and CH_3 can be of importance. The quantum yields of the main products were found to be almost independent of temperature, wave-length, pressure, and intensity, and this suggests, a non-free-radical mechanism. However, a mechanism such as the following could account for the results:



as they point out, however, this is completely speculative.

Dipropyl Ketone

Pearson and Purcell¹⁰³ detected the n-propyl radical in the photolysis of di-n-propyl ketone by its action on arsenic, antimony, tellurium, and lead mirrors, and by conversion to propyl mercuric bromide. In a later paper¹⁰⁴ they report a similar investigation of di-iso-propyl ketone. The result was the identification of n-propyl mercuric bromide rather than the iso-propyl compound. It follows that either the iso-propyl radical isomerized spontaneously, or else the isomerization occurred during the process of forming compounds for identification. The latter alternative appears to be the more likely one.

The photolysis of di-n-propyl ketone has been investigated by Bamford and Norrish,¹⁰⁵ who found that about 37 per cent decomposed via radicals, and 63 per cent underwent a "type I I" reaction, forming methyl propyl ketone and ethylene, followed by secondary reactions.

Dibutyl Ketone

In the course of another investigation Glazebrook and Pearson¹⁰⁶ made a few experiments with di-tert-butyl ketone. The results were indefinite but radicals were detected, which may have been tert-butyl.

Cyclic Ketones

Bamford and Norrish¹⁰⁷ have investigated the photolysis of a number of cyclic ketones: Cyclo-hexanone, suberone, 2-, 3-, and 4-methyl cyclo-hexanones, and menthone. It appears likely that at least a part of each of these photolyses proceeds by a mechanism which involves biradicals.

¹⁰³ T. G. Pearson and R. H. Purcell, *Nature*, **136**, 221 (1935), *J. Chem. Soc.*, **1936**, 253.

¹⁰⁴ T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, **1936**, 1777.

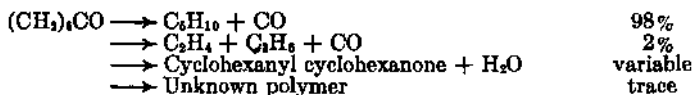
¹⁰⁶ C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 1504, **1938**, 1544.

¹⁰⁶ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1937**, 567.

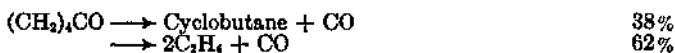
¹⁰⁷ C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, **1938**, 1521; O. D. Saltmarsh and R. G. W. Norrish, *J. Chem. Soc.*, **1935**, 455.

Benson and Kistiakowsky¹⁰⁸ have criticized Norrish's work on the ground that the substances were refluxed through the irradiated zone, and that part of the reaction thus occurred in the liquid draining back rather than in the vapor phase. They reinvestigated the problem using cyclohexanone, cyclopentanone, and cyclobutanone. The overall reactions were:

Cyclohexanone



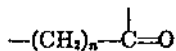
Cyclopentanone



Cyclobutanone



They suggest that the primary process is, in every case, a split to a biradical



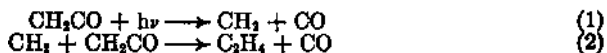
This may then (a) reform the original ketone, (b) react with another ketone molecule to give a condensation product, or (c) split further.

Acetophenone and Benzophenone

The photolyses of these substances have been investigated by Glazebrook and Pearson.¹⁰⁹ The products from acetophenone removed tellurium mirrors and diphenyl-, dimethyl-, and phenyl methyl-tellurides were identified. Benzophenone also removed tellurium mirrors, and although the products were not unequivocally identified, it is likely that the radicals were again phenyl and methyl. The transitory formation of the benzoyl radical, $\text{C}_6\text{H}_5\text{CO}$, and the phenacyl radical, $\text{C}_6\text{H}_5\text{COCH}_2$, is indicated.

11. Ketene

The photolysis of ketene was investigated by Norrish, Crone, and Saltmarsh,¹¹⁰ who concluded from the band spectrum that absorption was by the carbonyl group. The products were! quantitatively carbon monoxide and ethylene. They suggested the mechanism



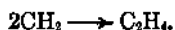
¹⁰⁸ S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 64, 80 (1942).

¹⁰⁹ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, 1939, 589.

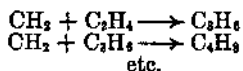
¹¹⁰ R. G. W. Norrish, H. G. Crone, and O. D. Saltmarsh, *J. Chem. Soc.*, 1933, 1533.

The reaction was re-investigated by Ross and Kistiakowsky,¹¹¹ who confirmed the fact that the gaseous products were exclusively carbon monoxide and ethylene, but found that a solid polymer was formed as well. The quantum yield was approximately unity for A3130, and considerably smaller, 0.2 to 0.4 for $\lambda 3660$.

There appears to be no doubt that the primary step is that postulated by Norrish, Crone, and Saltmarsh. This involves the breaking of a C = C bond, and since the energy available is only 80 kcal. or so, the CO formed in the reaction must be the "molecule" rather than the "radical" $>\text{CO}$, or else methylene is formed as the molecule CH_2 . Since the quantum yield is unity or less, however, reaction (2) cannot be the main secondary reaction, and it appears that the main reaction must be



The solid polymer has the composition $(\text{CH}_2)_n$, and must be formed by



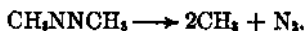
Pearson, Purcell, and Saigh¹¹² investigated the thermal and photochemical decomposition of ketene and of diazomethane using the mirror removal method. Methylene radicals were detected, and their rate of decay was investigated by means of standard mirrors. With ketene in an 11 mm. tube at a pressure of 0.15 mm. they found no appreciable decay in travelling 81 cm., corresponding to a time of 0.05 sec. On the other hand, if the radicals were prepared from diazomethane only about 1 per cent of the molecules decomposed contributed to mirror removal. It thus appears that although methylene reacts readily with diazomethane it has a very long life in the presence of ketene. Reaction (2) thus appears to be ruled out.

Burton, Davis, Gordon, and Taylor¹¹³ investigated the photolysis in the presence of excess ethylene and of nitric oxide. Methylene reacted readily with ethylene. Nitric oxide, however, had no appreciable effect on the reaction possibly because of the instability of the complex CH_2NO .

The photolysis in the presence of hydrogen has been investigated by Rosenblum.¹¹⁴ The results are discussed in section VI-20.

12. Azomethane

As discussed in section III—17, it appears to be well established that in the *thermal* decomposition of azomethane the primary step is



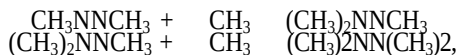
¹¹¹ W. F. Ross and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 1112 (1934).

¹¹² T. G. Pearson, R. H. Purcell, and G. S. Saigh, *J. Chem. Soc.*, **1938**, 409.

¹¹³ M. Burton, T. W. Davis, A. Gordon, and H. A. Taylor, *J. Am. Chem. Soc.*, **63**, 1956 (1941).

¹¹⁴ C. Rosenblum, *J. Am. Chem. Soc.*, **60**, 2819 (1938), **63**, 3322 (1941).

The reaction does not, however, appear to be a chain process. The main steps following the primary process are probably



followed by secondary reactions leading to the formation of nitrogen, ethane, and other hydrocarbons.

The photolysis of azomethane was first investigated by Ramsperger,¹¹⁵ who found that it has a strong absorption region between 4000 and 2800Å, with a maximum at about 3400Å. The photolysis was investigated with light in the range 3650 to 3663Å, and the reaction was followed by the pressure change, assuming complete decomposition to correspond to 2.04 times the initial pressure. On this basis the quantum yield had values of 1.91 to 2.22 at pressures from 25.7 to 0.12 cm. It thus appears that reaction chains are not involved. Ramsperger explained the quantum yield of about 2 on the basis of an excited molecule mechanism, but the work was done before free radical ideas had come into prominence.

Forbes, Heidt, and Sickman¹¹⁶ reinvestigated the reaction. The rate was again derived from pressure measurements, but their optical technique was superior to that of Ramsperger. A range of wave lengths from 3660 to 2080Å was used. At room temperature the quantum yield decreased as the reaction progressed, approached unity at low pressures and diminished at high, and was a maximum in the region from 3660 to 3350Å. The yield was independent of temperature from 20° to 226°.

In view of the discrepancy between the quantum yield values of Ramsperger and those of Forbes, Heidt, and Sickman, Kuchler¹¹⁷ reinvestigated the reaction. It was followed by measuring the evolved nitrogen, and only very small percentage decompositions were used (less than 1 per cent). His results were: (a) at 3130Å the quantum yield is approximately 2, independent of pressure, or of temperature up to 200°, (b) at 2535Å, the yield is less than 1 at room temperature, (c) in the presence of hydrogen at 3130Å, the yield is 2 at 20° and rises to about 6 at 225° for a 3:1 hydrogen-azomethane mixture.

Since 2535Å is on the edge of the second absorption region where absorption by the C—N bond is coming into play, while at longer wave lengths absorption is by the —N=N— bond, Kuchler suggests different primary processes at the two wave lengths, viz., an excited molecule mechanism at long wave lengths and a split into radicals at short wave lengths. This is, however, purely speculative.

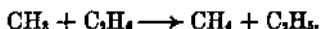
More recent investigations indicate that the quantum yield at longer

¹¹⁵ H. C. Ramsperger, *J. Am. Chem. Soc.*, 50, 123 (1928).

¹¹⁶ G. S. Forbes, L. J. Heidt, and D. V. Sickman, *J. Am. Chem. Soc.*, 57, 1935 (1935).

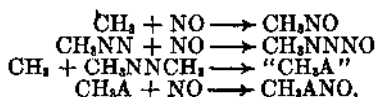
¹¹⁷ L. Kuchler, *Nach. Ges. Wiss. Göttingen III*, 1, 215 (1937).

ture on the photolysis,¹²³ using temperatures up to 257°. At higher temperatures ethane formation decreased strongly and methane became the main hydrocarbon product. This may be explained by the occurrence at higher temperatures of the reaction



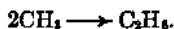
If this is the case, the comparatively small formation of propane and higher hydrocarbons must mean that most ethyl radicals disappear by reactions other than recombination, probably by association reactions with azomethane.

The effect of nitric oxide on the photolysis was investigated by Davis, Jahn, and Burton.¹²⁴ In the reaction at low temperatures in the presence of nitric oxide a pressure decrease occurred instead of the normal pressure increase. There was, however, no inhibition of the formation of nitrogen. The primary step thus appears to be predominantly a split into radicals, and in the presence of nitric oxide the radicals must form addition compounds, such as



where CH₃A is an addition product of methyl and azomethane, and is thus itself a free radical.

At higher temperatures there was a slight pressure increase, perhaps due to the decomposition of the polymers which are formed at lower temperatures. They rule out the reaction



in the normal photolysis on the following grounds: The work of Burton, Davis, and Taylor indicates that one out of every five methyl radicals formed in the normal photolysis disappears permanently by an association reaction with azomethane, which we may designate by



The other four radicals ultimately appear as ethane. They conclude that the ethane cannot be formed by a simple recombination of methyls, since in the nitric oxide inhibited reaction no ethane is formed but (1) still occurs readily in spite of the fact that the competing reaction



must be fast. Hence



¹²³ M. Burton, T. W. Davis, and H. A. Taylor, *J. Am. Chem. Soc.*, 59, 1989 (1937).

¹²⁴ T. W. Davis, F. P. Jahn, and M. Burton, *J. Am. Chem. Soc.*, 60, 10 (1938).

must be slow compared with (1), so that ethane must arise by some secondary reaction of the product CH₃A. The argument is weakened somewhat by the fact that the occurrence of (1) is inferred solely on the basis of material balances, and these are notoriously unreliable*

Blacet and Tauiog,¹¹⁹ who obtained results in excellent agreement with those of Burton, Davis, and Taylor, suggest that the results could be explained by a mechanism such as



Hence the nitric oxide results do not absolutely rule out the occurrence of a reaction leading directly to ethane in the normal photolysis, although they certainly favor such a conclusion.

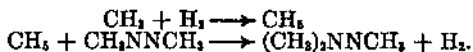
Blacet and Taurog also investigated the photolysis of acetaldehyde-azomethane mixtures, and found that acetaldehyde decomposed by a sensitized reaction, presumably initiated by methyl radicals from the photolysis of azomethane. However, the dissociation of acetaldehyde was inappreciable unless the acetaldehyde-azomethane ratio was greater than 10. This shows that methyl radicals also react very readily with azomethane and thus supports the conclusions of Davis, Jahn, and Burton.

Taylor and Flowers¹²⁵ investigated the photolysis of azomethane in the presence of hydrogen at temperatures from 20° to 200°. The ethane yield was found to be independent of the presence of hydrogen. At low temperatures hydrogen diminished the methane production considerably, but not at higher temperatures. These facts cannot be explained on a simple mechanism where both methane and ethane come from reactions of methyl. It thus seems highly probable that the reaction



occurs, and accounts for part of the methyls in the normal photolysis.

Taylor and Flowers suggest that in the presence of hydrogen the association reaction occurs by¹²⁶

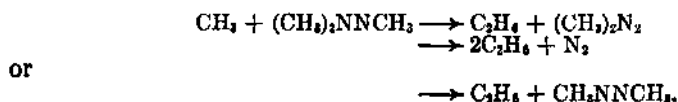


This removes any third-body restrictions which might apply to the simple association. In other words they are suggesting that in virtue of a very "sticky" collision between methyl and hydrogen, hydrogen will be a highly efficient third body for the association. (The weak point of this argument is that it would not be expected that third-body restrictions would be serious in the case of the formation of such a complex molecule.) The additional loss of methyl in this way when hydrogen is present will explain the facts

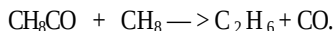
¹²⁵ H. A. Taylor and R. G. Flowers, *J. Chem. Phys.*, 10, 110 (1942).

¹²⁶ E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, 7, 633(1939).

provided that ethane arises by secondary reactions and not by the recombination of methyls. They suggest that ethane arises by a semi-Walden inversion of the $(\text{CH}_3)_2\text{NNCH}_3$ radical with a methyl, viz.,



This is analogous to the reaction which has been postulated in the acetone photolysis



As further evidence for their mechanism they cite the fact that no dimethyl hydrazine was found as a product. Henkin and Taylor¹²⁷ had found this to be a main product of the reaction of hydrogen atoms with azomethane by the discharge tube method. They therefore conclude that no hydrogen atoms are present and that the reaction



cannot be the source of the methane. It should be pointed out, however, that under the drastic conditions of the discharge tube method products may be formed which differ entirely from those formed in photolytic systems where the hydrogen atom concentration is very low.¹²⁸

13. Metal Alkyls

The photolysis of the metal alkyls appears in every case to involve splitting off alkyl radicals in the primary step. As a result they have been much used as a source of free radicals in sensitization experiments. (See II-4.)

The photolysis of mercury dimethyl was investigated by Terenin and his co-workers,¹²⁹ who found that the absorption spectrum showed a continuum below 2800A, together with diffuse bands in the region from 2100 to 1970A. They showed by the Paneth technique that free radicals were formed in the photolysis, the maximum yield of radicals occurring at about 2100A. In the photolysis of lead tetramethyl Leighton and Mortensen¹³⁰ similarly detected the methyl radical.

A more detailed investigation of the photolysis of mercury dimethyl was made by Linnett and Thompson,¹³¹ who used X2537 and found that ethane

¹²⁷ H. Henkin and H. A. Taylor, *J. Chem. Phys.*, 8, 1 (1940).

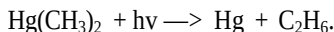
¹²⁸ See, for example, E. W. R. Steacie and N. A. D. Parlee, *Can. J. Research*, B17, 371 (1939); E. W. R. Steacie and D. J. Dewar, *J. Chem. Phys.*, 8, 571 (1940).

¹²⁹ A. Terenin, *J. Chem. Phys.*, 2, 441 (1934); *Acta Physicochimica* (U.R.S.S.), 1, 762 (1935); A. Terenin and N. Prileshajeva, *Tram. Faraday Soc.*, 31, 1483 (1935).

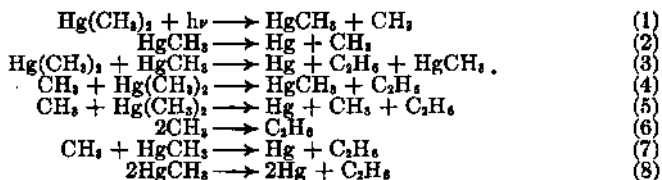
¹³⁰ P. A. Leighton and R. A. Mortensen, *J. Am. Chem. Soc.*, 58, 448 (1936).

¹³¹ H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, 33, 501 (1937).

was almost the sole product at room temperature. On this basis they suggested that the primary step was



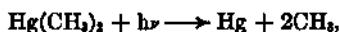
In a later paper¹³² they investigated the effect of temperature and of the presence of nitric oxide on the reaction. The results showed that the quantum yield increased at higher temperatures above the value of unity obtained at room temperature. The results in the presence of nitric oxide were complex, but favored the idea of a free radical mechanism. They suggested



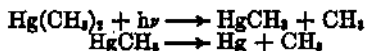
This explains the results provided that it is assumed that the activation energies of reactions (3), (4), and (5) are high. They will thus have no effect at room temperature and the quantum yield of unity will be due to the sequence (1), (2), (6), or to (1), (6), (7), (8). At higher temperatures the occurrence of (3), (4), and (5) will give the reaction chain characteristics and cause the quantum yield to rise. They estimate an activation energy of 10.7 kcal. for the chain carrying step. This probably corresponds to that of reaction (4) or (5).

Since Leighton and Mortensen found higher quantum yields for the photolysis of lead tetramethyl than were found here, Linnett and Thompson suggest that the activation energy of the reaction of methyl radicals with lead tetramethyl is lower than 10 kcal.

Cunningham and Taylor¹³³ investigated the photolysis in more detail, with special emphasis on the effect of hydrogen on the reaction. Their work in the presence of hydrogen is discussed in detail in section VI-27, and in the absence of hydrogen in section VI-28. Their results in the absence of hydrogen agree in general with those of Linnett and Thompson, the only important product at lower temperatures being ethane. At higher temperatures more and more methane is formed as well. As the primary step they accept



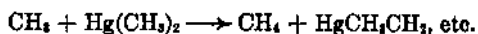
or



¹³² H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, 33, 874 (1937).

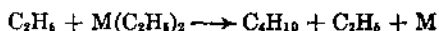
¹³³ J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.*, 6, 359 (1938).

At lower temperatures ethane formation is ascribed to reaction (6) in Linnett and Thompson's scheme, and at higher temperatures to (5). The production of methane in the absence of hydrogen must be due to



The photolysis of mercury and of zinc diethyl has been investigated by Moore and Taylor.¹³⁴ The bearing of this work on the recombination of ethyl radicals is discussed in section VI-53. The products at lower temperatures were ethylene and ethane in roughly equal amounts, and hydrogen and butene also in equivalent amounts, together with considerable butane. At higher temperatures ethane increased relative to ethylene and hydrogen was no longer a product.

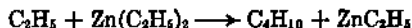
They account for the increased quantum yield at higher temperatures by a chain mechanism similar to that for mercury dimethyl, viz.,



or



In the case of zinc diethyl the proportion of butane is less at lower temperatures than is the case with mercury diethyl, but it increases to about the same amount at higher temperatures. This may be due to a higher activation energy for the reaction



on account of the greater strength of the Zn—C bond.

14. Alkyl Iodides

The photolysis of a considerable number of alkyl iodides has been investigated. We will discuss here only methyl and ethyl iodides, and leave the discussion of other iodides for the sections dealing with specific elementary reactions.

Methyl Iodide

For a discussion of early literature on the photolysis of methyl iodide see Emschwiller.¹³⁵

The organic iodides all show maximum continuous absorption in the region around 2500 to 2600Å, and there is no doubt that the primary process in all cases is¹³⁶



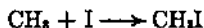
¹³⁴ J. W. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 396 (1940).

¹³⁵ G. Emschwiller, *Ann. Chim.*, 17, 413 (1932).

¹³⁶ G. Herzberg and G. Scheibe, *Z. physik. Chem.*, B7, 390 (1930); G. Emschwiller, *Compt. Rend.*, 191, 208 (1930); T. Iredale and W. N. W. Wallace, *Phil. Mag.*, 8, 1093 (1929).

Further support for such a primary process comes from numerous observations that the polymerization of ethylene and other reactions can be photosensitized by methyl and other iodides, undoubtedly through the agency of the radicals formed in the photolysis.¹³⁷

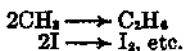
Bates and Spence¹³⁸ investigated the photolysis of methyl iodide, using the full radiation from a mercury arc. The reaction was very slow, being about 0.02, and they conclude that the small quantum yield is due to the re-formation of methyl iodide by one or both of the reactions



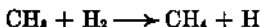
and



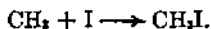
The final products thus result only from secondary reactions such as



Hydrogen had no effect on the rate, so that the reaction



must be slower than



West and Paul¹³⁹ studied the photolysis in hexane solution. At 2610Å ϕ was about 0.05, and at 3130Å about 0.008. The temperature coefficient of the reaction was practically unity, and the rate was independent of the concentration of the alkyl halide. Since the reaction was of zero order in the early stages they point out that the reaction



cannot be of much importance compared with



However the presence of a solvent might influence the situation in favor of the latter reaction.

West and Paul also investigated a number of other iodides. If, as seems reasonable, the quantum yield is largely determined by the efficiency of the back reaction



then the relative efficiencies of recombination of alkyl radicals with iodine atoms are, in the order of decreasing efficiency: methyl, allyl, vinyl, ethyl, propyl, isopropyl.

West¹⁴⁰ decomposed methyl iodide in the presence of para-hydrogen and

¹³⁷ See, e.g., J. C. Jungers and L. M. Yeddanapalli, *Trans. Faraday Soc.*, 36, 483 (1940), and other references in II—3 and 4.

¹³⁸ J. R. Bates and R. Spence, *J. Am. Chem. Soc.*, 53, 1689 (1931); *Trans. Faraday Soc.*, 27, 468 (1931).

¹³⁹ W. West and B. Paul, *Trans. Faraday Soc.*, 28, 688 (1932).

¹⁴⁰ W. West, *J. Am. Chem. Soc.*, 57, 1931 (1935).

found considerable conversion to the ortho modification. This indicates the presence either of radicals or of H-atoms produced by the reaction

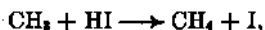


Further work on the photolysis was done by Spence and Wild¹⁴² using the full radiation from a mercury arc. The products consisted mainly of methane, with some ethane, and an amount of iodine much less than that to be expected from the quantities of hydrocarbons formed. This deficiency of iodine is undoubtedly due to the formation of methylene iodide, etc. The large formation of methane is not easy to account for, but may arise from the reaction



They confirmed the previous observations that the products were virtually unchanged by the addition of hydrogen and that the quantum yield was low (0.06).

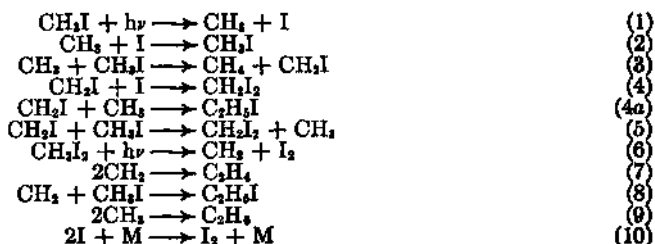
In the case of CH_3I — HI mixtures¹⁴³ containing more than 40 per cent of HI the quantum yield rose to 2. This points to the ready occurrence of the reaction



which prevents the re-formation of methyl iodide.

The gas phase reaction was investigated by West and Schlessinger¹⁴⁴ with special emphasis on the products. At 25° using X2537 and a pressure of methyl iodide vapor of 300 mm., the gaseous products were 80-90 per cent methane with small amounts of ethane and ethylene. About one-third of the iodide decomposed appeared as CH_2I_2 . In the presence of silver foil the rate was about 40 times greater than normal, all the iodine appeared as AgI , and the gaseous products were approximately 55 per cent C_2H_6 , 18 per cent C_2H_4 , and 28 per cent CH_4 .

They suggest the mechanism



The fact that (2) predominates over (3) in spite of the high concentration of methyl iodide must mean that while E_2 is approximately zero, E_z is of the

¹⁴¹ See F. Patat, *Z. physik. Chem.*, 32, 274 (1936).

¹⁴² R. Spence and W. Wild, *Proc. Leeds Phil. Soc.*, 3, 141 (1936).

¹⁴³ T. Iredale and D. Stephan, *Trans. Faraday Soc.*, 33, 800 (1937).

¹⁴⁴ W. West and L. Schlessinger, *J. Am. Chem. Soc.*, 60, 961 (1938).

order of 10 kcal. This is supported by analogy with ethyl iodide. It will also be noted that the considerable production of ethane requires that the association reactions (2) and (9)"should proceed readily. In this connection Bawn¹⁴⁶ has concluded on theoretical grounds that virtually every collision between CH₃ and I will be effective, while only 1 collision in 10⁴ or so will result in the formation of ethane from two methyls.

Iredale¹⁴⁶ investigated the photolysis in the presence of nitric oxide. The nitric oxide was found to accelerate the reaction by a factor of as much as 12. This is obviously caused by the removal of radicals by nitric oxide and the consequent prevention of the back reaction. He suggests a mechanism similar to that of West given above, except that he considers the reaction

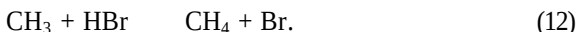


to be of importance.

Andersen and Kistiakowsky¹⁴⁷ have made certain experiments for the purpose of determining which of the reactions



was responsible for the low quantum yield in the methyl iodide photolysis. In the photolysis of CH₃I in the presence of HBr and iodine (see X-35) the methyl radicals formed in the primary step will disappear mainly by (2), (11), and



The total rate of disappearance of methyl radicals will then be

$$R = k_{12}[\text{HBr}][\text{CH}_3] + k_2[\text{CH}_3][\text{I}] + k_{11}[\text{CH}_3][\text{I}_2],$$

and the fraction appears

$$\frac{k_{12}[\text{HBr}]}{k_{12}[\text{HBr}] + k_2[\text{I}] + k_{11}[\text{I}_2]}.$$

The absolute rate of methane formation will be the above fraction multiplied by I^n , where I is the light intensity and n is a constant.

If reaction (2) is the main methyl iodide re-forming reaction, the ratio R/I^n will depend on $[\text{I}]$ and hence on the light intensity. Actually, however, a variation of a factor of 20 in the light intensity produced no appreciable change in R/I^n , and they therefore conclude that (11) is the only important reaction which leads to the re-formation of methyl iodide. This does not necessarily mean that (2) is not important in the absence of large amounts of added iodine, i.e., in the normal photolysis of methyl iodide alone.

¹⁴⁸ C. E. H. Bawn, *Trans. Faraday Soc.*, 31, 1536 (1935).

¹⁴⁶ T. Iredale, *Trans. Faraday Soc.*, 35, 458 (1939).

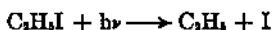
¹⁴⁷ H. G. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, 11, 6 (1943).

Ethyl Iodide

The photolysis of ethyl iodide has been frequently investigated¹⁴⁸ in the gas phase, the liquid, and in solution. In hexane solution West and Paul¹⁴⁹ found quantum yields of about 0.58 at 2610Å and **0.30 at 3130Å**. These values are somewhat high since they used monochloroacetic acid as an actinometer and assumed a quantum yield of unity for its decomposition. The quantum yield was independent of temperature over the narrow range investigated of 25° to 35°. It was independent of the ethyl iodide concentration, and for small amounts of iodine was independent of it as well. They assume a mechanism similar to that given above for methyl iodide.

For liquid ethyl iodide Norton¹⁵⁰ found quantum yield values of **0.31** at 3130Å, 0.38 at 2654Å, and 0.41 at 2537Å.

The photolysis of gaseous ethyl iodide was investigated by West and Ginsburg.¹⁵¹ At 2600Å the yield was virtually nil, at 2026Å about 0.1, and at 1962Å about 0.78. In the continuum (2600Å) there is no doubt that the primary process is



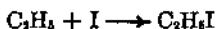
and that the very low yield is due to the efficiency of the back reaction or the reaction



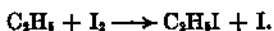
Hence other possible secondary reactions such as



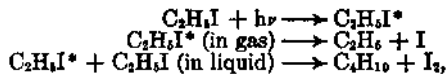
must be slow compared with



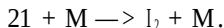
and



The relatively high yield in solution or in the liquid state might be due to an excited molecule mechanism, such as



or merely to the liquid or solvent providing efficient third bodies for the reaction¹⁵²



The latter seems the more probable alternative.

¹⁴⁸ For early work see K. A. Burke and F. G. Donnan, *J. Chem. Soc.*, **85**, 574 (1904); G. Emschwiller, *Compt. Rend.*, **190**, 741 (1930), **179**, 52 (1924); T. Iredale, *J. Phys. Chem.*, **33**, 290 (1929).

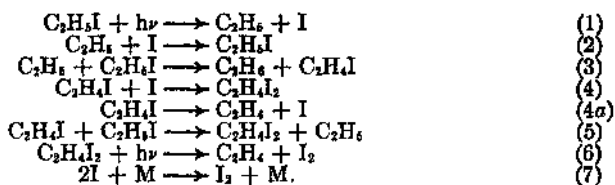
¹⁴⁹ W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

¹⁵⁰ B. M. Norton, *J. Am. Chem. Soc.*, **56**, 2294 (1934).

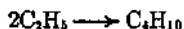
¹⁵¹ W. West and E. Ginsburg, *J. Am. Chem. Soc.*, **66**, 2626 (1934).

¹⁵² W. West and J. Fitelson, *J. Am. Chem. Soc.*, **62**, 3021 (1940).

A more thorough investigation of the photolysis of gaseous ethyl iodide, including analyses of the products was made by West and Schlessinger.¹⁵³ At 25° and 100 mm, pressure-with $\lambda 2537$ the products consisted of a small amount of methane together with approximately 50 per cent ethylene and 50 per cent ethane. At 2026A (in the banded region) under the same circumstances the products were about the same, except that a trace of hydrogen was formed as well. In the presence of a silver surface the products were not appreciably altered, but the rate was increased by a large factor. By analogy with the scheme proposed for the methyl iodide decomposition they suggest the mechanism

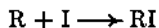


No butane was detectable, i.e., the reaction



does not occur to an appreciable extent in competition with (2) and (3). Even in the presence of silver no butane was formed. The predominant secondary reactions are (3), (4), and (6).

They point out that the fact that butane is formed in the case of other reactions involving the presence of ethyl, and similarly in other cases ethane is formed from methyls, while in the case of the iodides they are not formed, is evidence that the reactions



are very rapid, and the stationary radical concentrations in the photolysis of iodides are thus extremely low.

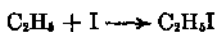
In view of the fact that the quantum yield is much greater in the liquid phase, apparently because of collisions with the solvent, they tried the effect of high pressures of foreign gases on the quantum yield. Large increases were obtained: thus 40 atm. of carbon dioxide raised the yield to about 1.7 that in hexane solution under the same conditions. They suggest that the main effect of a solvent or a foreign gas is to increase the rate of (7), and thus prevent the back reaction (2).

In the banded region (2026A) the situation is generally similar. The bands are underlaid by a continuum, and it is possible that a free radical split occurs here also. However, the very great increase in the quantum yield argues against this and it is probable that the mechanism in the banded region involves excited molecules.

¹⁵³ W. West and L. Schlessinger, *J. Am. Chem. Soc.*, 60, 961 (1938).

Joris and Jungers¹⁵⁴ investigated the polymerization of ethylene photosensitized by ethyl iodide. The results permit certain conclusions to be drawn concerning the photolysis of ethyl iodide itself. They found a very small quantum yield for the photolysis, in agreement with previous work. The yield was greatly increased by the presence of mercury, the action obviously being similar to that of silver. The fact that the polymerization of ethylene was sensitized is further evidence for the production of ethyl radicals in the photolysis of ethyl iodide.

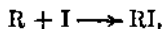
No sensitization of the ethylene polymerization occurred in the absence of mercury. This shows that the reaction



is much faster than



Jungers and Yeddanapalli¹⁵⁵ investigated the sensitization of the ethylene polymerization by a series of alkyl iodides. An increase in the effectiveness of photosensitization was found in the order methyl, ethyl, n-propyl, iso-propyl iodide. This is presumably due to a decrease in the same order in the efficiency of the reaction

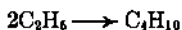


probably on steric grounds.

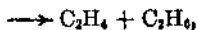
They conclude that in the ethyl iodide decomposition radicals disappear both by



and by recombination



or



the former predominating at low and the latter at high radical concentrations.

15. Photohalogenations

A very large number of photohalogenations have been investigated. These reactions are all similar in that in every case light is absorbed by the halogen molecule, which is split into atoms in the primary process. The secondary reactions which follow are the result of reactions of atomic chlorine, bromine, or iodine. The subject has been frequently reviewed,¹⁸⁶

¹⁵⁴ G. G. Joris and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 47, 135 (1938).

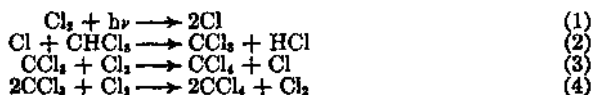
¹⁵⁵ J. C. Jungers and L. M. Yeddanapalli, *Trans. Faraday Soc.*, 36, 483 (1940).

¹⁵⁶ W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases*, New York, 1941; G. K. Rollefson and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions*, New York, 1939; H. J. Schumacher, *Z. angew. Chem.*, 49, 613 (1936), 60, 483 (1937), 63, 501 (1940); *Z. Elektrochem.*, 42, 522 (1936); *Trans. Electrochem. Soc.*, 71, 409 (1937); *Atti X^o Congr. Intern. Chim.*, 4, 464 (1939).

and in the treatment below we will follow the classification used by Schumacher.

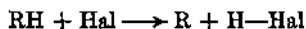
(a) *The Change of a C—H to a C—Hal Bond*

An example of this type of reaction is the photochlorination of chloroform, which has a chain length of over 100. The mechanism appears to be



The main points to be noted are that the mechanism involves chlorine atoms and that the radical CCl_3 arises from a reaction of atomic chlorine which has a very small activation energy. CCl_3 and Cl are the chain carriers, and it is evident that the mechanism is the analogue of the Nernst chain mechanism for the hydrogen-chlorine reaction. This same general mechanism appears to hold for all the chlorine substituted methanes, and for many other reactions.

Reaction (2) is an important step in the mechanism, and Schumacher¹⁵⁷ points out that its equivalent



is exothermic in the case of chlorine, while with bromine it is slightly endothermic, and with iodine it is strongly so. The activation energies are therefore considerably higher with bromine and iodine, in general the activation energy being 5-10 kcal. higher in the case of bromine, and about 30 kcal. in the case of iodine. The chlorine reaction is thus very much faster.

Conversely, the reverse of the above reaction is slightly endothermic with chlorine, but is strongly exothermic with bromine and iodine. It is thus much more important in the latter cases.

Schumacher concludes that reactions in solution will in general occur by the same mechanism, except that recombination and chain ending processes may be favored because of:

(a) The Franck-Rabinowitsch principle¹⁶⁸ according to which the products of a dissociation are unable to separate sufficiently because of surrounding molecules of solvent, and hence recombine.

(6) Third body processes will be favored since the solvent furnishes a more or less continual third body.

As a result reactions in solution are often slower. Examples are the chlorination of chloroform in carbon tetrachloride solution,¹⁵⁹ and the bromination of dichlor ethylene.¹⁶⁰ On the other hand the chlorination of

¹⁵⁷ H. J. Schumacher, *Angew. Chem.*, 63, 501 (1940).

¹⁵⁸ J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, 30, 120 (1934).

¹⁵⁹ G. M. Schwab and U. Heyde, *Z. physik. Chem.*, B8, 147 (1930).

¹⁶⁰ J. C. Ghosh and S. K. Bhattacharyya, *Z. physik. Chem.*, B52, 145 (1936).

tetrachlor ethylene proceeds with the same speed in the liquid and gaseous phases.¹⁶¹

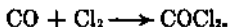
A large number of reactions with mechanisms of this type have been investigated. Examples are: the chlorination of methane,¹⁶² chloroform,¹⁶³ pentachlorethane,¹⁶⁴ pentane,¹⁶⁵ heptane,^{166a} and benzene,¹⁶⁶ the bromination of chloroform,¹⁶⁷ benzene,¹⁶⁸ cyclohexane,¹⁶⁹ methane,¹⁷⁰ and ethane.¹⁷⁰ The reactions are discussed in detail in the sections dealing with the specific part reactions.

$$\begin{array}{c} \text{Hal} \quad \text{Hal} \\ | \quad | \\ \text{C} - \text{C} \end{array}$$

(6) *The Change of a C=C to a C—C Bond*

The general mechanism of the addition of halogens to a double bond is similar to that of the phosgene synthesis. This has been much investigated, and we will merely summarize the present status of the problem.

The overall reaction in the phosgene synthesis is



At room temperature and at reasonably high pressures the rate law is¹⁷¹

$$\frac{d}{dt} [\text{COCl}_2] = k I_{\text{abs.}} \frac{1}{2} [\text{CO}] \frac{1}{2} [\text{Cl}_2].$$

At high temperatures, around 300°, the rate law changes to¹⁷²

$$\frac{d}{dt} [\text{COCl}_2] = k I_{\text{abs.}} \frac{1}{2} [\text{CO}] [\text{Cl}_2].$$

At room temperature and low pressures the high temperature rate law also holds.¹⁷³

¹⁶¹ R. G. Dickinson and J. A. Leermakers, *J. Am. Chem. Soc.*, **54**, 3852 (1932); J. A. Leermakers and R. G. Dickinson, *J. Am. Chem. Soc.*, **54**, 4648 (1932).

¹⁶² L. T. Jones and J. R. Bates, *J. Am. Chem. Soc.*, **56**, 2282 (1934); A. Coehn and H. Cordes, *Z. physik. Chem.*, **B9**, 1 (1930); M. Tamura, *Rev. Phys. Chem., Japan*, **16**, 86 (1941).

¹⁶³ G. M. Schwab and U. Heyde, *Z. physik. Chem.*, **B8**, 147 (1930); D. G. Hill, *J. Am. Chem. Soc.*, **54**, 32 (1932); H. J. Schumacher and K. Wolff, *Z. physik. Chem.* **B25**, 161 (1934).

¹⁶⁴ H. J. Schumacher and W. Thurauf, *Z. physik. Chem.*, **A189**, 183 (1941).

¹⁶⁵ T. D. Stewart and B. Weidenbaum, *J. Am. Chem. Soc.*, **57**, 1702 (1935).

^{166a} J. Stauff and H. J. Schumacher, *Z. Elektrochem.*, **48**, 271 (1942).

¹⁶⁶ C. E. Lane and W. A. Noyes, *J. Am. Chem. Soc.*, **64**, 161 (1932); W. A. Noyes and E. J. Hart, *J. Am. Chem. Soc.*, **55**, 4444 (1933).

¹⁶⁷ J. Willard and F. Daniels, *J. Am. Chem. Soc.*, **57**, 2240 (1935); V. Braunwarth and H. J. Schumacher, *Kolloid-Z.*, **89**, 184 (1939).

¹⁶⁸ W. Meidinger, *Z. physik. Chem.*, **B5**, 29 (1929); E. Rabinowitsch, *Z. physik. Chem.*, **B19**, 190 (1932).

¹⁶⁹ W. Jost, *Z. physik. Chem. Bodenstein-Festband*, 291 (1931).

¹⁷⁰ H. G. Andersen, G. B. Kistiakowsky, and E. R. Van Artsdalen, *J. Chem. Phys.*, **10**, 305 (1942).

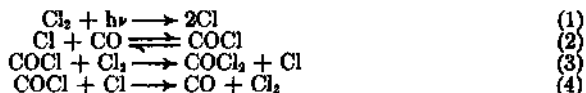
¹⁷¹ M. Bodenstein, *Z. physik. Chem.*, **130**, 422 (1927).

¹⁷² M. Bodenstein and T. Onoda, *Z. physik. Chem.*, **181**, 153 (1927).

¹⁷³ H. J. Schumacher and G. Stieger, *Z. physik. Chem.*, **B13**, 157 (1931).

Two main mechanisms have been proposed to account for these results:

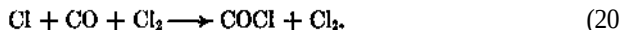
I. Bodenstein, Lenher, and Wagner¹⁷⁴



This agrees with the experimental rate expression, provided it is assumed that the equilibrium in (2) is maintained, *i.e.*, that (3) is slow compared with the reverse of (2).

II. Lenher and Rollefson¹⁷⁵

This is the same as the above, except that in place of (2) we have



In other words chlorine is assumed to be a specific third body for the association reaction

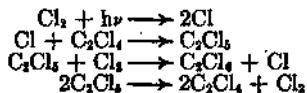


It will be seen that this is not very different from the assumption of Cl_3 as an intermediate in photohalogenations, as is consistently done by Rollefson and his school. In view of the arguments against Cl_3 (see below) and the fact that it is now generally considered unnecessary to postulate it (see, for example, footnote 176), it may be considered that mechanism I is rather definitely established.

Recent papers from Bodenstein's laboratory have given estimates of the activation energies of the part reactions,¹⁷⁷ viz., $E_3 = 2.6$ kcal., $E_4 = 1.94$ kcal., and $E = 23.0$ kcal. for the reverse of (3), *i.e.*,



Analogous to this we have in the case of tetrachlor ethylene, for example,



It seems to be possible to explain the photochlorination of almost all unsaturated compounds on such a basis.

The data for photobrominations and photoiodinations are much more scanty. It appears possible, however, to explain the facts on the basis of

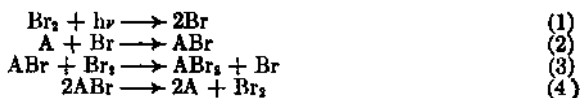
¹⁷⁴ M. Bodenstein, S. Lenher, and C. Wagner, *Z. physik. Chem.*, B3, 459 (1929).

¹⁷⁶ S. Lenher and G. K. Rollefson, *J. Am. Chem. Soc.*, 62, 500 (1930).

¹⁷⁷ W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases*, New York, 1941, p. 279.

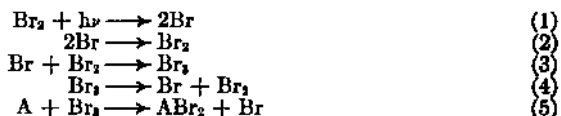
¹⁷⁷ M. Bodenstein, W. Brenschede, and H. J. Schumacher, *Z. physik. Chem.*, B40, 121 (1938).

mechanisms of the same type. Thus, for example, Berthoud and his collaborators¹⁷⁸ have investigated the photobromination in solution of a number of unsaturated organic acids. The mechanism given by them is consistent with the above scheme, i.e.,



where A represents the acid.

Ghosh¹⁷⁹ has criticized this scheme on the ground that reaction (2) will not occur readily since it is an association. However, it seems very unlikely that three body restrictions will be of importance for such complex molecules, and in solution where the solvent molecules act as a sort of continuous third body at all times. Ghosh¹⁸⁰ considers that the mechanism is



This also will lead to a rate expression in agreement with experiment.

Similar mechanisms involving Cl_3 and Br_3 have been frequently postulated in other cases.¹⁸¹ Schumacher discusses the question of the postulation of Cl_3 and Br_3 in considerable detail. He concludes that the facts can be readily explained without such an assumption.¹⁸² The mechanism has also been discussed by Daniels.¹⁸³ He concludes that it is not possible to reach a definite decision between the Br atom and Br_3 theories, although he favors the former. However, the main difficulty is that the rate of photobromination of acids appears to be proportional to I_{abs} , rather than to $I_{\text{abs}}^{1/2}$, as predicted by the mechanism. Later work, however, in which precautions were taken to exclude oxygen¹⁸⁴ gave results which are in every way compatible with the standard atom-chain mechanism.

¹⁷⁸ A. Berthoud and J. Beraneck, *Helv. Chim. Acta*, 10, 289 (1927); A. Berthoud, *ibid.*, 13, 385 (1930); A. Berthoud and D. Porret, *ibid.*, 17, 1548 (1934); A. Berthoud and J. Beraneck, *J. Chim. Physique*, 24, 213 (1927); A. Berthoud and G. Nicolet, *ibid.*, 26, 40 (1928); *Helv. Chim. Acta*, 10, 417 (1927), etc.

¹⁷⁹ J. C. Ghosh, *Z. physik. Chem.*, B9, 154 (1930); J. C. Ghosh and R. Purkayastha, *J. Indian Chem. Soc.*, 2, 261 (1926), 4, 409 (1927).

¹⁸⁰ J. C. Ghosh and R. Purkayastha, *Z. physik. Chem.*, B9, 154 (1930), B32, 145 (1936).

¹⁸¹ G. K. Rollefson and H. Eyring, *J. Am. Chem. Soc.*, 64, 170 (1932); G. K. Rollefson, *J. Am. Chem. Soc.*, 66, 579 (1934); A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, 66, 2014 (1934).

¹⁸² M. Bodenstein, W. Brenschede, and H. J. Schumacher, *Z. physik. Chem.*, B28, 81 (1935).

¹⁸³ F. Daniels, *Chemical Kinetics*, Ithaca, 1938, p. 157.

¹⁸⁴ R. F. Brown and F. Daniels, *J. Am. Chem. Soc.*, 62, 2820 (1940); J. L. Magee and F. Daniels, *J. Am. Chem. Soc.*, 62, 2825 (1940).

Sherman and Sun¹⁸⁶ have used the transition state method to calculate the activation energies of a number of reactions which are pertinent to the above discussion. With the usual assumptions, and assuming the following bond strengths C—I = 44.0 kcal., C—Br = 58.0 kcal., C—Cl = 78.6 kcal., they obtained the results listed below:

	Activation energy
$\text{C}_2\text{H}_4 + \text{I}_2 \longrightarrow \text{C}_2\text{H}_4\text{I}_2$	22.4 kcal.
$\text{C}_2\text{H}_4 + \text{I}_2 \longrightarrow \text{C}_2\text{H}_3\text{I}_2 + \text{I}$	29.7
$\text{C}_2\text{H}_4 + \text{Br}_2 \longrightarrow \text{C}_2\text{H}_4\text{Br}_2$	24.4
$\text{C}_2\text{H}_4 + \text{Br}_2 \longrightarrow \text{C}_2\text{H}_3\text{Br}_2 + \text{Br}$	35.6
$\text{C}_2\text{H}_4 + \text{Cl}_2 \longrightarrow \text{C}_2\text{H}_4\text{Cl}_2$	25.2
$\text{C}_2\text{H}_4 + \text{Cl}_2 \longrightarrow \text{C}_2\text{H}_3\text{Cl}_2 + \text{Cl}$	48.2

As a result they conclude that the Br_3 and Cl_3 type of mechanism is ruled out, since the direct addition of CU and Br_2 to a double bond is faster than the reaction involving Cl_3 or Br_3 . This is, of course, speculative and it is difficult to know how much reliance can be placed in this type of calculation. On the whole, however, the evidence seems strongly in favor of the atom mechanism, and the postulation of Cl_3 or Br_3 appears to be unnecessary.

Examples of reactions which appear to proceed by a mechanism of this type are the chlorination of ethylene,¹⁸⁶ dichlorethylene,¹⁸⁷ trichlorethylene,¹⁸⁷ and tetrachlorethylene,¹⁸⁸ the bromination of ethylene,¹⁸⁹ dichlorethylene,¹⁹⁰ and tetrachlorethylene.¹⁹¹ These are discussed fully in later chapters.

Hal Hal

(c) The Change of a $\text{C}\equiv\text{C}$ to a $\text{C}=\text{C}$ Bond

The bromination of acetylene¹⁹² is the only reaction of this type which has been investigated in any detail. The mechanism appears to be similar to those of reactions involving $\text{C}=\text{C}$ bonds.

¹⁸⁵ A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, **56**, 1096 (1934).

¹⁸⁶ T. D. Stewart and M. H. Hanson, *J. Am. Chem. Soc.*, **63**, 1121 (1931); T. D. Stewart and B. Weidenbaum, *J. Am. Chem. Soc.*, **67**, 2036 (1935); H. Schmitz, H. J. Schumacher, and A. Jager, *Z. physik. Chem.*, **B61**, 281 (1942).

¹⁸⁷ K. L. Muller and H. J. Schumacher, *Z. physik. Chem.*, **B36**, 285, 455 (1937); *Z. Elektrochem.*, **43**, 807 (1937).

¹⁸⁸ J. A. Leermakers and R. G. Dickinson, *J. Am. Chem. Soc.*, **54**, 4648 (1932); R. G. Dickinson and J. L. Carrico, *J. Am. Chem. Soc.*, **56**, 1473 (1934).

¹⁸⁹ H. Schmitz, H. J. Schumacher, and A. Jager, *Z. physik. Chem.*, **B51**, 281 (1942).

¹⁹⁰ J. C. Ghosh and S. K. Bhattacharyya, *Z. physik. Chem.*, **B32**, 140 (1936); K. L. Muller and H. J. Schumacher, *Z. physik. Chem.*, **B42**, 327 (1939).

¹⁹¹ J. Willard and F. Daniels, *J. Am. Chem. Soc.*, **57**, 2240 (1935); R. G. Dickinson and J. L. Carrico, *J. Am. Chem. Soc.*, **56**, 1473 (1934).

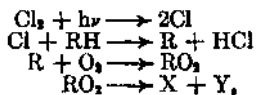
¹⁹² J. E. Booher and G. K. Roilefson, *J. Am. Chem. Soc.*, **66**, 2288 (1934); W. K. Franke and H. J. Schumacher, *Z. physik. Chem.*, **B34**, 181 (1936); G. K. Roilefson, *Z. physik. Chem.*, **B57**, 472 (1937); K. L. Muller and H. J. Schumacher, *Z. physik. Chem.*, **B39**, 352 (1938), **B40**, 318 (1938).

(d) *The Substitution of One Halogen for Another*

A number of reactions of this type have been investigated. The mechanisms are similar to those of the type discussed in (a).

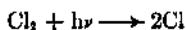
16. Halogen Sensitized Photooxidations

The photohalogenation reactions discussed above are all inhibited by small amounts of oxygen. If, however, enough oxygen is present, the reaction changes its nature and becomes a halogen sensitized oxidation, without any consumption of halogen.¹⁹³ Thus from chloroform, chlorine, and oxygen the product is phosgene,¹⁹⁴ from dichloromethane, chlorine, and oxygen the product is CO, which is then further oxidized to CO₂,¹⁹⁶ and from CCl₄, chlorine, and oxygen trichloroacetyl chloride¹⁹⁶ is formed. In all cases the rate is independent of the oxygen concentration, and the quantum yields are high (300 to 500). The mechanisms all appear to be of the same type, viz.,

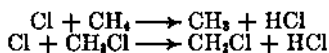


where X continues the chain.

As an example we may consider the chlorine sensitized oxidation of methane, methyl chloride, and methylene chloride, which have been investigated by Brenschede and Schumacher.¹⁹⁵ In all three cases the main products were HCl and CO, together with small amounts of phosgene, water, etc. The quantum yield increased from about 80 for methane to 800 for CH₂Cl₂. The mechanism is uncertain. The primary step is certainly



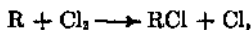
in all cases. This is undoubtedly followed by



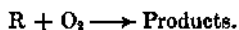
or



followed by the chlorination of the products by reactions of the type



and reactions with oxygen



¹⁹³ See H. J. Schumacher, *Z. Elektrochem.*, **42**, 522 (1936).

¹⁹⁴ H. J. Schumacher and K. Wolff, *Z. physik. Chem.*, **B26**, 453 (1934); A. T. Chapman, *J. Am. Chem. Soc.*, **57**, 416 (1935).

¹⁹⁵ W. Brenschede and H. J. Schumacher, *Z. physik. Chem.*, **A177**, 245 (1936).

¹⁹⁶ R. G. Dickinson and J. L. Carrico, *J. Am. Chem. Soc.*, **56**, 1453 (1934).

Other examples are the chlorine sensitized oxidation of chloroform,¹⁹⁷ trichlor brom methane,¹⁹⁸ trichlor ethylene,¹⁹⁹ and chloral,²⁰⁰ and the bromine sensitized oxidation of carbon tetrabromide,²⁰¹ trichlor brom methane,¹⁹⁸ and chloral.²⁰²

¹⁹⁷ H. J. Schumacher and K. Wolff, *Z. physik. Chem.*, **B26**, 453 (1934).

¹⁹⁸ W. K. Franke and H. J. Schumacher, *Z. physik. Chem.*, **B42**, 297 (1939).

¹⁹⁹ K. L. Muller and H. J. Schumacher, *Z. physik. Chem.*, **B37**, 365 (1937).

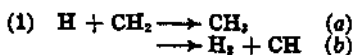
²⁰⁰ W. A. Alexander and H. J. Schumacher, *Z. physik. Chem.*, **B44**, 313 (1939).

²⁰¹ W. Koblitz, H. Meissner, and H. J. Schumacher, *Ber.*, 70, 1080 (1937).

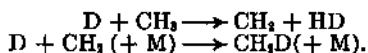
²⁰² J. Stauff and H. J. Schumacher, *Z. physik. Chan.*, **B48**, 154 (1941).

Chapter VI

Systems Containing Carbon and Hydrogen Only

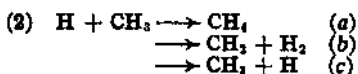


Reaction (1a) has been postulated as a rapid step in the exchange of methyl radicals and atomic deuterium viz.,

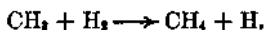


(See VI-2 for further details.)

Since Bonhoeffer and Harteck² found that CH bands were emitted when H-atoms and many hydrocarbons were brought together, it seems probable that (1b) occurs to some extent.

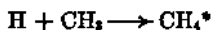


Reaction (2a) is very frequently assumed in free radical mechanisms. It is, of course, strongly exothermic, and probably has a very small activation energy. It is very difficult to assess its importance in $\text{H}-\text{H}_2-\text{CH}_3$ systems compared with the reaction



In view of the simplicity of the methane molecule it seems probable that three-body restrictions play some part, and that the recombination will only occur readily at the wall or in the presence of a third body.

Kimball³ has calculated the mean lives of the complexes formed in association reactions from vibration frequencies. He concludes that the complex



has a mean life of 3.2×10^{-12} sec. This would indicate that (2a) would in general occur only at a triple collision.

Rice⁴ assumes an activation energy of 8 kcal. for reaction (2a), and all other radical recombinations, in order to obtain agreement between his

¹ N. R. Trenner, K. Morikawa, and H. 8. Taylor, *J. Chem. Phys.*, 5, 203 (1937)
E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, 7, 633 (1939).

² K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, 139, 64 (1928).

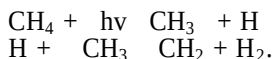
³ G. E. Kimball, *J. Chem. Phys.*, 6, 310 (1937).

⁴ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

free radical mechanisms and experiment; it seems certain, however, that this value is much too high.

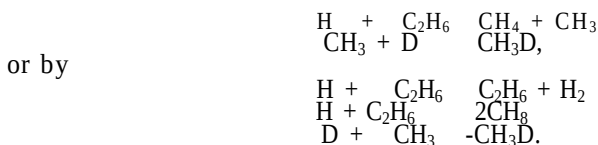
There is no real information regarding the occurrence of (26). It has, however, been suggested¹ as a possible mechanism for the exchange of methyl radicals, as pointed out in section VI-1.

Its occurrence has also been suggested by Groth and Laudenklos⁵ as a secondary reaction in the photodecomposition of methane, viz.,

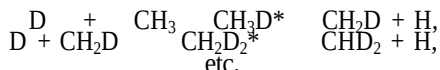


Their whole mechanism is, however, open to question.

In an investigation of the reaction of atomic deuterium with ethane Trenner, Morikawa, and Taylor¹ found that the methane in the products was very highly exchanged (up to 63 per cent). This is much more than can be accounted for on the basis of



They therefore suggested that deuterium atoms and methyl radicals must interact according to (2c),



On the basis of their results either reaction (26) or reaction (2c) has an activation energy equal to or less than 5 kcal.⁶

Similar results were obtained by Steacie, Alexander, and Phillips⁷ in an investigation of the reaction of hydrogen atoms, produced by mercury photosensitization, with ethane. The same reaction was postulated by Steacie and Parlee⁸ to explain the high deuterization of the methane produced in the reaction of deuterium atoms with propane.

Gorin, Kauzmann, Walter, and Eyring,¹ however, object to this mechanism on the grounds that reaction (2c) is improbable since the deuterium atom approaches along an axis of symmetry and hence when the energy is redistributed the three other hydrogen atoms must move out symmetrically, and the energy could not become concentrated in a single C—H bond. They therefore prefer the mechanism involving reaction (26).

⁵ W. Groth and H. Laudenklos, *Naturwiss.*, **24**, 796 (1936).

⁶ K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Chem. Phys.*, **5**, 212 (1937).

⁷ E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research*, **B16**, 314 (1938).

⁸ E. W. R. Steacie and N. A. D. Parlee, *Can. J. Research*, **B17**, 371 (1939).



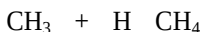
The reactions of various hydrocarbons with hydrogen atoms were investigated by the discharge-tube method by Bonhoeffer and Harteck.² They point out that from an energetic standpoint both C—H and C—C bonds can be broken in the reaction of a hydrocarbon with hydrogen atoms, and there are thus three possibilities, hydrogenation, dehydrogenation, and splitting of the hydrocarbon chain.

Methane was found to be surprisingly inert in the presence of atomic hydrogen^{2,9} and no reaction could be detected at room temperature, although the reaction



might have been expected. These results were confirmed by v. Wartenberg and Schultze,¹⁰ who also found that no appreciable heat was developed on mixing H-atoms with methane (apart from the normal amount produced by recombination of the atoms). Further confirmation of the inertness of methane was furnished by the work of Chadwell and Titani.¹¹

Geib and Harteck¹² investigated the process over a range of temperatures and showed that no reaction occurred up to 183°. They therefore concluded that reaction (3a) had an activation energy of at least 17 kcal. It might be suggested that the reaction really occurs readily, but that



proceeds more rapidly than other possible reactions of the methyl radical such as



so that methane is reformed as fast as it is consumed. Geib and Harteck ruled out such a suggestion on the grounds that (a) it is exceedingly unlikely that no other secondary reactions of the methyl radical should occur, and (b) the presence of methane causes no appreciable alteration in the hydrogen atom concentration, whereas the above mechanism would involve the consumption of hydrogen atoms by both steps.

The second objection could be overcome, however, by assuming the secondary reaction to be



and thus regenerating the hydrogen atom lost in the primary step. The rate of reaction (1) is discussed in detail in section VI-27, and it appears that this explanation is not valid. In any case, however, as will be seen from the following discussion, the investigation of the reaction of deuterium

⁹ E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

¹⁰ H. v. Wartenberg and G. Schultze, *Z. physik. Chem.*, B2, 1 (1929).

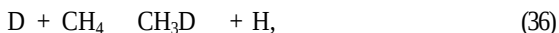
¹¹ H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, 55, 1363 (1933).

¹² K. H. Geib and P. Harteck, *Z. physik. Chem.*, **A170**, 1 (1934).

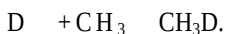
atoms with methane proves conclusively that methane is not attacked readily by atomic hydrogen.

The first investigation of the deuterium atom reaction was made by Taylor, Morikawa, and Benedict,¹³ the atoms being produced by photosensitization with mercury, and the resulting deuterio-methanes detected by infra-red spectroscopy. This paper was only a preliminary note and their results will be discussed later in connection with their more detailed paper.

Geib and Steacie¹⁴ investigated the same reaction by the Wood-Bonhoeffer method. They found no detectable reaction of deuterium atoms with methane up to 100°, indicating that the activation energy of the exchange reaction is not less than 11 kcal., and suggested that the reaction concerned was probably the analogue of the ortho-para hydrogen conversion, viz.,



rather than reaction (3a) followed by



In any case, a lower limit of 11 kcal. is set for both (3a) and (36). Subsequent work to be discussed later furnishes further confirmation of the absence of a reaction at low temperatures between deuterium atoms produced by a discharge and methane.

A few preliminary experiments on the thermal exchange reaction between deuterium and methane at temperatures in the neighbourhood of 1000°K were made by Farkas.¹⁵ His results show that the thermal reaction proceeds by an atomic mechanism, i.e., the primary step is the reaction



While the temperature coefficient of the reaction was not determined, an activation energy of about 11 to 12 kcal. was indicated by comparison with other processes. Farkas interprets his results on the basis of exchange occurring by reaction (36).

The mercury photosensitized reaction was reinvestigated at room temperature by Steacie and Phillips,¹⁶ who found an activation energy for the exchange of 11.7 kcal., assuming a steric factor of 0.1.

A further investigation over a wide range of temperature was made by Farkas and Melville,¹⁷ who found an activation energy of 13 kcal. In their investigation the atom concentration was determined by using ortho-deuterium-methane mixtures and measuring the rate of the ortho-para con-

¹³ H. S. Taylor, K. Morikawa, and W. S. Benedict, *J. Am. Chem. Soc.*, **57**, 383 (1935).

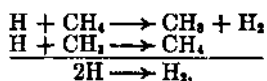
¹⁴ K. H. Geib and E. W. R. Steacie, *Z. physik. Chem.*, **B29**, 215 (1935).

¹⁵ A. Farkas, *J. Chem. Soc.*, **1936**, 36.

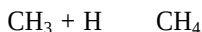
¹⁶ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, **4**, 461 (1936).

¹⁷ A. Farkas and H. W. Melville, *Proc. Roy. Soc. (London)*, **A157**, 625 (1936).

version as well as that of the exchange. They concluded that the reaction occurring was (36). They found, however, that at high temperatures the deuterium atom concentration fell off greatly. The obvious way to account for this would be to assume that atoms are consumed by reaction (3a) at higher temperatures. Farkas and Melville ruled this out, however, on the grounds that if the atoms disappeared by a bimolecular process the D-atom concentration in the presence of methane should be proportional to the light intensity, which is not the case. In view of the complexity of the system, this argument is not compelling. However, it should be noted that this explanation of the loss of hydrogen atoms is equivalent to



i.e., to another mechanism for the recombination of H-atoms. This, as Farkas and Melville point out, will only be effective if the reaction



occurs rapidly compared with the ordinary recombination



Hence this explanation really hinges on the methyl radical concentration, *i.e.*, on how far over to the right the equilibrium is in the reaction



For this equilibrium to be sufficiently over to the right the reaction must be exothermic as written, *i.e.*, the C—H bond strength in methane must not be greater than the heat of dissociation of hydrogen, and this appears to be the case. In any case, in view of the complexity of the system and the possibility of the disappearance of methane in other ways, it does not seem valid to rule out reaction (3a), and in fact Farkas and Melville's work may be taken as supporting its occurrence, at least at high temperatures.

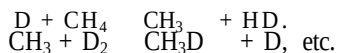
The quantum yields of the exchange reaction determined by Farkas and Melville are given in Table XLIV.

TABLE XLIV. QUANTUM YIELD OF METHANE EXCHANGE REACTION
(FARKAS AND MELVILLE)

Temperature	Quantum yield
189	0.10
340	0.18
453	0.27
610	1.2

Since the quantum yield is above unity at 610°, they argue that the mechanism must be of the true exchange type, *i.e.*, reaction (36), since this does not consume hydrogen atoms. This argument does not seem to be valid

for two reasons. In the first place Farkas and Melville determined the light input using a monochloroacetic acid actinometer. Since Rudberg's value¹⁸ of the quantum yield of this reaction has been shown to be too high by Leighton, Smith, and Leighton,¹⁹ the quantum yields in Table XLIV are too high by a factor of about 2. Hence the quantum yield of the exchange reaction as determined by Farkas and Melville never rises above unity. Secondly, the argument is inconclusive in any case since exchange by the sequence



could lead to a chain reaction.

Morikawa, Benedict, and Taylor⁶ made a further very thorough investigation of the mercury photosensitized exchange reaction. They discovered a fact which had been overlooked by previous investigators, viz., that methane itself is attacked by excited mercury atoms, presumably by



As a result in methane-deuterium mixtures, some of the exchange observed occurs by (2) followed by



Their value of the collision yield of the observed exchange at 100° leads to an overall activation energy of 12.5 to 14 kcal. in satisfactory agreement with previous values. In view of the complications introduced by the photosensitized decomposition of methane, however, they conclude that it is difficult to obtain much information about the activation energy of the reaction of deuterium atoms with methane from their work. In the low temperature range they ascribe exchange mainly to reactions (2) and (4), together with exchange of the methyl radical by



Here the sensitized decomposition of methane by reaction (2) will be the rate determining factor, and this has an activation energy of ca. 4.5 kcal. (It has, however, the low quantum yield of about 0.08 at 20° owing to the low quenching efficiency of methane relative to that of hydrogen.) Around 200° exchange sets in by reaction (1) to which they assign an activation energy of 11 kcal. They conclude that the reaction



only becomes appreciable around 300°, its activation energy being about 15 kcal. Since (1) and (3a) together yield a chain process, the quantum yield now rises rapidly.

¹⁸ E. Rudberg, *Z. Physik*, 24, 247 (1924).

¹⁹ W. G. Leighton, R. N. Smith, and P. A. Leighton, *J. Am. Chem. Soc.*, 60, 2566 (1938).

Apart from interpretation, the main discrepancy between the results of Farkas and Melville and those of Morikawa, Benedict, and Taylor is the quantum yield of the exchange at high temperatures. Thus at 450 to 500° Farkas and Melville give the quantum yield as 0.27, while Morikawa, Benedict, and Taylor found a value of 71. The difference is in part due to the experimental conditions, since Morikawa, Benedict, and Taylor used approximately 6 times higher pressures, 1J30 the light intensity, and a vessel 2.3 times wider than that of Farkas and Melville. All these factors would tend to decrease recombination of hydrogen atoms and thus to increase the quantum yield in the investigation of Morikawa, Benedict, and Taylor. However, it seems impossible to account for the whole discrepancy in this way. In view of the much more comprehensive nature of the investigation of Morikawa, Benedict, and Taylor their results would appear to be the more reliable.

Further investigations of the reaction with deuterium atoms produced by the Wood-Bonhoeffer method have also been made by Trenner, Morikawa, and Taylor¹ and by Steacie.²⁰ Steacie investigated the reaction up to 500° and obtained an activation energy of 12.9 ± 2 kcal., the values calculated from the temperature coefficient and the collision yield being in good agreement.

Trenner, Morikawa, and Taylor by the same method found no reaction from 25° to 208°, from which they calculate a minimum activation energy of 15.6 kcal. From a single run at 310° they calculate $E = 18$ kcal. These values are somewhat higher than those obtained by other workers. The discrepancy is partly due to the fact that they assume that the process under investigation is reaction (3a), followed by a rapid exchange of the methyl radical. Hence to get the rate of the initial step they divide the observed rate by three. This raises their value of the activation energy by about 1 kcal.

In a review of atomic reactions Geib²¹ points out that further evidence of the stability of methane to attack by hydrogen atoms is furnished by the fact that it is obtained as an end product in many reactions of hydrogen atoms.

All things considered, it appears that the main body of evidence favors an activation energy of about 13 kcal. for the exchange reaction between deuterium atoms and methane. The values obtained by various workers are summarized in Table XLV. There is some difference of opinion as to whether the primary reaction concerned is



or



but it seems certain that the latter alternative is the correct one.

²⁰ E. W. R. Steacie, *Can. J. Research*, 15B, 264 (1937).

²¹ K. H. Geib, *Ergeb. exakt. Naturwiss.*, 15, 68 (1936).

In connection with the mechanism of the reaction there have been two theoretical papers of some importance. Gorin, Kauzmann, Walter, and Eyring²² have investigated the system from the point of view of Eyring's semi-empirical method. They calculate for the reaction



an activation energy of 37 kcal. This is in good qualitative agreement with calculations of Rice and Teller²³ based on spectroscopic data. They suggest therefore that this reaction must be ruled out as a method of exchange between D-atoms and methane, and that the primary reaction must be

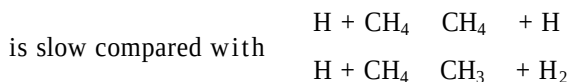


In view of all the other evidence this conclusion appears to be valid. For the latter reaction they calculate an activation energy of about 10.5 kcal., which is in satisfactory agreement with the experimental values of around 12-13 kcal. for the exchange reaction. They also estimated the steric factor to be of the order of 0.1, as has been assumed by most experimenters.

TABLE XLV. VALUES OF VARIOUS WORKERS FOR THE ACTIVATION ENERGY OF REACTION (3)

Author	Method	E, kcal.
Geib and Steacie	Discharge-tube	> 11
Steacie and Phillips	Hg photosensitization	11.7
Farkas	Thermal (<i>E</i> estimated by analogy with his results for $\text{D} + \text{NH}_3$)	11
Farkas and Melville	Hg photosensitization	13
Morikawa, Benedict, and Taylor	Hg photosensitization	12.5-14
Trenner, Morikawa, and Taylor	Discharge-tube at temperatures up to 300°	15.6
Steacie	Discharge-tube at temperatures up to 500°	12.9 ± 2

They conclude further that the reaction is endothermic by 7.6 kcal. This is unquestionably in error. If it were true, the C—H bond in methane would have a strength of approximately 110 kcal., which is far too high. Further, this value means that the calculated activation energy of the back reaction (1) is 10.5 — 7.6 = 2.9 kcal., which is entirely out of the question. It would appear therefore that the qualitative conclusion that



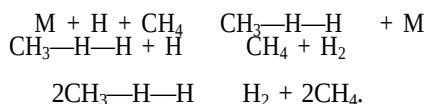
²² E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, 7, 633 (1939). See also S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, New York, 1941.

²³ F. O. Rice and E. Teller, *J. Chem. Phys.*, 6, 489 (1938).

may be accepted, but that the finer details of their calculation cannot be relied upon.

One other interesting result emerges from their calculations. In the potential energy surface they find a basin 8 kcal. in depth corresponding to a stable Coulomb bond between methane and a hydrogen atom. They interpret the decrease in hydrogen atom concentration in Farkas and Melville's work in terms of this $\text{CH}_3\text{—H—H}$ complex as follows:

"The catalytic effect of methane in causing the recombination of hydrogen atoms can thus be interpreted in terms of the reactions



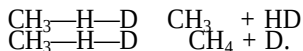
Our quantum mechanical calculations have led us to the conclusion that before a hydrogen atom can be absorbed, on methane it must go over a potential barrier 10 kcal. in height. This is in agreement with the data of Farkas and Melville since they find that the catalytic efficiency of methane for the recombination of hydrogen atoms rises rapidly with temperature, reaches a maximum and then decreases beyond 280°. The decrease at high temperatures is explained since because of the weak nature of the Coulomb bond between a hydrogen atom and methane, the equilibrium would be in favor of the dissociated state at moderately high temperatures.

"It should be remarked that according to our calculations the potential barrier for the formation of $\text{CH}_3\text{—H—H}$ is the same as for the reaction $\text{H} + \text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}_2$. It is therefore to be expected that unless the $\text{CH}_3\text{—H—H}$ complex is stabilized by a collision this reaction will take place. If the reaction were carried out in the presence of deuterium, there would thus be a competition between the exchange reaction and the catalytic recombination of the deuterium atoms."

It might be remarked that it would be possible to have exchange by this mechanism by the steps



That is, if $\text{CH}_3\text{—H—D}$ is formed in the primary step, we could then have a competition between



A "mixed" mechanism for the exchange is thus possible.

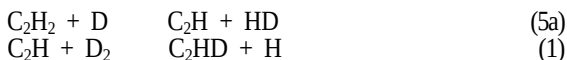
This suggested catalytic recombination is of decided interest. However, in view of the defects of the calculations pointed out above, the conclusion that the complex $\text{CH}_3\text{—H—H}$ has appreciable stability must be taken with considerable reserve.



This reaction probably occurs readily, and it is a possible step in the mechanism of the exchange of deuterium atoms and acetylene (VI-5), viz.,



The reaction of hydrogen atoms with acetylene was investigated by Bonhoeffer and Hardeck² and by von Wartenberg and Schultze.¹⁰ In the presence of acetylene it was found that the recombination of hydrogen atoms was strongly catalysed, heat was given out, and there was a strong emission of light corresponding to the CH and C₂ bands. However, practically all the acetylene was recovered unchanged, so that presumably a series of reactions occur which consume hydrogen atoms and eventually regenerate acetylene. That such is the case is proved by an investigation of the reaction of acetylene with deuterium atoms by Geib and Steacie.¹⁴ It was found that the acetylene recovered after the reaction was almost completely exchanged to deuterio-acetylene. Apparently, then, the acetylene must be alternately hydrogenated and dehydrogenated. The reaction occurs so quickly that three-body processes are ruled out, and the activation energy must be less than 5 kcal. Also, a mechanism of the type



can be eliminated because the atoms removed from the system by reaction (5a) would be regenerated by (1) and no "catalytic" recombination would occur. The mechanism, therefore, must either be analogous to that previously discussed in the case of ethane, viz.,



or else the exchange occurs through the formation of a quasi-molecule, C₂H₂D, i.e.,



However, if the quasi-molecule had a long enough life to make such a mechanism possible, we would also expect the reaction



to occur, and actually no appreciable quantity of ethylene is formed. As von Wartenberg and Schultze point out, the absence of hydrogenation to ethylene is somewhat surprising, since acetylene is very easily hydrogenated to ethylene by metal catalysts. Hydrogenation of acetylene to ethylene was also reported in early work to be absent when the hydrogen atoms were

produced by photosensitization with mercury.²⁴ LeRoy and Steacie²⁶ have recently confirmed the absence of hydrogenation by the discharge tube method. By mercury photosensitization, however, they found that ethane, butane, and a partially hydrogenated polymer were produced. The rate of hydrogenation increased considerably with increasing temperature in the range 25° to 300°. Regardless of which of the alternative mechanisms of Geib and Steacie is accepted for the primary step, it would seem to be necessary for vinyl radicals to be formed before any hydrogenation can occur. This could take place by either



or by



followed by



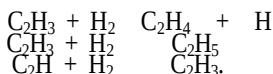
The absence of hydrogenation by the discharge tube method could then be explained on the assumption that the reactions



or

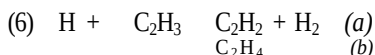


occur much more readily in the presence of high hydrogen atom concentrations than the reactions



Ethane and butane would then arise by recombination and disproportionation of ethyl radicals.

Geib and Harteck²⁶ have also investigated the reaction of hydrogen atoms with acetylene at liquid air temperature. They find that no addition compounds, stable or unstable, are formed.



Some evidence for the occurrence of reaction (6a) comes from the work of von Wartenberg and Schultze¹⁰ and Klemenc and Patat²⁷ on the reaction of hydrogen atoms with ethylene. A small amount of acetylene is formed, which presumably arises by



It is also possible, as mentioned in section VI-5, that the reaction might be involved in the reaction of H-atoms with acetylene. It is surprising that

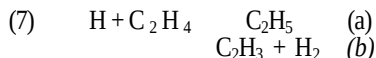
²⁴ J. R. Bates and H. S. Taylor, *J. Am. Chem. Soc.*, 49, 2348 (1927).

²⁵ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* 12, 369 (1944).

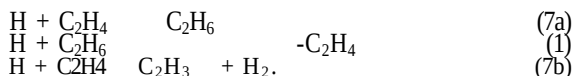
²⁶ K. H. Geib and P. Harteck, *Ber.*, 66, 1815 (1933).

²⁷ A. Klemenc and F. Patat, *Z. physik. Chem.*, B3, 289 (1929).

ethylene is not formed via (66) in the reaction of hydrogen atoms, produced by the discharge tube method, with acetylene. In the mercury photosensitized reactions of acetylene; however, C₂ hydrocarbons are produced to some extent,²⁵ possibly via (66).



The reaction of hydrogen atoms with ethylene was first investigated by the discharge-tube method by von Wartenberg and Skultze.¹⁰ They found that chemiluminescence occurred, the emitted light corresponding to the C—C and C—H bands, and that the reaction was rapid and yielded principally ethane, with a little acetylene. This suggests that both hydrogenation and dehydrogenation occur, *i.e.*,

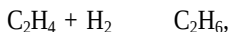


Similar results were obtained by Klemenc and Patat,²⁷ using hydrogen atoms produced both by mercury photosensitization and by the discharge-tube method.

Geib and Harteck²⁶ found that ethane was also formed when ethylene and hydrogen atoms were brought together at liquid air temperature. This points to an activation energy for reaction (7a) of less than 5 kcal., but under these circumstances it is in all probability a surface catalysed reaction.

By mercury photosensitization the reaction was first investigated in a qualitative way by Taylor and Marshall,²⁸ using a cooled mercury arc as a source. They found that there was a steady drop in pressure, presumably owing to the formation of ethane. The rate was very high for the intensity of the light used, suggesting a chain reaction.

Olson and Meyers²⁹ also investigated the reaction by the same method. They found that the drop in pressure was not quite that corresponding to



perhaps owing to the formation of some methane. In a later paper³⁰ they showed by mass-spectrographic analysis that methane, ethane, propane, and butane were formed. When hydrogen and ethylene were present in about equal quantities, considerable higher hydrocarbons were formed and very little methane. Thus with initial pressures of 39 cm. of hydrogen and 25 cm. of ethylene the relative amounts of the products were as follows: CH₄ = 0.018, C₂H₆ = 1, C₃H₈ = 0.64, C₄H₁₀ = 0.42. If, however, hy-

²⁸ H. S. Taylor and A. L. Marshall, *J. Phys. Chem.*, 29, 1140 (1925).

²⁹ A. R. Olson and C. H. Meyers, *J. Am. Chem. Soc.*, 48, 389 (1926).

³⁰ A. R. Olson and C. H. Meyers, *J. Am. Chem. Soc.*, 49, 3131 (1927).

drogen was in large excess, the situation was reversed and very little propane and butane were formed. For example, with 40 cm. of hydrogen and 2 cm. of ethylene they found: $\text{CH}_4 = 0.22$, $\text{C}_2\text{H}_6 = 1$, $\text{C}_3\text{H}_8 = 0.04$, $\text{C}_4\text{H}_{10} = 0.0008$. They conclude that three primary processes occur,



(The last of these is certainly impossible on energetic grounds, since there appears to be no doubt that the $\text{C}=\text{C}$ bond strength in ethylene is much greater than 112 kcal.) In later work³¹ Stewart and Olson point out that the above analyses are not to be taken too seriously, since secondary chemical reactions may occur in the ion stream of the mass-spectrograph.

Bates and Taylor²⁴ also found that some polymerization accompanied the formation of ethane. The occurrence of the reaction was also noted by Hirst.³²

A more thorough investigation was made by Taylor and Hill,⁸³ who found that when hydrogen was in large excess the products were practically exclusively ethane, but with relatively more ethylene higher hydrocarbons were formed (average C_4), and a liquid of molecular weight about 230. Some methane was also formed. There is thus good general agreement between the work of Taylor and Hill and that of Olson and Meyers. Since the heavier products react as fast or faster than the lighter under the influence of excited mercury atoms, the process becomes extremely complicated once higher products have started to form, and the liquid product undoubtedly results from secondary reactions. Taylor and Hill conclude that the apparently simple results of von War ten berg and Schultze were due to the low pressure and large excess of hydrogen used in their experiments. They discuss the possible reaction steps in some detail, and conclude that they are very complex, and that one of the main steps is reaction (7a).

The reaction has also been investigated by Klemenc and Patat.²⁷ They agree with Taylor and Hill in general, but consider that the hydrogenation process is never as smooth as found by them, and is always accompanied by some polymerization. The polymerization process is complicated, but they suggest that it occurs mainly by the preliminary formation of acetylene and hydrogen, followed by polymerization of the acetylene as suggested by Taylor and Hill.

Melville³⁴ compared the reactions of ethylene with hydrogen and with deuterium atoms. He found no detectable difference in rate, and therefore

³¹ H. R. Stewart and A. R. Olson, *J. Am. Chem. Soc.*, 53, 1236 (1931).

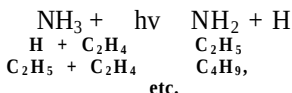
³² H. S. Hirst, *Proc. Cambridge Phil Soc.*, 23, 162 (1926).

³³ H. S. Taylor and D. G. Hill, *Z. physik. Chem.*, B2, 449 (1929); *J. Am. Chem. Soc.*, 51, 222 (1929).

³⁴ H. W. Melville, *J. Chem. Soc.*, 1934, 1243.

concludes that the rate-controlling step must be a hydrogen or deuterium atom reaction, since otherwise the difference in zero-point energies would make itself felt.

Taylor and Emeleus³⁵ have shown that the ethylene polymerization can be photosensitized by ammonia, presumably owing to hydrogen atoms or to radicals from the ammonia decomposition, i.e.,

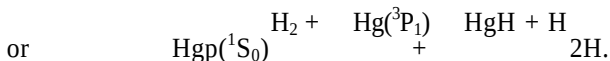


Similar results were obtained using methylamine and ethylamine.³⁶

By far the most thorough investigation is that of Jungers and Taylor,³⁷ who investigated the mercury photosensitized hydrogenation of C_2H_4 and C_2D_4 . They found that when hydrogen was in large excess the products of the reaction were predominantly butane, irrespective of variations in concentration, pressure, and intensity. No appreciable amount of methane was found. This disagrees with Taylor and Hill, who found mainly ethane at high hydrogen concentrations, together with some methane. Jungers and Taylor suggest that this was due to a deposit of polymer, $(\text{CH}_2)_n$, on the walls in the case of Taylor and Hill's experiments: they themselves torched the reaction vessel in a stream of air after each run, and thus always worked with clean vessels. The discrepancies between their results and those of von Wartenberg and Schultze are obviously due to the very high hydrogen atom concentration used by the latter, which favours the reactions



Jungers and Taylor found that when the hydrogen-ethylene ratio was greater than 3, the rate of reaction was independent of the ethylene concentration. This points to the primary process being exclusively



However, on the basis of the quenching cross-sections of hydrogen and ethylene³⁸ it would be expected that about one-fourth of the radiation would be absorbed by ethylene under these conditions, unless deactivation of excited ethylene molecules by hydrogen occurs. There is no doubt that the next step must be



³⁵ H. S. Taylor and H. J. Emeleus, *J. Am. Chem. Soc.*, 52, 2150 (1930).

³⁶ H. S. Taylor and H. J. Emeleus, *J. Am. Chem. Soc.*, 53, 3370 (1931).

³⁷ J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, 6, 325 (1938).

³⁸ E. W. R. Steacie, *Can. J. Research*, B18, 44 (1940).

Since little, if any, ethane is formed, the reactions

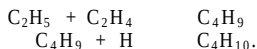


and



do not occur to any appreciable extent. The absence of (2) is in agreement with previous estimates of its activation energy (VI-49). The absence of (1) is apparently due to the rapid occurrence of (7a) (to which all the evidence points), with an activation energy not over 5 kcal. Reaction (7a) therefore "cleans up" all the hydrogen atoms in the system. This type of reaction is evidently the cause of the inhibitory effect of ethylene in chain reactions involving atomic hydrogen and free radicals.³⁹

The low hydrogen atom concentration rules out butane formation by the mechanism



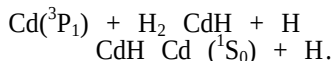
Butane must therefore be formed by



This is in agreement with the fact that ethylene polymerization by free radical sensitization occurs readily only at temperatures above 125° to 150°.

Moore and Taylor⁴⁰ obtained results similar to those of Jungers and Taylor. Thus at room temperature with a 6H2--IC2H4 mixture they obtained as products 2 per cent methane, 14 per cent ethane, and 84 per cent butane. Work on the mercury-photosensitized polymerization of ethylene (see IV-4) also leads to the conclusion⁴¹ that the reaction $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$ occurs readily.

The reaction of atomic hydrogen with ethylene has also been investigated by cadmium photosensitization^{42, 43} using the resonance line at 3261Å. There appears to be no doubt that in the presence of hydrogen the primary process is⁴⁴



These experiments were carried out at a much higher temperature than those using mercury photosensitization, it being necessary to work at 280° in order to obtain a sufficiently high cadmium vapor pressure. The products of the reaction are therefore more complex, consisting of methane,

³⁹ L. A. K. Staveley, *Proc. Roy. Soc. (London)*, **A162**, 557 (1937).

⁴⁰ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 504 (1940).

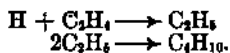
⁴¹ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, **9**, 829 (1941), **10**, 676 (1942).

⁴² J. R. Bates and H. S. Taylor, *J. Am. Chem. Soc.*, **60**, 771 (1938).

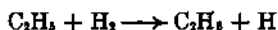
⁴³ E. W. R. Steacie and R. Potvin, *Can. J. Research*, **B16**, 337 (1938), **B18**, 47 (1940).

⁴⁴ P. Bender, *Phys. Rev.*, **37**, 1535 (1930); L. O. Olsen, *J. Chem. Phys.*, **6**, 307 (1938).

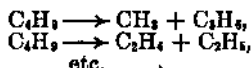
ethane, propane, butane, and higher hydrocarbons. It appears probable that the mechanism is in the main that proposed by Taylor and Jungers, *i.e.*



The additional products presumably arise from the ready occurrence of

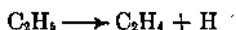


at the higher temperature, and from the undoubted instability of the butyl radical at this temperature, and we thus have



The reaction photosensitized by ($^3\text{P}_1$) zinc atoms appears to be very similar.⁴⁵ The reactions photosensitized by $\text{Cd}(^1\text{P}_1)$ ⁴⁶ and $\text{Zn}(^1\text{P}_1)$ atoms⁴⁵ also appear to involve the reaction $\text{H} + \text{C}_2\text{H}_4 \longrightarrow \text{C}_2\text{H}_6$ as an important step.

Bawn⁴⁷ from transition state calculations concludes that the reverse reaction



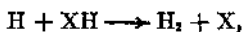
is endothermic to the extent of 35 kcal., and that its activation energy is ca. 49 kcal. This corresponds to an activation energy of ca. 14 kcal. for the reaction



There appears to be no doubt that this is far too high. However, Bawn's values can only be expected to be reliable in so far as the order of magnitude is concerned.

To obtain agreement between free radical mechanisms and experimental results on thermal reactions, Rice and Herzfeld⁴⁸ assume an activation energy of 10 kcal. for reaction (7a). This again seems much too high. A value of 5 kcal. or less is much more probable, and low values have often been assumed in photochemical mechanisms.⁴⁹

Since atomic hydrogen usually acts as a dehydrogenating agent, *i.e.*,



reaction (76) might also be expected in systems containing hydrogen atoms and ethylene. There is some evidence for its occurrence. Thus both von Wartenberg and Schultze¹⁰ and Klemenc and Patat²⁷ found that when hydrogen atoms produced by a discharge reacted with ethylene at room

⁴⁵ H. Habeeb, D. J. LeRoy, and E. W. R. Steacie, *J. Chem. Phys.*, 10, 261 (1942).

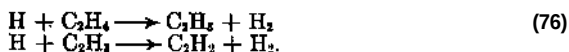
⁴⁶ E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, 10, 22 (1942).

⁴⁷ C. E. H. Bawn, *Trans. Faraday Soc.*, 34, 598 (1938).

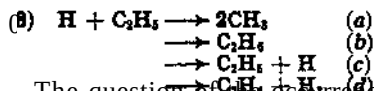
⁴⁸ F. O. Rice and K. F. Herzfeld, *J. Chem. Phys.*, 7, 671 (1939).

⁴⁹ See *e.g.*, R. D. McDonald and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A167**, 480 (1936).

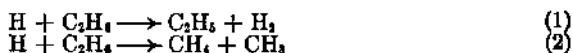
temperature some acetylene was produced in addition to ethane, *i.e.* presumably



This indicates an activation energy of the order of 10 kcal. for reaction (76).



The question of the occurrence of reaction (8a) is intimately connected with the reaction $\text{H} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2$, for details of which see VI-9. The production of large quantities of methane in the reaction of hydrogen atoms with ethane is definitely established.^{1,50} This was originally explained on the assumption that of the two possible reactions



the latter must be the faster. In support of this Steacie and Phillips⁵¹ concluded from an investigation of the mercury photosensitized decomposition of ethane that (2) must be at least 4 times faster than (1) at room temperature.

This assumption would make still more difficult the application of the Rice theory to the ethane decomposition (see III-5). The only way to avoid this difficulty (if it is to be avoided) is to postulate some other mechanism in which reaction (1) is the primary step, and methane is ultimately formed from the ethyl radicals produced by (1). Rice and Teller⁶² suggested that methane formation could be accounted for without the postulation of reaction (2) if we assume the reactions



In their original paper on the reaction of H-atoms with ethane (VI-9) Trenner, Morikawa, and Taylor had ruled out the possibility of methane formation by (8a) followed by (3) on the grounds that in the mercury photosensitized hydrogenation of ethylene,⁵³ ethylene is completely hydrogenated successively to ethyl and ethane without the formation of methane. They further suggested as additional evidence against (8a) that the C—H bond is stronger in ethyl than in ethane.

On the other hand, Klemenc and Patat⁵⁴ always obtained some methane

⁶⁰ E. W. R. Steacie, *J. Chem. Phys.*, 6, 37 (1938).

⁵¹ E. W. R. Steacie and N. W. F. Phillips, *Can. J. Research*, B16, 303 (1938).

⁵² F. O. Rice and E. Teller, *J. Chem. Phys.*, 6, 489 (1938); see also H. S. Taylor, *Phys. Chem.*, 42, 763 (1938).

⁶³ H. S. Taylor and D. G. Hill, *J. Am. Chem. Soc.*, 51, 2922 (1929).

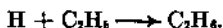
⁶⁴ A. Klemenc and F. Patat, *Z. physik. Chiem.*, B3, 289 (1929).

in the mercury photosensitized hydrogenation of ethylene. However, a more thorough investigation by Jungers and Taylor⁵⁵ showed that in vessels which were carefully kept free from traces of higher hydrocarbons no methane was formed.

Taylor⁵⁶ points out, however, that this argument is by no means compelling. Under the conditions of Jungers and Taylor's work the predominant product is butane. This is obviously formed by the combination of ethyl radicals. Now the reaction of hydrogen atoms with ethylene is exceedingly rapid, and apparently in the presence of ethylene hydrogen atoms are "cleaned up," and their concentration is reduced to a very low value. As a result ethyl radicals combine to form butane, since the H-atom concentration is too low for reaction (8a) to be appreciable. What ethane is formed probably arises from the disproportionation reaction



rather than from the reaction



It follows that work on the photosensitized hydrogenation of ethylene has no bearing on the question of the occurrence of reaction (8a) in cases where the H-atom concentration is appreciable.

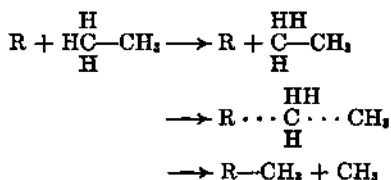
Reaction (8a) has received considerable theoretical and experimental support. Rice and Teller⁵² have discussed the possibilities of the occurrence of reactions of the general types



and



from the standpoint of the "principle of least motion." They conclude that reaction (4) should occur readily. In the case of reaction (5) they make what appears to be the reasonable assumption that on account of the shielding of the carbon atom by the surrounding hydrogen atoms it will first be necessary to force the hydrogen atoms into the plane of the carbon, and then to bring up the atom or radical, R, while the methyl group moves off. *I.e.*,



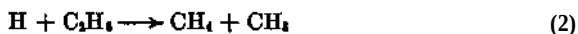
From the known bending vibrations of the methane molecule they calculate the energy necessary to move the hydrogen atoms into the plane of

⁵⁵ J. C. Jungers and H. 8. Taylor, *J. Chem. Phys.*, 6, 325 (1938).

⁵⁶ H. S. Taylor, *J. Phys. Chem.*, 42, 763 (1938).

the carbon, and thus arrive at an estimate of approximately 40 kcal. for the activation energy of reaction (5). They therefore conclude that the only appreciable reaction of hydrogen atoms with ethane will be reaction (4), and that methane formation must be due to subsequent reactions of the ethyl radical.

The same conclusion is also reached on theoretical grounds by Gorin, Kauzmann, Walter, and Eyring.²² The reaction



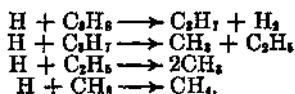
is of the same "inversion" type as the reaction



which was discussed in detail in Section VI-3. They therefore conclude that (2) must also have a high activation energy of the order of 37 kcal., and hence methane formation in systems containing ethyl radicals must arise by



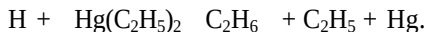
From the experimental point of view strong evidence for the occurrence of reaction (8a) comes from the work of Steacie and Parlee⁶⁷ on the reaction of hydrogen atoms with propane. As discussed in Section VI-12, it is impossible to account for the products of the reaction at room temperature unless the predominant reactions are



Work on the reaction of hydrogen atoms with butane,⁶⁸ discussed in Section VI-15, leads similarly to the conclusion that reaction (8a) is a major step in the process.

Further experimental support comes from the work of Moore and Taylor.⁵⁹ In an investigation of the photolysis of mercury diethyl they found that at 100° and 160° no detectable methane was formed, the products being hydrogen, ethane, ethylene, butane, and some higher hydrocarbons. However, at 100° the irradiation with mercury resonance radiation of a mixture of mercury diethyl and hydrogen leads to a large formation of methane. Since ethyl radicals do not react appreciably with molecular hydrogen at this temperature, this points to the occurrence of reaction (8a) with an activation energy of not over 5 kcal.

This evidence is not, perhaps, entirely conclusive. To explain other features of their work Moore and Taylor postulate the occurrence of the reaction

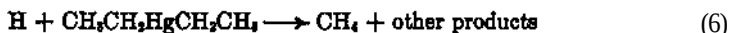


⁵⁷ E. W. R. Steacie and N. A. D. Parlee, *Trans. Faraday Soc.*, 35, 854 (1939); *Can. J. Research*, **B17**, 371 (1939).

⁵⁸ E. W. R. Steacie and E. A. Brown, *J. Chem. Phys.*, 8, 734 (1940).

⁵⁹ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 396 (1940).

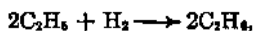
However, there is the possibility that the reaction



might occur, *i.e.*, that the C—C bond nearest the approaching H-atom might break rather than the Hg—C bond. Against this are (a) the relative weakness of the Hg—C bond, and (b) the fact that in the normal photolysis in the presence of hydrogen it seems fairly certain that the reaction

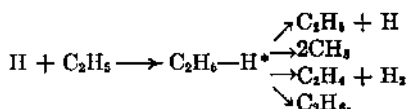


occurs, but no methane results from further reactions of the atomic hydrogen. However, if ethane formation in the normal case were to follow a mechanism analogous to that suggested for methane by Taylor and Burton,⁶⁰ *i.e.*,

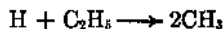


then methane formation when resonance radiation is used in the presence of hydrogen might be due to the occurrence of (6) rather than (8a). However, Moore and Taylor's own explanation of their results is far more plausible.

The various possibilities when a hydrogen atom reacts with an ethyl radical are summed up diagrammatically below



It may be assumed that the first product of the reaction between H and C₂H₅ is in every case a complex or quasi-molecule C₂HB—H* with high energy. This quasi-molecule may by collision with a third body or with the wall be stabilized to C₂H₆. If it is not so stabilized, it may dissociate again, either into the original H and C₂H₅, or into C₂H₄ and H₂, or into 2CH₃. In view of the relative weakness of the C—C bond the reaction



may be expected to occur readily, and this conclusion appears to be substantiated experimentally, as discussed above.

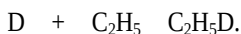
The reaction



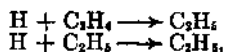
does not appear to occur to any great extent under most circumstances. In investigations of the reactions of deuterium atoms with ethane (see VI-9) both by the discharge tube method and by mercury photosensitization it was found that unreacted ethane was exchanged to only a slight extent, while the products of the reaction were strongly deuterized. Since relatively large concentrations of deuterium atoms and ethyl radicals were undoubt-

⁶⁰ H. A. Taylor and M. Burton, *J. Chem. Phys.*, 7, 676 (1939).

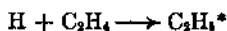
edly present, especially in Trenner, Morikawa, and Taylor's investigation, this appears to be strong evidence against the occurrence of the reaction



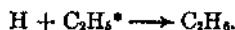
On the other hand, Geib and Harteck⁶¹ found that hydrogen atoms reacted with ethylene to give ethane even at liquid air temperature. This presumably occurred by the steps



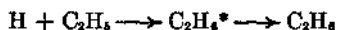
and points to a very low activation energy for both reactions, but at these temperatures the reactions probably occur at the wall. Also ethane is the main product of the reaction of H-atoms with ethylene at room temperature, while little methane is formed. These results are difficult to reconcile with experiments on the reaction of H-atoms with ethane and on the mercury photosensitized reactions of ethane. Possibly the reaction



occurs, and at sufficiently high H-atom concentrations this is followed by



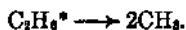
Kimball⁶² from a consideration of vibration frequencies has discussed the mean lives of the complexes formed in association reactions. He concludes that the $\text{C}_2\text{H}_5\text{—H}$ complex has a life of 2.1 sec, and thus should always be stabilized by collision before dissociation occurs. This would indicate that the reaction



should be an efficient one, while



should not occur to an appreciable extent. However, Kimball's calculations are based only on a consideration of the dissociation into C_2H_5 and H, and he does not consider the possibility of



Kimball's results, therefore, have no bearing on the possibility of the occurrence of this reaction, and indeed the possibility of its occurrence makes Kimball's discussion of little real significance. In any case Kassel⁶³ has severely criticized Kimball's treatment, and he concludes that it is fundamentally unsound.

Rice and Herzfeld⁶⁴ to obtain agreement with experiment in their free radical mechanisms assume a small activation energy, or none at all, for

⁶¹ K. H. Geib and P. Harteck, *Ber.*, 66, 1815 (1933).

⁶² G. E. Kimball, *J. Chem. Phys.*, 6, 310 (1937).

⁶³ L. S. Kassel, *J. Chem. Phys.*, 5, 922 (1937).

⁶⁴ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, 56, 284 (1934).

the recombination of H and C₂H₅ to give ethane. The Ktichler and Theile⁶⁵ modification of their scheme for ethane (III-5), however, which Rice and Herzfeld accept,⁶⁶ does not involve this reaction as an important step, and hence the success or failure of the Rice-Herzfeld mechanism has no bearing on the occurrence of (86).

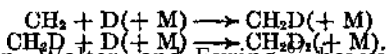
There is considerable evidence that the reaction



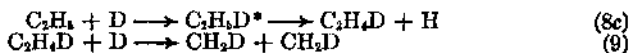
occurs readily, the activation energy being about 5 kcal. As pointed out above, in their investigation of the reaction of deuterium atoms with ethane Trenner, Morikawa, and Taylor found that the recovered ethane was deuterized to a negligible extent. The methane formed in the reaction, however, was highly deuterized (up to 63 per cent). They explained this as due to exchange of the methyl radical by reactions such as



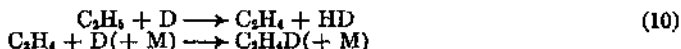
followed by



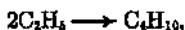
Gorin, Kauzmann, Walter, and Eyring,⁶⁷ however, consider that reaction (7) is improbable since the D atom approaches along an axis of symmetry, and hence on redistribution of the energy they consider that the three other hydrogens would move out symmetrically, and the energy could not become concentrated in a single C—H bond. They prefer as the mechanism



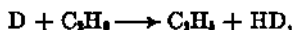
or else



More direct evidence for the occurrence of (8c) comes from the work of Steacie, Alexander, and Phillips.⁶⁸ They found in the mercury photosensitized reaction of ethane-deuterium mixtures that methane, propane, and butane were formed, and that all three were highly deuterized. Since butane is certainly formed by the reaction



and since the ethyl radicals result from



⁶⁵ L. Kuchler and H. Theile, *Z. physik. Chem.*, **B42**, 359 (1939).

⁶⁶ F. O. Rice and K. F. Herzfeld, *J. Chem. Phys.*, **7**, 671 (1939).

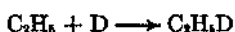
⁶⁷ E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

⁶⁸ E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research*, **B16**, 314 (1938).

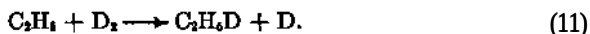
it is apparent that the deuterization of butane must have resulted from deuterization of the ethyl radicals after their formation. This must almost certainly be due to the occurrence of the reaction



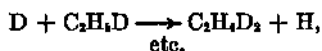
Further evidence for this reaction was obtained by Steacie and Parlee⁵⁷ in an investigation of the reactions of deuterium atoms with propane. In this case ethane is a product of the reaction at higher temperatures. This undoubtedly results from the reactions



and



The ethane formed was, however, too highly deuterized to account for in this way, and it appears probable that exchange of the ethyl radicals occurred, although it is possible that the deuterization might have resulted from the alternate occurrence of (11) and



Reaction (8d) was also one of the important steps in the original Rice-Herzfeld mechanism for the ethane decomposition, and it was assumed to have a low activation energy. In the Kuchler and Theile modification of this mechanism, however, it is no longer an important step.

There appears to be little information about its occurrence. Intrinsically it would seem to be not unlikely, since the reaction



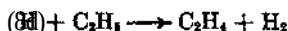
has a low activation energy, and the strength of binding of the second hydrogen atom in ethane is probably not greatly different from that of the first.

Gorin, Kauzmann, Walter, and Eyring consider that the reaction probably has a low activation energy, for reasons not stated.

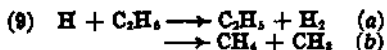
In general, there is little evidence of the occurrence at low temperatures of ethylene in systems containing hydrogen atoms and ethyl radicals (although ethylene does occur in such systems at higher temperatures in some cases). However, all the evidence indicates (Section VI-7) that the reaction



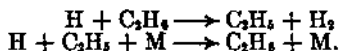
occurs with a very low activation energy, and hence any ethylene formed by



would be expected rapidly to reform C_2H_5 by (12).



Bonhoeffer and Harteck² and von Wartenberg and Schultze¹⁰ found that luminescence occurred on mixing hydrogen atoms and ethane, bands due to CH and CC being observed. The major part of the ethane was recovered unchanged, however. The latter authors found that there was a considerable loss of gas in their experiments (up to 25 per cent), which might have been due to methane formed in the reaction, and which with their technique would have passed through the liquid-air trap and been lost. They suggested that the main reactions were

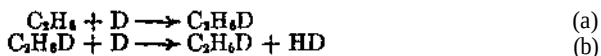


Since a complex mixture of products is not formed, it is apparent that the emission of the C₂ and CH bands is due to the presence of only minute amounts of these substances, produced by secondary reactions. If the main process went by dehydrogenation to C₂ and CH, it seems impossible that these could be quantitatively hydrogenated back to ethane without the formation of appreciable amounts of other products.

Chadwell and Titani⁶⁹ in the course of another investigation made two experiments with ethane and hydrogen atoms. They found that (a) 25 cc. of ethane gave 5 per cent methane, 1.4 per cent carbon dioxide, and 1.6 per cent ethylene, and (6) 150 cc. of ethane gave 3 per cent methane, 3 per cent carbon dioxide, and 1.7 per cent ethylene. The carbon dioxide obviously comes from a reaction involving the water or phosphoric acid used to poison the walls of the apparatus to prevent too rapid recombination of hydrogen atoms. They suggest that the gas lost in the investigation of von Wartenberg and Schultze was ethane which passed the liquid-air trap, rather than methane. It is certainly to be expected that some ethane would be lost under the experimental conditions of von Wartenberg and Schultze. On the other hand Kemula⁷⁰ found that some methane was produced in the reaction of ethane with hydrogen atoms formed by mercury photo-sensitization.

Steacie and Phillips⁷¹ investigated the reaction of deuterium atoms with ethane, using the Wood-Bonhoeffer method, and found an activation energy of 6.3 kcal. for the exchange reaction. They point out that there are three main possibilities for the mechanism of the reaction:

I. Hydrogenation

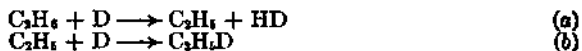


⁶⁹ H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, 55, 1363 (1933).

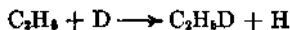
⁷⁰ W. Kemula, *Roczniki Chem.*, 10, 273 (1930).

⁷¹ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 4, 461 (1936).

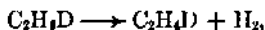
II. Dehydrogenation



III. Exchange by Metathesis



As with methane, the direct exchange by III can probably be ruled out. They conclude that⁷² "Mechanism I is very unlikely, since reaction 1(a) would have to occur at a triple collision (or else have a very low steric factor), and this would make the reaction far too slow to enable ethane to exert a strong catalytic effect on the recombination of hydrogen atoms. (It should be remarked that this 'catalytic effect' can by no means be considered to be definitely established.) Also, even if reaction 1(a) occurred sufficiently rapidly, the very unstable molecule $\text{C}_2\text{H}_5\text{D}$ would have little chance of surviving long enough (10^{-6} sec.) to meet a deuterium atom and give I(b). Hence in general reaction I(a) would be followed by



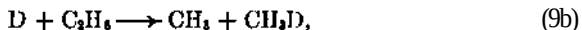
which would make the process indistinguishable from reaction II(a)."

Hence they conclude that mechanism II is correct, and that the measured activation energy (6.3 kcal.) is that of reaction II(a). The companion reaction

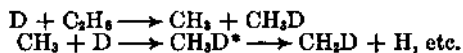


has therefore also an activation energy of the same order of magnitude.

The reaction was reinvestigated by the same method by Trenner, Morikawa, and Taylor.⁷³ At first sight their results appeared to differ sharply from those of Steacie and Phillips. They concluded that at room temperature the main reaction is



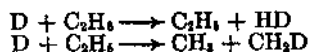
with an activation energy of 7.2 kcal., and that the exchange reaction is only appreciable at temperatures from 100° up, with an activation energy of 11.4 kcal. (See Figure 25.) In their experiments from 10 to 20 per cent of the ethane was found to be decomposed to methane. They made very thorough analyses of the products of the reaction, and determined the deuterium content of each separately. The methane formed was found to be about 50 per cent deuterized, but the ethane was entirely light at temperatures below 100°. They suggested that methane is formed by the reactions



⁷² E. W. R. Steacie, *Chem. Reviews*, 22, 311 (1938).

⁷³ N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, 5, 203 (1937).

They ruled out



as the mechanism of methane formation, since Taylor and Hill⁷⁴ found that in the mercury photosensitized hydrogenation of ethylene



without the formation of methane.

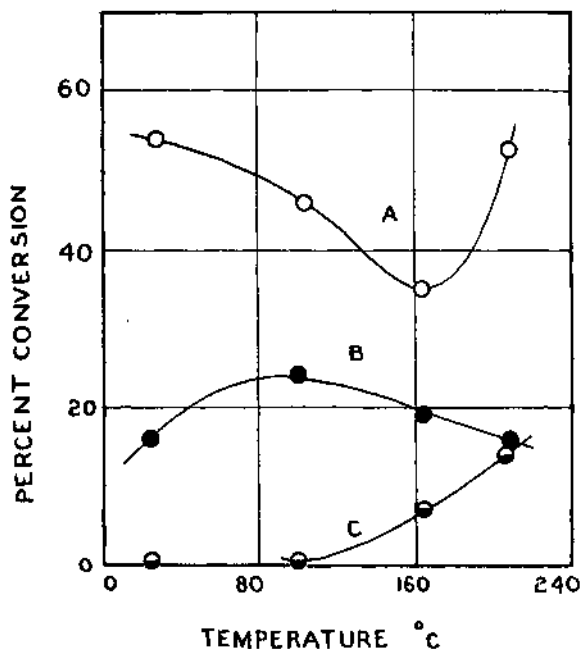
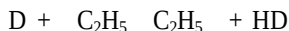


Figure 25. Reaction of deuterium atoms with ethane (Trenner, Morikawa and Taylor).

A, Methane deuteration. B, Ethane decomposition. C, Ethane deuteration.

Trenner, Morikawa, and Taylor suggest that above 100° reaction also occurs by

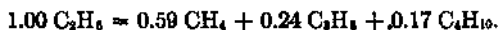


as suggested by Steacie and Phillips. There is, however, a considerable discrepancy in the activation energy of this process between the two investigations (6.3 and 11.4 kcal.). In Steacie and Phillips' investigation the separate products were not isolated, it being assumed from the work of Chadwell and Titani that the formation of methane was negligible. In a further investigation under conditions identical with those employed by Steacie and Phillips, the production of methane was confirmed.⁷⁶

⁷⁴ H. S. Taylor and D. G. Hill, *J. Am. Chem. Soc.*, 51, 2922 (1929).

⁷⁵ E. W. R. Steacie, *J. Chem. Phys.*, 6, 37 (1938).

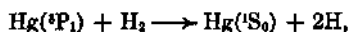
The reaction of hydrogen atoms with ethane has been investigated qualitatively by mercury photosensitization by a number of workers.^{70,74,76-78} It was reinvestigated by Steacie and Phillips⁷⁹ in a flow system with improved trapping methods to cut down secondary reactions. In the absence of hydrogen they found that the products of the reaction consisted entirely of methane, propane, and butane, as expressed by the stoichiometric equation



If the decomposition were carried out in the presence of added hydrogen, the yield of methane was increased and hydrogen was consumed, as indicated by



The above results were obtained with a circulating type of system. In later work using a "single-pass" flow system, they found that hydrogen was produced in the reaction of ethane alone, but that in the circulating system it was consumed again by the reaction

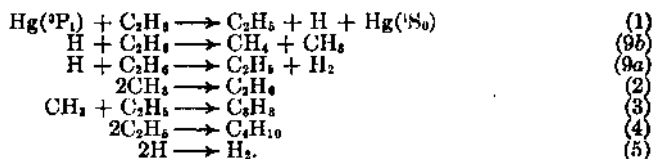


followed by reactions of atomic hydrogen.

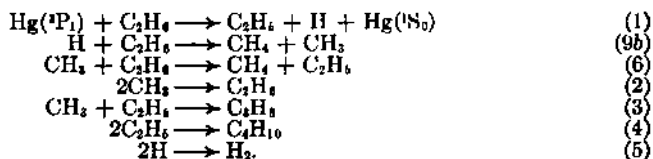
In discussing the mechanism of the reaction they point out that the primary step must be a C—H bond split. The only other alternative would be a C—C split followed by some reaction of methyl or ethyl radicals with ethane which consumes hydrogen. Such reactions are unquestionably too slow to account for the observed hydrogen production.

Accepting a C—H bond split as the primary step, we then have as alternatives:

Mechanism I



Mechanism II



⁷⁶ S. Tolloczko, *Przemysl Chem.*, 11, 245 (1927)

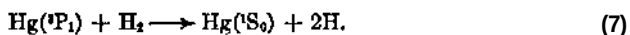
⁷⁷ H. S. Taylor and D. G. Hill, *Z. physik. Chem.*, B2, 449 (1929).

⁷⁸ W. Kemula, S. Mrazek, and S. Tolloczko, *Coll. Czech. Chem. Comm.*, 5, 263 (1933).

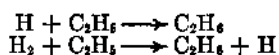
⁷⁹ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 6, 179 (1938); *Can. J. Research*, B16, 303 (1938); E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research*, B16, 314 (1938).

These schemes assume the same primary step and the same radical recombination reactions to produce the final products. They differ fundamentally, however, in the presence or absence of reaction (6) as a means of production of ethyl radicals and of loss of methyl radicals. With appropriate assumptions as to the relative rates of the various steps both schemes will account stoichiometrically for the products of the reaction. However, as discussed later, the work of Smith and Taylor⁸⁰ and other evidence indicates that reaction (6) is too slow to be of importance at room temperature. Steacie and Phillips therefore rule out Scheme I I, and consider Scheme I to be established.

In the presence of hydrogen, on account of its very high quenching efficiency, the primary step is unquestionably

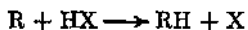


The other steps are then the same as in the absence of hydrogen. Both in the absence and in the presence of hydrogen this mechanism accounts satisfactorily for the products of the reaction, provided it is assumed that reaction (96) is four times as fast as reaction (9a). Steacie and Phillips remark in this connection "The only way to avoid such an assumption would be to postulate some reaction of velocity comparable to (9a) which consumes hydrogen and destroys ethyl radicals. The former requisite is necessary to account for the over-all hydrogen consumption, and the latter to account for the low yield of propane and butane relative to methane." They rule out the reactions



on the grounds that they are too slow, and also because work on the reaction of deuterium atoms, produced by photosensitization, with ethane⁷⁹ shows that little of the unchanged ethane in the reaction mixture is deuterized. They therefore conclude that reaction (96) occurs four times as fast as reaction (9a) at room temperature.

This assumption is directly opposed to the Rice theory⁸¹ of the thermal ethane decomposition (III—5), since it brings in reaction (96) as a major step in the process. Actually, however, the occurrence of reaction (96) would have much more serious consequences than this. All the Rice mechanisms are based on the idea that reactions of the type



occur readily, but that hydrocarbon chain splitting reactions of the type



⁸⁰ J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, 7, 390 (1939).

⁸¹ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, 56, 284 (1934).

never occur to an appreciable extent. Hence the ready occurrence of reaction (96) is contrary to the general postulates of the Rice mechanisms for all substances.

In order to account for the production of methane, but at the same time avoid the postulation of chain splitting reactions like (96), Rice and Teller⁸² suggested that methane formation occurs by



This mechanism has received considerable theoretical and experimental support. (See VI-8.)

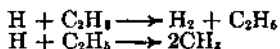
The postulation of (8) as the source of methane in the reaction of H-atoms with ethane, removes the discrepancies between the work of Trenner, Morikawa, and Taylor, and that of Steacie and Phillips. The activation energy of 7.2 kcal. found by the former is now to be ascribed to reaction (9a) as is the value of 6.3 kcal. found by Steacie and Phillips. We may therefore put

$$E_{9a} = 6.7 \pm 1 \text{ kcal.}$$

This is much lower than the value of 17 kcal. assumed by Rice and Herzfeld⁸¹ in connection with the mechanism of the ethane decomposition.

Work on the mercury photosensitized reactions of ethane at high temperatures (up to 475°)⁸³ indicates that the same general mechanism holds.

Darwent^{83a} has pointed out that there are certain discrepancies between the results with ethane, propane, and butane, as far as the participation of reaction (8) is concerned. In all cases the reaction of H-atoms with the hydrocarbons leads to the production of much methane, when the discharge-tube method is used. This is to be expected, since the concentration of atomic hydrogen is very high, and a sequence of reactions such as



is favored.

In the case of the mercury photosensitized reactions, however, there is a surprising difference between ethane and propane and the butanes. In the case of ethane, as discussed above, large quantities of methane are formed. With propane and the butanes, however, as discussed in sections VI-12, VI-15, and VI-16, the overall reaction at higher pressures is almost entirely that corresponding to



and it is difficult to see how reaction (8) can be the sole source of methane in the case of ethane, and be negligible with propane and the butanes. Recent

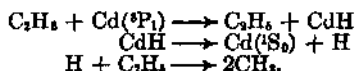
⁸² F. O. Rice and E. Teller, *J. Chem. Phys.*, 6, 489 (1938); see also H. S. Taylor, *Phys. Chem.*, 42, 763 (1938).

⁸³ E. W. R. Steacie and R. L. Cunningham, *J. Chem. Phys.*, 8, 800 (1940).

^{83a} B. deB. Darwent, *Ph.D. Thesis*, McGill University, 1943.

work, however, has shown^{83b} that at lower pressures methane, ethane, and C₄ and C₈ hydrocarbons are formed from propane. There is, however, a surprising difference in the conditions necessary to obtain similar products from the two hydrocarbons. (See Section VI-12 for a more detailed discussion.)

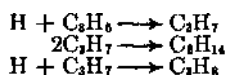
The cadmium photosensitized reactions of ethane and of ethane-hydrogen mixtures⁸⁴ appear to be essentially similar to the mercury photosensitized reactions. Steacie and Potvin suggest an identical mechanism, with the methane formed in the reaction arising by



Moore and Taylor⁸⁶ investigated the mercury photosensitized reaction of hydrogen-propylene mixtures. The experiments were carried out with 40 mm. of propylene and a 6-fold excess of hydrogen. The main products were

CH_4	2 per cent	C_2H_{10}	5 per cent
C_2H_6	1 " "	C_2H_{12}	2 " "
C_3H_8	26 " "	C_3H_{14}	64 " "

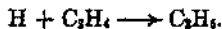
This indicates that the main reactions are



or



together with various other reactions of lesser importance. The indications are that reaction (10) has a low activation energy, as is the case with the analogous reaction of ethylene,



The reaction of H-atoms with propylene has been investigated by the discharge-tube method by Rabinowitch, Davis, and Winkler.⁸⁶ The products were methane, ethane, and propane, in amounts of approximately 0.45 mole, 0.68 mole, and 0.33 mole respectively per mole of C₃H₆ reacting, and were independent of temperature over the range 30° to 250°. The most striking feature of the results was that the extent of reaction exceeded the available concentration of hydrogen atoms.

^{83b} B. de B. Darwent and E. W. R. Steacie, *J. Chem. Phys.*, in press.

⁸⁴ E. W. R. Steacie and R. Potvin, *J. Chem. Phys.*, 7, 782 (1939).

⁸⁵ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 504 (1940).

⁸⁶ B. S. Rabinowitch, S. G. Davis, and C. A. Winkler, *Can. J. Research*, B21, 251 (1943).

The results are summarized in Table XLVI.

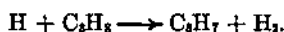
TABLE XLVI. REACTION OF HYDROGEN ATOMS WITH PROPYLENE

Temperature	% Reaction	Collision Yield X 10 ⁶	E (assuming A = 0.1)
30	44.9	0.918	7.0
100	42.3	1.63	8.3
170	39.0	1.95	9.6
250	38.8	2.92	10.8

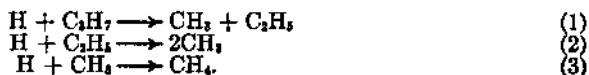
There appears to be no question that the primary step is



Once the primary step has occurred, it would be expected that the following reactions would be similar to those of propane (VI-12), since the propyl radical is there produced in the primary act also, by



Thus we might expect the reactions



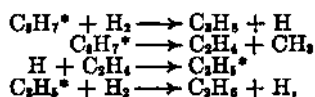
However there are two discrepancies:

- (a) Ethane is formed here at room temperature, but not with propane.
- (b) The H-atom concentration is too low to account for all these H-atom consuming steps.

They conclude therefore that after the formation of C₃H₇ the reaction must follow a course different from that of the propane reaction. Now reaction (10) is about 40 kcal. exothermic, and hence it may be written



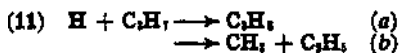
the resulting propyl radical having high energy. Such a radical might then, at room temperature, undergo reactions which would normally be expected only at high temperatures, viz.,



the ethyl radical being assumed to be "hot" for similar reasons. On this basis it is possible to account for their experimental results, including the temperature independence of the products.

They consider the room temperature value of the activation energy to be the most reliable. This value is, however, probably high because the large extent of reaction would reduce the H-atom concentration much below that found in blank experiments and used for the calculation. They

therefore consider that a value of about 5 kcal. is probably the best estimate for E_m .



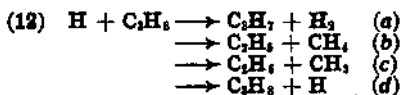
Trenner, Morikawa, and Taylor,¹ and Steacie and Parlee⁶⁷ in investigations of the reactions of deuterium atoms with propane found that although the products of the reaction (methane and ethane) were highly exchanged, the unreacted propane was deuterized to a negligible extent. This means that over a temperature range from room temperature to 250° the reaction



has not occurred to an appreciable extent. It must therefore be considerably slower than the reaction



The evidence for the occurrence of the latter reaction is discussed in some detail in section VI-12. There seems to be little doubt that it occurs readily, with an activation energy probably of 5 kcal. or less.



By mercury photosensitization Taylor and Hill⁸⁷ found that propane reacts somewhat faster with hydrogen atoms than does ethane, but more slowly than butane. In the course of another investigation Trenner, Morikawa, and Taylor* made two runs with propane and deuterium atoms produced by the Wood-Bonhoeffer method. They found that the products of the reaction were roughly 85 per cent methane and 15 per cent ethane at room temperature, and 65 per cent methane, 35 per cent ethane at 109°. The amount of decomposition was quite small, being 2.4 per cent at room temperature, and about 10 per cent at 109° when the deuterium atom concentration was 20 per cent. Propane is thus considerably less reactive than ethane, contrary to Taylor and Hill's findings. The methane and ethane were found to be highly deuterized, while the propane was not exchanged. They found no evidence of a catalytic recombination of hydrogen atoms in the presence of propane as reported previously by Bonhoeffer and Har-teck.²

The reaction of hydrogen atoms and propane has been investigated in more detail by the same method by Steacie and Parlee.⁵⁷ The most striking feature of their results was that the products of the reaction consisted ex-

⁸⁷ H. S. Taylor and D. G. Hill, *Z. physik. Chem*, B2, 449 (1929); *J. Am. Chem. Soc.*, 51, 2922 (1929).

clusively of methane at lower temperatures. At 100° ethane made its appearance, and at 250° there was over twice as much ethane as methane. At higher temperatures some ethylene was also formed. The results are illustrated in Figure 26.

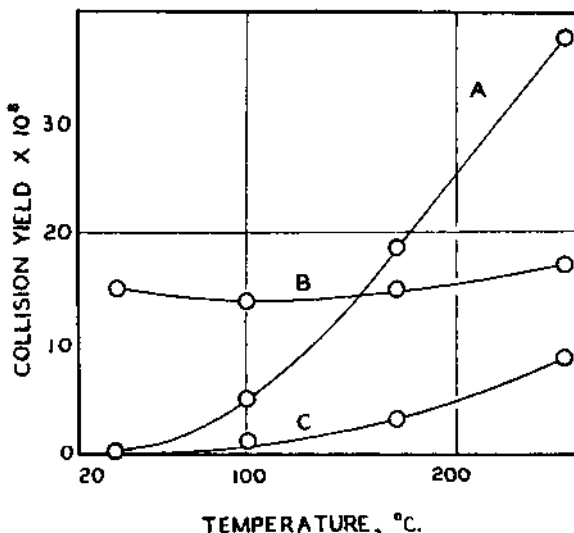
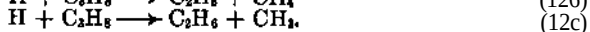
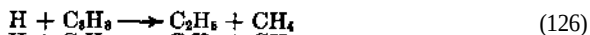


Figure 26. Collision yields of products in the reaction of hydrogen atoms with propane. A, Ethane. B, Methane. C, Ethylene.

There are obviously two possibilities for the primary reaction step, the abstraction of a hydrogen atom



or a hydrocarbon-chain splitting reaction



Conclusive evidence that (12a) is the primary step is obtained from an investigation by Steacie and Dewar⁸⁸ of the reaction of hydrogen atoms produced by mercury photosensitization with propane. They found the products under these circumstances to be virtually exclusively hydrogen and hexane at temperatures from 25° to 323°. This only can be the case if the primary step is reaction (12a). The non-appearance of hexane as a product in Steacie and Parlee's work is not surprising. In the mercury photosensitized reaction the pressure is high and the hydrogen atom concentration is very low. These conditions favor radical recombination reactions, and hexane is therefore to be expected if the propyl radical is present

⁸⁸ E. W.-R. Steacie and D. J. Dewar, *J. Chem. Phys.*, 8, 571 (1940).

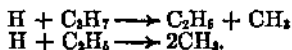
and has an appreciable life. Under the low pressure and high relative hydrogen concentration (atomic and molecular) of the discharge-tube method collisions between propyl radicals will be relatively rare, and the chance of a propyl radical reacting with hydrogen will be great. From these considerations the absence of hexane is to be expected.

Results of the investigation of the cadmium photosensitized reaction⁸⁹ also show that hydrogen and hexanes are the main products, and confirm (12a) as the primary step in the reaction of hydrogen atoms with propane.

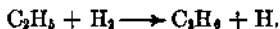
If the primary step is (12a) in Steacie and Parlee's investigation, then the propyl radicals produced must disappear at low temperatures without the formation of ethane. We cannot postulate appreciable decomposition of the propyl radical by the reaction



since all the evidence indicates that it is stable at room temperature. (See VI-59.) In any case the assumption of (1) as an important step would lead to difficulties since as shown in (VI-7) the main product of the reaction of hydrogen atoms with ethylene is ethane, and neither ethylene nor ethane occurs as a product at low temperatures. It must therefore be concluded that the propyl radicals disappear by a series of atomic cracking reactions

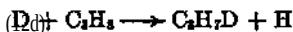


At higher temperatures ethylene and ethane are formed. The ethylene undoubtedly arises from the decomposition of the propyl radical by (1). Ethane is presumably formed by the reaction



From the temperature coefficient of the reaction Steacie and Parlee obtain a value of the activation energy of 10 ± 2 kcal. This is presumably the activation energy of reaction (12a). The reaction of hydrogen atoms with propane is therefore considerably slower than the reaction with ethane.

Experiments with deuterium atoms show that while the products (ethane and methane) are highly deuterized, the undecomposed propane is not appreciably deuterized, even at 250°. Any exchange reaction of the type



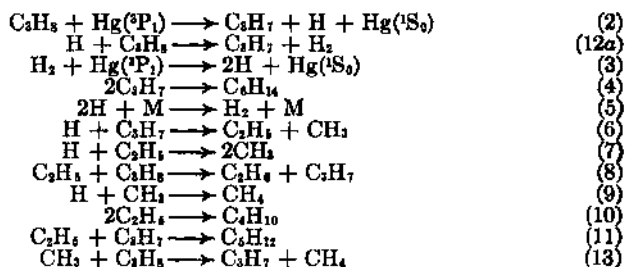
is therefore ruled out.

As discussed in section VI-9, there is a surprising difference between propane and ethane from the point of view of mercury photosensitization. With ethane much methane is formed even at room temperature and with single-pass flow experiments where hydrogen is not allowed to accumulate.

⁸⁹ E. W. R. Steacie, D. J. LeRoy, and R. Potvin, *J. Chem. Phys.*, 9, 306 (1941).

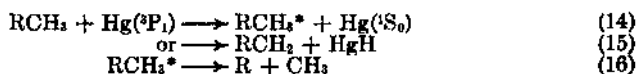
With propane, on the other hand, methane is not formed even when hydrogen accumulates in static runs. To obtain further light on this point an investigation was made^{89a} of the mercury photosensitized decomposition of propane over a wider range of pressure. At high propane pressures, methane production was negligible, in agreement with the results of Steacie and Dewar. At low pressures, however, of the order of 3 to 10 mm., the gaseous products contained over 30 per cent methane. The experiments were made in a circulating system in which higher products were removed continuously to prevent secondary reactions.

The results with propane at low pressures thus agree with those with ethane at high pressures. The production of C₂ and C₄ hydrocarbons also increased with decreasing propane pressure. The complete mechanism proposed by Steacie and Dewar for the mercury photosensitized reaction at higher pressures was:



At higher pressures their results led to the conclusion that only reactions (12a), (2), (3), and (4) were of much importance. At low pressures this mechanism will give agreement with the facts, since a decrease in [C₃H₈] will lead to an increase in the rate of reaction (6) relative to (12a), and methane will therefore be produced at the expense of hexane. It therefore appears that the reactions of propane and ethane with excited mercury are fundamentally of the same type. The difference in the extent of atomic cracking with ethane and propane at a given pressure is, however, surprisingly large. It seems very difficult to explain this since the atomic cracking reactions with ethyl and propyl must both have very low activation energies. Further since the activation energy of (12a) is *higher* than that of the analogous reaction with ethane, it seems certain that the stationary H-atom concentration under comparable conditions is *higher* in the case of propane than it is with ethane.

It is possible that the results are to be explained on the basis of an excited molecule mechanism of the type:



^{89a} B. deB. Darwent and E. W. R. Steacie, unpublished results.

This would explain the facts if it were assumed that (15) is preferred in the case of propane because of the weaker secondary C—H bonds. This is, however, purely speculative, and at the moment no really satisfactory explanation of the difference between propane and ethane exists.

In the presence of added hydrogen it was found that at low pressures (0.75 to 3 mm.) of propane, the rate of disappearance of propane decreased with increasing hydrogen pressure, while the relative amount of methane produced increased. There is no question that with increasing amounts of hydrogen present more and more of the quenching will be by hydrogen rather than by propane. The stationary H-atom concentration will therefore increase and more atomic cracking will occur. The decreased total rate is presumably to be attributed to increased recombination of H-atoms.



This reaction with a low activation energy appears to be a step in the mercury photosensitized polymerization and hydrogenation of butadiene.⁸⁹⁶ (See IV-9.)



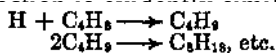
This reaction is probably a step in the mechanism of the mercury photosensitized hydrogenation of butadiene.⁸⁹⁶ (See IV-9.)



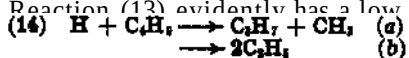
Moore and Taylor⁸⁶ investigated the products of the mercury photosensitized reactions of butene-hydrogen mixtures, and obtained results similar to those with propylene, viz.,

CH_4	3 per cent
C_2H_4	1 " "
C_2H_6	1 " "
C_4H_{10}	29 " "
C_3H_{10}	66 " "

The mechanism of the reaction is undoubtedly similar to that of propylene:

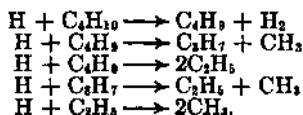


Reaction (13) evidently has a low activation energy.



The reaction of H-atoms with n-butane has been investigated by Steacie and Brown.⁵⁸ (See VI-15.) The results were similar to those of the reaction with propane. At room temperature methane was the sole product of^{89b} H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, 12,484 (1944).

the reaction, and they conclude that its exclusive formation **can only be** accounted for by a series of atomic cracking reactions



The reaction of H-atoms with iso-butane is similar to that with n-butane,⁹⁰ and the reaction



thus appears to occur readily. (See also VI-66.)

(15) $\text{H} + n\text{-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2$

Taylor and Hill⁸⁷ found, using mercury photosensitization, that butane reacts somewhat faster with hydrogen atoms than propane. Trenner, Morikawa, and Taylor⁷³ made one run with n-butane and deuterium atoms produced by the discharge-tube method. They found about **11** per cent decomposition (with a deuterium atom concentration of 20 per cent) at 110° to give methane, ethane, and propane as products. The methane and ethane were highly exchanged, while the recovered butane was not deuterized at all. The amount of reaction was slightly greater than that of propane under identical conditions, but the difference is almost certainly within the experimental error.

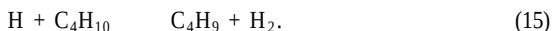
A more comprehensive investigation by the discharge-tube method was made by Steacie and Brown.⁵⁸ They investigated the reaction of n-butane over the temperature range 35° to 250°, and found results exactly parallel to those obtained with propane by Steacie and Parlee.⁵⁷ The products of the reaction were solely methane and ethane, as shown in Table XLVII.

TABLE XLVII. PRODUCTS OF THE REACTION OF HYDROGEN ATOMS
WITH n-BUTANE

Temperature	Per cent butane converted to	
	CH ₄	C ₂ H ₆
35	11.8	0.0
100	7.9	2.8
170	5.8	8.3
250	4.4	10.5

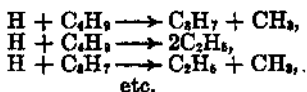
The results correspond to an activation energy of 9 ± 1.5 kcal., assuming a steric factor of 0.1.

Using the arguments previously cited in the case of propane, they conclude that the primary step is the reaction

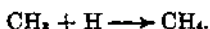


⁹⁰ W. H. White, C. A. Winkler, and B. J. Kenalty, *Can. J. Research*, B20, 255 (1942).

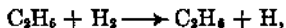
At low temperatures this is assumed to be followed by a series of atomic cracking reactions



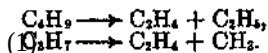
and ultimately by



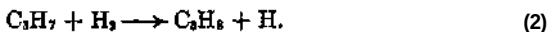
At higher temperatures ethane formation undoubtedly occurs by



and decomposition reactions of radicals also occur, such as



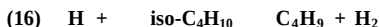
The absence of propane requires explanation, since it would be expected that it would be formed by



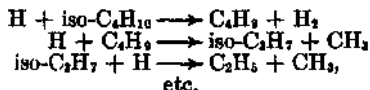
Its absence must be due to the fact that (2) only becomes appreciable at temperatures where (1) is fast enough to destroy the propyl radicals before they can react.

White, Winkler, and Kenalty,⁹⁰ in the course of an investigation of the reaction of H-atoms with iso-butane (VI-16), compared the rate with that of n-butane. They conclude that the H-atom concentrations in Steacie and Brown's work were really higher than those reported. In view of their work it appears that the activation energy reported by Steacie and Brown is somewhat low, and 10 ± 1.5 kcal. is probably a more reliable value.

Reaction (15) is also probably involved⁹¹ in the mercury photosensitized decomposition of n-butane. (See VI-66.)

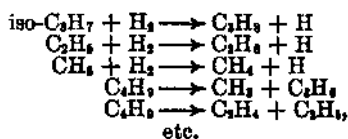


The reaction of hydrogen atoms with iso-butane has been investigated in a manner similar to that with n-butane by White, Winkler, and Kenalty.⁹⁰ The reaction resembles that of n-butane but is somewhat slower. The activation energy is 10.5 ± 1.5 kcal. At lower temperatures methane is the only product, while at higher temperatures ethane and a small amount of propane are formed. They propose a mechanism similar to that for n-butane in every way, viz.,



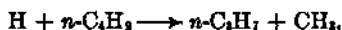
⁹¹ A. W. Hay and C. A. Winkler, *Can. J. Research*, B21, 149 (1943).

At higher temperatures reactions such as



also come into play.

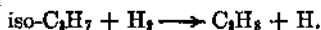
The only difference in the products as compared with n-butane is the presence of a small amount of propane. They point out that perhaps the reaction of H with n-butyl is



while with iso-butyl



If this is the case, considering that there is some evidence that the iso-propyl radical is more stable than the n-propyl,⁹² this might explain the survival of some iso-C₃H₇ for long enough to yield appreciable amounts of C₃H₈ by the reaction



Reaction (15) is also probably involved in the mercury photosensitized reaction of iso-butane. (See VI-66.)

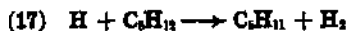
Comparison of the reactions of Hydrogen Atoms with the lower paraffins

The activation energies of these reactions, on the basis of the results discussed in previous sections, are:

$\text{H} + \text{CH}_4$	$13 \pm 2 \text{ kcal.}$
$\text{H} + \text{C}_2\text{H}_6$	6.7 ± 1
$\text{H} + \text{C}_2\text{H}_4$	10 ± 2
$\text{H} + n\text{-C}_4\text{H}_{10}$	10 ± 1.5
$\text{H} + \text{iso-C}_4\text{H}_{10}$	10 ± 1.5

From the relative rates of the reactions under comparable conditions there is no question that the reaction with methane is slower than the others, and that with ethane is faster. The difference between methane and ethane is undoubtedly to be ascribed to the large decrease in C—H bond strength on going from methane to ethane. In view of the uncertainties of the data, the possibility cannot be excluded that at least a part, and perhaps all, of the difference between the higher hydrocarbons and ethane might be due to a diminished steric factor rather than to an increased activation energy. Actually under comparable conditions n-butane reacts faster than iso-butane or propane. Whether this is due to different steric factors or to small differences in activation energy cannot be decided with the data available.

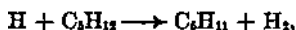
⁹² H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, 1936, 1777.



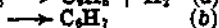
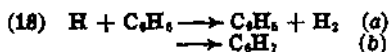
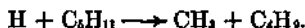
Comparatively little work has been done on the reactions of hydrogen atoms with the higher paraffins.

Bonhoeffer and Harteck² investigated in a purely qualitative way the reaction of hydrogen atoms produced by the discharge-tube method with pentane. Methane, ethylene, acetylene, and propane were identified among the products. From their work it may be estimated that the activation energy of the reaction is not over 10 kcal.

Frankenburger and Zell⁹³ investigated the same reaction using hydrogen atoms produced by photosensitization with mercury. With their technique they were unable to detect methane, ethane, and other low-boiling substances, but they detected higher hydrocarbons with 6, 7, 8, and 10 carbon atoms. They suggest, therefore, that the primary step is not exclusively the reaction



but that hydrocarbon chain splitting reactions also occur. However, in view of more recent work on the lower paraffins, it is probable that the hydrocarbons with 6 to 8 carbon atoms arise by atomic cracking reactions such as



A qualitative investigation of the reaction of hydrogen atoms with benzene, by the discharge-tube method, was made by Bonhoeffer and Harteck,² who found that much methane was produced together with some ethane, ethylene, and acetylene. Since the reaction occurred readily under their experimental conditions, the activation energy must be not over 10 kcal., if a steric factor of 0.1 is assumed.

Geib and Harteck²⁶ found that at liquid-air temperature hydrogen atoms still reacted with benzene. The only process occurring under these circumstances was hydrogenation, so that the primary process is presumably (186). Under these conditions the reaction probably occurs at the wall.

Forbes and Cline⁹⁴ investigated the mercury photosensitized reactions of benzene and benzene-hydrogen mixtures using X1849. On the grounds that the results were the same with benzene alone even when mercury vapor was "pretty completely trapped out at -8° ," they conclude that the mercury photosensitized reaction of benzene alone is negligible, and that with mercury-benzene-hydrogen mixtures the primary act is entirely



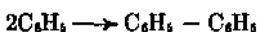
⁹³ W. Frankenburger and R. Zell, *Z. physik. Chem.*, B2, 395 (1929).

⁹⁴ G. S. Forbes and J. E. Cline, *J. Am. Chem. Soc.*, 63, 1713 (1941).

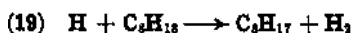
The second reaction is assumed on the ground that the products were mainly hydrogenated diphenyls and cyclohexadiene. Their conclusions are, however, open to question. In the first place the use of a trap at -8° will not reduce the mercury vapor pressure sufficiently to have any effect since the absorption coefficient of X1849 is extremely high. Hence the main primary reaction may well be



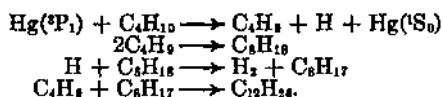
Secondly, the hydrogenated diphenyls can equally well be accounted for by the formation of diphenyl by the reaction



and its subsequent hydrogenation. Their results therefore give little information concerning the relative probabilities of reactions (18a) and (186).

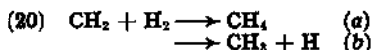


Hay and Winkler⁹¹ found dodecanes as one of the principal products of the mercury photosensitized reactions of n-butane. There appears to be no doubt that they arise, at least in part by the sequence



(See section VI-66 for details.)

The mercury photosensitized reaction of iso-butane appears to proceed by a similar mechanism.^{94a} (See VI-66.)



Kassel⁹⁵ investigated the thermal decomposition of methane. On the basis of a rather complex mechanism for the reaction he assigned an activation energy of 32 kcal. to reaction (20a). His mechanism is, however, highly speculative. (See III-4.)

Bawn and Milsted⁹⁶ investigated the reaction of methylene bromide with sodium. The primary step is undoubtedly



In the absence of hydrogen the main product was ethylene, i.e.,



^{94a} B. deB. Darwent and C. A. Winkler, *J. Phys. Chem.*, in press.

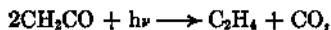
⁹⁵ L. S. Kassel, *J. Am. Chem. Soc.*, 54, 3949 (1932).

⁹⁶ C. E. H. Bawn and J. Milsted, *Trans. Faraday Soc.*, 35, 889 (1939); see also C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, 35, 185 (1939).

Similar results were obtained with methylene iodide. In the presence of hydrogen, however, methane was the main product, presumably as a result of the occurrence of reaction (20a). To account for the rapid occurrence of (20a) at 300°, it must be assumed to have a relatively low activation energy. They point out that (20a) is strongly exothermic, while (206) would be somewhat endothermic, and hence would be negligible compared with (20a).

Results which appear to be fundamentally different from those of Bawn and Milsted were obtained by Rosenblum⁹⁷ who investigated the photolysis of ketene in the presence of hydrogen. At 35° of the ketene decomposed 1 per cent gave methane, 74 per cent gave a gas with an average composition C2.56 H7.12, and 25 per cent gave a non-volatile residue. At 200° 9.6 per cent gave methane, 69 per cent gave a gas of similar composition to the above, and 21 per cent gave the residue.

In a later paper⁹⁸ Rosenblum reported a more detailed investigation of the photolysis, especially at smaller percentage conversions. With ketene alone the overall photolysis is

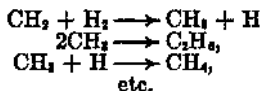


followed by polymerization of ethylene, presumably sensitized by methylene. In the presence of added gases the amount of ketene decomposed is independent of what other processes may occur, which suggests that



is the only primary reaction occurring, and that all other reactions are due to the methylene radicals produced in (1).

In the presence of hydrogen saturated hydrocarbons appear as products. Rosenblum suggests that these are formed by



He considers the reaction

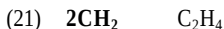


to be unlikely since increase in intensity (*i.e.*, in $[\text{CH}_2]$) does not increase methane production. On the other hand, as pointed out above reaction (206) is somewhat endothermic.

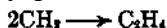
In view of the fact that Bawn and Milsted's results were obtained at 300°, and that Rosenblum found a definite increase in methane with increasing temperature, the two investigations are not necessarily in conflict. There is, however, a decided difference of opinion as to whether (20a) or (20b) is the predominant reaction of methylene with hydrogen.

⁹⁷ C. Rosenblum, *J. Am. Chem. Soc.*, 60, 2819 (1938).

⁹⁸ C. Rosenblum, *J. Am. Chem. Soc.*, 63, 3322 (1941).



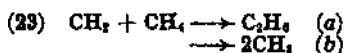
Pearson, Purcell, and Saigh⁹⁹ photodecomposed ketene and detected the methylene radical in the products by the mirror method. The half-life of the radicals was unusually great, about 0.2 sec, and hence the reaction



is slower than other radical recombinations, and must have an appreciable activation energy. There is, however, little doubt that it does occur in the photolysis of ketene^{98,100} at room temperature, and in the reaction of methylene halides with sodium vapor at 300°. ⁹⁶ (See XII-18 and XII-20.)



This reaction has been postulated by Rosenblum⁹⁸ to explain the formation of saturated hydrocarbons when ketene is photolysed in the presence of hydrogen.



Kassel⁹⁵ investigated the thermal decomposition of methane and concluded that the primary step was

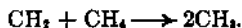


and that this was followed by



From an analysis of the mechanism Kassel assigned an activation energy of 44 kcal. to reaction (23a). His mechanism is, however, highly speculative (see III-4), and this value cannot be given much weight.

Pearson, Purcell, and Saigh⁹⁹ prepared methylene by the decomposition of ketene and diazomethane, and investigated its properties. The life of the methylene radical at room temperature was found to be relatively great (ca. 0.2 sec), and methane had little effect on this life, so that reaction (23) must be slow at room temperature, although it must occur at higher temperatures. They suggest that the methyl radicals detected by Rice and Dooley in the decomposition of methane were the result of the secondary reaction



However, as we have seen previously (III-4), it is doubtful if this is the case.

Bawn and his co-workers,⁹⁶ in the investigation referred to in section V I - 20 found that ethane was not produced at 300° in the reaction of methylene

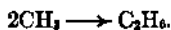
⁹⁹ T. G. Pearson, R. H. Purcell, and G. S. Saigh, *J. Chem. Soc.*, **1938**, 409.

¹⁰⁰ W. F. Ross and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 1112 (1934).

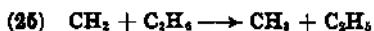
bromide with sodium, and they therefore conclude¹⁰¹ that reaction (23a) is negligible at this temperature.

In the investigation of Rosenblum,⁹⁸ referred to in VI-20, it was found that in the presence of methane saturated hydrocarbons were formed at the expense of the methane, just as with added hydrogen. He therefore suggests the occurrence of (236).

All in all the evidence for reaction (23) is thus rather sketchy. The activation energy is probably considerable. There also appears to be a definite divergence of opinion as to whether (23a) or (236) is occurring under any given set of conditions. It seems likely, however, that (236) is the important reaction, and that if ethane is formed by the reaction of methylene and methane it arises by (236), followed by



It has been shown^{97,98, 102} that the polymerization of ethylene can be sensitized by methylene from the photolysis of ketene at room temperature. The mechanism probably involves reaction (24), and if this is true it must have a very small activation energy.



Rosenblum⁹⁸ found polymerization in systems containing methylene and ethane, possibly owing to the occurrence of (25), etc.



Rice and Glasebrook¹⁰³ investigated the decomposition of diazomethane by their usual technique, using butane as a carrier gas. At temperatures below 550° methylene radicals were detected, but at higher temperatures only methyl radicals were found. They conclude that the disappearance of methylene and appearance of methyl at higher temperatures is satisfactorily explained provided that the reaction



has an activation energy of about 15 ± 5 kcal.



The activation energy of this reaction was first estimated to be about 8 kcal. by von Hartel and Polanyi,^{103a} who investigated the reaction of

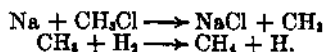
¹⁰¹ C. E. H. Bawn, *Trans. Faraday Soc.*, 35, 898 (1939).

¹⁰² M. Burton, T. W. Davis, and H. A. Taylor, *J. Am. Chem. Soc.*, 63, 1956 (1941).

¹⁰³ F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, 55, 4329 (1933), 66, 2381 (1934).

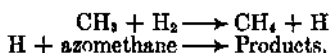
^{103a} H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, B 11, 97 (1930).

sodium vapor with methyl chloride using hydrogen as a carrier gas for the sodium. A certain amount of methane is formed under these conditions, which they assume arises by the mechanism



By using the hydrogen consumption over a range of temperature as a measure of the latter step, they estimated its activation energy. The result is not very certain, however, since they were not really very sure of the exact mechanism of the formation of methane, and there is also the possibility of an alteration in the concentration of methyl radicals with increased temperature owing to other secondary reactions.

Indirect information about the reaction was obtained by Sickman and Rice.¹⁰⁴ In an investigation of the effect of foreign gases on the azomethane decomposition they found that hydrogen is not an "inert gas," while deuterium is. They conclude that this is due to the occurrence of the processes



one of the two reactions being much faster with hydrogen than with deuterium. In view of the lack of plausibility of such an explanation, and of the indirect nature of the evidence, not much can be deduced from this work about the reaction under discussion, except perhaps that it occurs to some extent around 200°.

Considerable information about the reaction between methyl radicals and hydrogen comes from the work of Patat and Sachsse¹⁰⁵ on the rate of the para-ortho hydrogen conversion in systems containing decomposing organic compounds. This rate is higher than would be expected from the thermal equilibrium concentration of hydrogen atoms. On the assumption that methyl radicals are formed by the pyrolysis of organic compounds, and that these produce atomic hydrogen by reaction (27) they have calculated the methyl radical concentration in a number of organic decomposition reactions. In all cases a radical concentration is found which is much smaller than that predicted by the Rice-Herzfeld theory.¹⁰⁶ In particular Patat investigated the concentration of methyl radicals and of hydrogen atoms present during the photodecomposition of acetaldehyde. He found that, with certain assumptions regarding the mechanism of the photodecomposition, in order to get agreement with v. Hartel and Polanyi's experimental value of E_{27} it was necessary to assume the very low steric

¹⁰⁴ D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, **4**, 608 (1936).

¹⁰⁵ F. Patat and H. Sachsse, *Z. physik. Chem.*, **B31**, 105 (1935); H. Sachsse, *Z. physik. Chem.*, **B31**, 79 (1935); F. Patat, *Z. physik. Chem.*, **B32**, 274, 294 (1936).

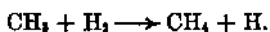
¹⁰⁶ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **66**, 284 (1934).

¹⁰⁷ See W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 396 (1940).

factor of 10^{-4} . If the steric factor is taken as unity, Patat's results lead to a value of 20 kcal. It should, however, be pointed out that Eyring's activated complex theory leads to the expectation of small steric factors in such reactions.⁶

In order to get the best agreement with free radical mechanisms, Rice¹⁰⁸ arbitrarily put the activation energy of (27) equal to 23 kcal. He points out that if v. Hartel and Polanyi's estimate of 8 kcal. were correct, it should be impossible to get appreciable quantities of methyl radicals in the presence of hydrogen, whereas in fact it is possible to do so. However, there seems to be no doubt that Rice's estimate is too high. In any case the argument would not be valid if the steric factor were very low.

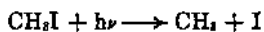
Paneth, Hofeditz, and Wunsch¹⁰⁹ investigated the rate of recombination of methyl radicals, using both hydrogen and helium as carrier gases. They found that the loss of methyl radicals was more rapid in hydrogen than in helium, even at room temperature. Under these conditions methane is formed, presumably by



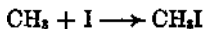
Their data indicate that the activation energy of the reaction is about 15 kcal. (or lower if a low steric factor is assumed).

On the ground that methyl radicals do not appear to react with hydrogen at temperatures below 165°, Trenner, Morikawa, and Taylor¹¹⁰ assumed an activation energy of 11.1 kcal., combined with a steric factor of 0.1.

Spence and Wild¹¹¹ found that hydrogen has little influence on the photolysis of methyl iodide. There is no question that the primary step is



and that the low quantum yield of the reaction (ca. 0.02) is due to the ready occurrence of the reverse reaction. The absence of appreciable methane formation in the presence of hydrogen shows that reaction (27) is slow compared with the reaction



and Spence and Wild conclude that E_{27} must be at least as great as 8 kcal.

H. S. Taylor and Rosenblum¹¹² investigated the photolysis of acetone in the presence of hydrogen. (See V-6 and VI-28.) Assuming that the increased methane production when hydrogen is present is due to reaction (27)

¹⁰⁸ F. O. Rice, *J. Am. Chem. Soc.*, 56, 488 (1934).

¹⁰⁹ F. Paneth, W. Hofeditz, and A. Wunsch, *J. Chem. Soc.*, 1935, 372.

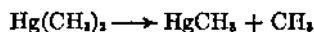
¹¹⁰ N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, 6, 203 (1937); K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Chem. Phys.*, 5, 212 (1937).

¹¹¹ R. Spence and W. Wild, *Proc. Leeds Phil. Soc.*, 3, 141 (1936); see also J. R. Bates and R. Spence, *Trans. Faraday Soc.*, 27, 468 (1931); *J. Am. Chem. Soc.*, 63, 1689 (1931).

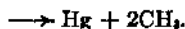
¹¹² H. S. Taylor and C. Rosenblum, *J. Chem. Phys.*, 6, 119 (1938).

they estimate in a way which they admit is not "unequivocal" an activation energy of 11 ± 2 kcal. for (27). While this estimate is somewhat doubtful, it at least appears to be of the right order of magnitude.

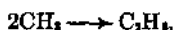
More definite information is obtained from the work of Cunningham and H. S. Taylor,¹¹³ who investigated the thermal and photochemical decomposition of mercury dimethyl. There is no doubt that this decomposition yields methyl radicals.¹¹⁴ The primary process in the photodecomposition may yield 2 methyl radicals, or may involve the intermediate formation of HgCH_3 , i.e.,



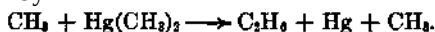
or



Ethane formation occurs by the reaction



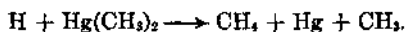
and also probably by



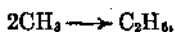
In the presence of hydrogen the rate increases several fold, and the formation of methane is greatly increased. They interpret this as due to



and



On the basis of this mechanism a steady state treatment of the results yields a value of 8.1 kcal. for the activation energy of reaction (27), if it is assumed that $E = 0$ for the reaction



or a somewhat lower value if a small activation energy be assumed for this reaction. Cunningham and H. S. Taylor conclude that from their investigation and that of H. S. Taylor and Rosenblum, the "best" value of the activation energy of reaction (27) is 9 ± 2 kcal.

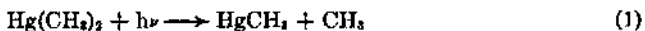
In a further investigation Smith and H. S. Taylor¹¹⁵ studied the reaction of methyl radicals with deuterium by the above method. Their results lead to an apparent activation energy of 8.1 kcal. for the temperature coefficient of methane formation. They point out that the following principal facts have to be explained: (1) The formation of ethane in the absence and presence of hydrogen or deuterium remains unchanged. (2) The formation of methane increases rapidly with temperature, and this increase is paralleled by an increase in the rate of decomposition of mercury dimethyl.

¹¹³ J. P. Cunningham and H. S. Taylor, *J. Chern. Phys.*, 6, 359 (1938).

¹¹⁴ J. W. Linnett and H. W. Thompson, *Trans. Faraday Soc.*, 33, 501, 874 (1937); P. A. Leighton and R. A. Mortensen, *J. Am. Chem. Soc.*, 68, 448 (1936); A. Terenin, *J. Chem. Phys.*, 2, 441 (1934); *Acta Physicochimica* (U.R.S.S.), 1, 762 (1935); A. Terenin and N. Prileshajeva, *Trans. Faraday Soc.*, 31, 1483 (1935).

¹¹⁵ J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, 7, 390 (1939).

(3) The formation of ethane shows a first-order dependence on light intensity, while the methane production shows an order between 0.5 and 1, increasing toward unity with increasing temperature. (4) Packing the vessel at 200° cuts down the amount of methane formed, but does not affect the ethane production. (5) The mercury dimethyl decomposes photochemically into free radicals. (6) The rate of mercury dimethyl decomposition is independent of its concentration. To satisfy these requirements they propose the mechanism:

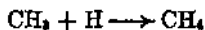


Whence by the usual stationary state method they obtain the expression

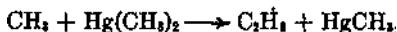
$$\frac{d[\text{CH}_4]}{dt} = k_{\text{CH}_4} = \frac{2k_4k_1I_{\text{abs.}}}{k_3} + 2k_{27} \left(\frac{k_1I_{\text{abs.}}}{k_3} \right)^{\frac{1}{2}} [\text{D}_2].$$

They assume that k_1 , $I_{\text{abs.}}$, k_3 , and k_4 are independent of temperature, and hence calculate k_{27} from the "observed variation of the methane production with temperature. The constancy of k_1 and $I_{\text{abs.}}$ over the temperature range appears to be established. k_3 is assumed to be independent of temperature, since in general the evidence points strongly to a very low activation energy for this reaction. (There are, however, some contrary indications.¹¹⁶) k_4 is probably unimportant in any case. On this basis they obtain a value of E_{27} of 8.1kcal.

The reason that reaction (4) is assumed at all is that the rate of methane formation is dependent on a power of the light intensity between 0.5 and 1.0. This points in part to a bimolecular formation of methane. Smith and H. S. Taylor assume reaction (4) because they feel that the reaction



cannot be important since otherwise the accelerating effect of hydrogen on the dimethyl decomposition is hard to explain. There is, however, the possibility of this reaction occurring to some extent, and also the reaction



or others of a similar type.

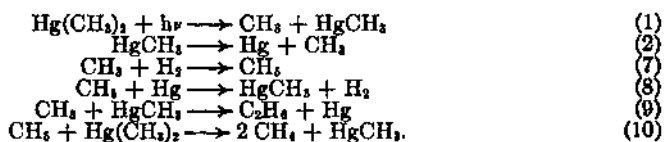
An objection to this mechanism has been raised by H. A. Taylor and Burton.¹¹⁷ Leighton and Mortensen¹¹⁴ in studying the analogous decomposition of lead tetramethyl pointed out that the observed quantum yield of 1.11 might be a compensated result of chains together with recombination

¹¹⁶ T. W. Davis, F. P. Jahn, and M. Burton, *J. Am. Chem. Soc.*, 60, 10 (1938).

¹¹⁷ H. A. Taylor and M. Burton, *J. Chem. Phys.*, 7, 676 (1939).

of metal atoms with alkyl radicals. (Such a recombination must occur to some extent since metal mirrors can be used as detectors for radicals.) H. A. Taylor and Burton suggest that this recombination may also be important in Cunningham and H. S. Taylor's investigation, and that the accelerating effect of hydrogen is due to a reduction in recombination.

H. A. Taylor and Flowers¹¹⁸ have discussed the mechanism of the mercury dimethyl photolysis in the presence of hydrogen. They suggest that CH₅ formation from CH₃ and H₂ may be important. (In effect this is merely equivalent to assuming unusually "sticky" collisions between methyl and hydrogen, and hence assuming that hydrogen will be an unusually efficient third body in recombination reactions involving methyl.) They postulate the following mechanism:



Whence by the usual steady state method

$$\begin{aligned}
 \frac{d[\text{C}_2\text{H}_6]}{dt} &= k_1 I_{\text{abs.}} \\
 \frac{d}{dt} [\text{CH}_4] &= \frac{2}{(k_8[\text{Hg}]/k_{10}[\text{Hg}(\text{CH}_3)_2]) + 1} \left(\frac{k_1 I_{\text{abs.}} k_2 k_7 [\text{H}_2]}{k_9} \right)^{\frac{1}{2}}
 \end{aligned}$$

On this basis, therefore, the rate of production of ethane is independent of the concentration of hydrogen and mercury dimethyl as found experimentally. From the mechanism the rate of production of methane should be proportional to the square root of the hydrogen concentration. Hence the overall rate of decomposition

$$-\frac{d}{dt} [\text{Hg}(\text{CH}_3)_2] = \frac{d}{dt} [\text{C}_2\text{H}_6] + \frac{1}{2} \frac{d}{dt} [\text{CH}_4]$$

should be somewhat dependent on the hydrogen concentration and on the mercury dimethyl concentration. Actually, the effects are complex and are also dependent on the concentration of mercury, and may well be within the experimental error.

Very roughly from the above E_M , the activation energy of methane production should be given by

$$E_M = E_{10} - \frac{1}{2} E_7.$$

Saunders and H. A. Taylor found $E = 13 - 14$ kcal. for the reaction of methyl with mercury dimethyl and hence infer that E_{10} is probably about 13 kcal. In the opinion of the writer, however, there is no justification whatever for this conclusion. A rough calculation by Eyring's method,

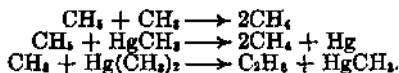
¹¹⁸ H. A. Taylor and R. G. Flowers, *J. Chem. Phys.*, 10, 110 (1942).

assuming the $\text{CH}_3\text{—Hg}$ bond to be 35 kcal., gave 10 kcal. for E_9 . Hence they conclude

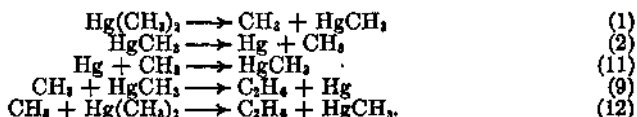
$$E_M = 13 - 5 = 8 \text{ kcal.}$$

This agrees with Cunningham and H. S. Taylor's value of 8.1 kcal., and they therefore suggest that E_M as deduced by Cunningham and H. S. Taylor is without significance. Whatever the status of H. A. Taylor and Flowers' suggested mechanism may be, however, it is evident that the above calculation has little meaning.

H. A. Taylor and Flowers also suggest the occurrence to a lesser degree of the reactions



Cunningham and H. S. Taylor found ethane production, in the presence or absence of hydrogen, to have a temperature coefficient equivalent to 1.5 kcal. In the absence of hydrogen, where the situation is relatively simple, H. A. Taylor and Flowers suggest the mechanism



This, very approximately, yields for the activation energy of ethane production,

$$E_E = E_{12} - \frac{1}{2}(E_1 + E_{12}).$$

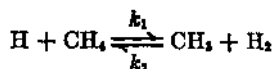
Putting $E_{12} = 13$, $E_9 = 10$, we get $E_E = 1.5$ kcal. in agreement with experiment. Since this value is obtained from the difference between two uncertain values, it is without much significance. On the basis of their calculations H. A. Taylor and Flowers conclude: "The decomposition of mercury dimethyl is thus adequately explained, and the similarity to the azomethane scheme lends credence to the suggested mechanism. The reaction of methyl radicals with hydrogen would not appear to involve hydrogen atoms and the *observed* value 9 ± 2 kcal. is complex and in no way specific of methane production from methyl and hydrogen." We will return again later to the question. It may be remarked here, however, that none of the alternatives to the mechanism of H. S. Taylor and Cunningham appears to possess much plausibility, and their mechanism seems to be on firm ground.

The strength of the C—H bond in methane

From the foregoing summary and the discussion of the reaction



the main body of evidence indicates that the activation energies for the reaction



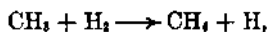
are about $E_1 = 13 \pm 2$ kcal., $E_2 = 9 \pm 2$ kcal. It follows, therefore, that the reaction as written is 4 ± 4 kcal. endothermic. Hence since

$$\text{H}_2 \approx 2\text{H} - 102.5 \text{ kcal.},$$

we have

$$\text{CH}_4 = \text{CH}_3 + \text{H} - 106.5 \text{ kcal.}$$

In other words the C—H bond strength in methane is about 106.5 ± 4 kcal. A value of this magnitude was first derived in the manner indicated by Trenner, Morikawa, and H. S. Taylor.¹¹⁰ At the time the estimate was made the consensus of opinion was that the C—H bond strength in methane was not over 95 kcal., and the calculated value thus appeared to be very high. It did not appear possible, furthermore, to reconcile the values on the basis of experimental errors in E_1 or E_2 , since both these values were well established by the results of a number of different methods of investigation. Recently a number of different methods have indicated (see section III—1) that the correct value of the C—H bond strength in methane is about 102 ± 1 kcal., and there is thus no discrepancy. At the time, however, a discrepancy appeared very definitely to exist, and H. A. Taylor and Burton¹¹⁷ suggested the following explanation: They pointed out that in most investigations bearing on the subject what is observed is not direct evidence for the reaction

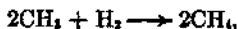


but rather that the addition of hydrogen to a system containing methyl radicals leads to the formation of methane and to a diminution in ethane formation by recombination of methyl radicals. They suggested that instead methane production is a result of the reaction

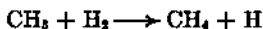


and that the evidence for the formation of hydrogen atoms accompanying the disappearance of methyl radicals is in most cases not conclusive. "Perhaps the most convincing evidence for the production of hydrogen atoms from methyl radicals and molecular hydrogen is to be found in the observations by Patat and Sachsse¹⁰⁵ of a rate of para- to ortho-hydrogen conversion in systems containing methyl radicals which is higher than that to be expected from the equilibrium concentration of hydrogen atoms at the temperature of the experiments. On the assumption that methyl radicals produce hydrogen atoms by reaction with hydrogen, they have measured the radical concentration in numerous organic pyrolyses. It is extremely significant that they find in all cases a radical concentration that is much smaller than that to be expected on the basis of current theory. It

is surprising that the possibility of a disappearance of methyl radicals other than by a reaction producing hydrogen atoms has not been seriously considered." H. A. Taylor and Burton therefore suggested that the experimentally determined activation energy of ca. 9 kcal. is to be assigned to the reaction

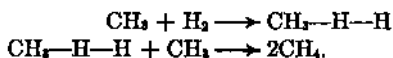


and that the reaction

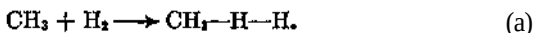


has a considerably higher activation energy, which they tentatively put at 19 kcal. If we accept this estimate, and combine it with a value of 13 kcal. for the back reaction, we obtain for the C—H bond strength in methane a value of $102.5 - 6 = 96.5$ kcal.

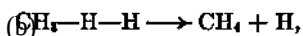
It is possible to combine this mechanism with the suggestions of Gorin, Kauzmann, Walter, and Eyring,¹¹⁹ and substitute two bimolecular steps for the termolecular mechanism proposed above, viz.,



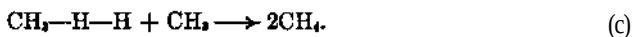
It will be observed that this mechanism is equivalent to assuming that the first reaction of methyl with hydrogen is in every case



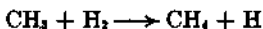
The complex can then decompose



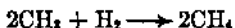
or react with a further methyl radical



If we assume that (c) has a lower activation energy than (6), then at high temperatures or low methyl radical concentrations (b) will predominate, and the overall process will be



with an activation energy of about 20 kcal. At lower temperatures, or high methyl radical concentrations, (c) will predominate, and the overall process will be

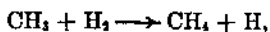


with an activation energy of about 10 kcal. This mechanism can be easily reconciled with the results of v. Hartel and Polanyi, and of most of the other workers. The main argument against it comes from the work of H. S. Taylor and his collaborators. It is very difficult to see how the results of Cunningham and H. S. Taylor and of Smith and H. S. Taylor on the reactions of mercury dimethyl, discussed above, can be reconciled with H. A. Taylor and Burton's mechanism. The main feature of their results is that

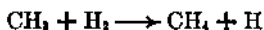
¹¹⁹ E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, 7, 633 (1939).

the addition of hydrogen to the system greatly increases the overall production of methane. H. A. Taylor and Burton's suggested explanation of their results has been discussed above.

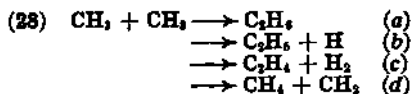
In view of the fact that the recent values of the C—H bond strength are in good agreement with that calculated on the assumption, that the activation energy of the reaction



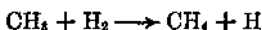
is 9 kcal., it is no longer necessary to find another mechanism and H. A. Taylor and Burton's suggestion loses its original objective. On account of the very frequent occurrence of reactions between methyl and hydrogen, the question is an important one. In, the opinion of the writer the evidence very strongly favors the simple mechanism, and we may take it to be rather definitely established that the reaction occurring in systems containing methyl radicals and hydrogen molecules is



with an activation energy of approximately 9 kcal.



Paneth and Hofeditz¹²⁰ in the original experiments on the free methyl radical found a rapid disappearance of the radicals once formed. At room temperature the half-life was 0.006 sec. under their experimental conditions. Paneth and Lautsch¹²¹ found that the rate of disappearance of methyl radicals was not appreciably different in the presence of nitrogen, helium, neon, or argon as carrier gases at room temperature. This indicates that the predominant reaction is recombination, and that reactions such as



are not prominent under their experimental conditions.

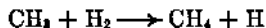
They also showed that surface had a pronounced effect. In the first place the tube diameter is of importance. Thus the half-life of methyl radicals at room temperature increased from 5×10^{-3} to 15×10^{-3} sec. when the quartz tube was increased in diameter from 0.5 cm. to 1.5 cm. On the other hand quartz, soft glass, soft glass etched with HF, and iron were all similar in their effect. These two results taken together indicate that the recombination is mainly a surface reaction under their experimental conditions, but that the nature of the surface is not of much importance.

¹²⁰ F. Paneth and W. Hofeditz, *Ber.*, 62, 1335 (1929).

¹²¹ F. Paneth and W. Lautsch, *Ber.*, 64, 2708 (1931); F. Paneth and K. F. Herzfeld, *Z. Elektrochem.*, 37, 577 (1931).

Paneth and Hofeditz also showed that if a small section of the tube through which methyl radicals were flowing was cooled to -180° no radicals passed by. Apparently at this low temperature every collision with the wall results in adsorption and subsequent recombination to ethane. Similar results were obtained by Rice, Johnston, and Evering.¹²² Their experiments also showed that every collision of a methyl radical with a lead mirror at room temperature results in its capture to form an organo-metallic compound.

Paneth, Hofeditz, and Wunsch¹²³ repeated the experiments of Paneth and Hofeditz with greater precision. They investigated the rate of disappearance of methyl radicals from tetramethyl lead in the presence of both hydrogen and helium. At room temperature in hydrogen, at a pressure of 1 to 2 mm., a streaming velocity of 1035 cm. per sec, with a quartz tube 1 cm. in diameter and 170 cm. long, they found a half-life of 5.2×10^{-3} sec. The life increased with increasing wall temperature up to 350° and then decreased again at higher temperatures. They analysed the products of the reaction under these conditions, and found that of the radicals disappearing 1 per cent formed C_2H_4 , 59 per cent formed C_2H_6 , and 40 per cent formed CH_4 . Somewhat indirectly they conclude that at 350° 90 per cent form CH_4 and 10 per cent form C_2H_6 . This is strong evidence that at higher temperatures the reaction



is coming into play as a homogeneous reaction and is outweighing the effect of the wall recombination to ethane. They also investigated the effect of the concentration of methyl, and found as might be expected that high radical concentrations favor the recombination to ethane, while low radical concentrations favor methane production. In the presence of helium at a temperature of 500° they found a very greatly increased life, 0.1 sec. They conclude that the optimum condition for a long life would be attained "immediately before the inception of a cracking process."

Rice¹²⁴ considers radical recombination reactions such as (28a) to be the chain-ending processes in free-radical chain decompositions, and assigns an activation energy of about 8 kcal. to all of them.

The fact that ethane is the main product of the thermal decomposition of lead tetramethyl when the experiments are carried out by a flow method at low pressures indicates that recombination by (28a) is the main fate of the methyl radicals under these conditions.¹²⁶ In static experiments methane predominates in the products owing to the occurrence of reactions between methyl radicals and lead tetramethyl.

¹²² F. O. Rice, W. R. Johnston, and B. L. Evering, *J. Am. Chem. Soc.*, **54**, 3529 (1932).

¹²³ F. Paneth, W. Hofeditz, and A. Wunsch, *J. Chem. Soc.*, **1935**, 372.

¹²⁴ F. O. Rice and K. F. Herzfeld, *J. Chem. Phys.*, **7**, 672 (1939).

¹²⁶ J. H. Simons, R. W. McNamee, and C. D. Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

Bawn¹²⁶ by assuming that the decomposition reaction



has a rate constant given by $k = 10^{13} e^{-80000/2T}$, and calculating the equilibrium constant by evaluating the partition functions (with some rather drastic assumptions) concludes that if the reaction



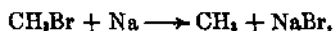
has zero activation energy, the steric factor is 8×10^{-6} . If 8 kcal. is assumed for the activation energy, he gets 10^{-4} for the steric factor, and with 70,000 cal. for the activation energy of (1) and zero activation energy for (28a) he gets 2×10^{-4} . The detailed calculation is probably unreliable ; but the general conclusion of a low steric factor appears worthy of some weight. In the treatment this conclusion follows from the low probability of the transition state in reactions involving radicals or molecules of moderate complexity.

Kimball¹²⁷ has calculated on classical grounds a mean life of 10^{12} sec. for the collision complex



It might therefore be concluded that this reaction would occur only in a three-body collision or at the wall. Kassel,¹²⁸ however, has criticized Kimball's calculations and concludes that they are fundamentally unsound.

Allen and Bawn¹²⁹ investigated the recombination of methyl radicals by the diffusion flame method. Methyl radicals were formed by the reaction



and were detected by means of antimony mirrors. At 350° it was found that the concentration of methyl did not decrease as the distance from the reaction zone to the mirror was increased up to a distance where about 10 collisions between methyls occurred. The results, therefore, constitute an experimental proof that either reaction (28a) has at least a small activation energy, or that it has a steric factor equal to or less than 0.1.

The recombination of methyl radicals has been discussed theoretically by Gorin, Kauzmann, Walter, and Eyring.¹¹⁹ They make use of an expression for the absolute rate of recombination of free radicals derived by Gorin,¹⁸⁰

$$k_{\text{CH}_3} = \frac{3\pi}{(2)} \left(\frac{kT}{2} \right)^{\frac{1}{2}} \frac{1}{\sigma_{ab}} \frac{(\alpha_a \alpha_b I_a I_b)^{\frac{1}{2}}}{(I_a + I_b)} \frac{(M_a M_b)}{(M_a + M_b)^{\frac{1}{2}}} K,$$

where the α 's are polarizabilities, the I 's moments of inertia, the M 's masses, and a is a symmetry number (= 2 in this case), and K , the trans-

¹²⁶ C. E. H. Bawn, *Trans. Faraday Soc.*, 31, 1536 (1935).

¹²⁷ G. E. Kimball, *J. Chem. Phys.*, 5, 310 (1937).

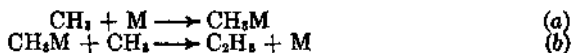
¹²⁸ L. S. Kassel, *J. Chem. Phys.*, 5, 922 (1937).

¹²⁹ A. O. Allen and C. E. H. Bawn, *Trans. Faraday Soc.*, 34, 463 (1938).

¹³⁰ E. Gorin, *Acta Physicochimica* (U.R.S.S.), 9, 681 (1938).

mission coefficient, can be put equal to unity. This expression was derived on the assumption that there is no activation energy in the true sense of the word, the radicals being assumed to attract one another by polarization forces. This attraction is opposed by the centrifugal force of the rotation of the two radicals considered as a diatomic rotator. These two forces together give rise to a potential barrier, the top of which corresponds to the activated complex.

With certain assumptions as to a 's, etc., they obtain for the rate of recombination of two methyls at 600° , 2.54×10^{-11} , taking the transmission coefficient K as unity. Actually on account of various assumptions they suggest that the observed rate may be two or three times smaller than this. At low pressures, the rate will fall off due to redissociation before stabilization. It will be noted that the above treatment corresponds to zero activation energy for reaction (28a). They discuss Rice's assumption of 8 kcal., and conclude that perhaps when we have

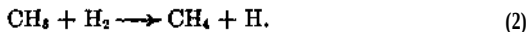


step (6) may have some activation energy.

Indirect information regarding reaction (28a) is obtained from the work of Taylor and Rosenblum¹³¹ who investigated the photolysis of acetone, alone and in the presence of hydrogen. The reaction produces methyl radicals, and these may combine to form ethane



or react with hydrogen to form methane,



Other secondary processes also occur, but the above are the main fates of a methyl radical, and Taylor and Rosenblum measured the amounts of methane and ethane produced in order to infer the relative rates of (28a) and (2). They found that over the temperature range 160° to 300° the amount of acetone decomposed per unit time was independent of temperature and of the presence or absence of hydrogen. In the absence of hydrogen ethane formation decreased with increasing temperature, while methane formation increased. In the presence of hydrogen the decrease in ethane and increase in methane with rising temperature was much more marked.

By plotting the log of the methane production against $1/T$ they obtained an activation energy of 8.6 kcal., with a rather large experimental error. In the presence of hydrogen the activation energy was smaller, viz., 5.9 kcal. calculated directly from the methane production, or 6.4 kcal. calculated from the hydrogen consumption. A log $(\text{CH}_4/\text{C}_2\text{H}_6)$ vs. $1/T$ plot gave a

¹³¹H. S. Taylor and C. Rosenblum, *J. Chem. Phys.*, 6, 119 (1938).

straight line corresponding to an activation energy of 11.4 kcal. The increase over that for methane is due to the decrease in ethane with rising temperature, which obviously results from a decrease in the methyl radical concentration owing to reaction (2) swamping out (28a).

They give the following kinetic analysis of the results:

"We may represent the reaction producing methane in presence of hydrogen by means of the equation:

$$\frac{d}{dt}[\text{CH}_4] = k_1[\text{H}_2][\text{CH}_3]e^{-E_M/RT}.$$

The process producing ethane may be unimolecular at the wall, a bimolecular association of methyl radicals, or a three-body combination of two radicals, representable by an equation

$$\frac{d}{dt}[\text{C}_2\text{H}_6] = k_2[\text{CH}_3]^x e^{-E_E/RT},$$

where x may be either 1 or 2, and k_2 in the case of a termolecular reaction would include a concentration of a third body.

Taking the unimolecular case first with $x = 1$, $[\text{H}_2]$ constant, and the activation energy $E_E = 0$, we obtain

$$\begin{aligned} \frac{d[\text{CH}_4]}{d[\text{C}_2\text{H}_6]} &= \frac{k_1[\text{H}_2][\text{CH}_3]e^{-E_M/RT}}{k_2[\text{CH}_3]} \\ &= k_3 e^{-11.4/RT} \end{aligned}$$

from the slope of the curve $\log [\text{CH}_4]/[\text{C}_2\text{H}_6]$ vs. $1/T$. On this assumption $E_M = 11.4$ kcal. The difference between this value and the observed slope $\log [\text{CH}_4]/[\text{CO}]$ vs. $1/T = 6.4$ kcal., must represent the variation of stationary state concentration of methyl with temperature,

$$[\text{CH}_3] = k_4 e^{5.0/RT}.$$

In the interval from 160° to 300° the quantity $e^{5.0/RT}$ changes by the factor $e^{-1.42}$ or approximately 0.24. This is almost exactly the ratio in which ethane production in presence of hydrogen decreases in the same interval. This concordance therefore strongly suggests a unimolecular reaction at the wall with negligible activation energy.

In the bimolecular case, $x = 2$, we have

$$\begin{aligned} \frac{d[\text{CH}_4]}{d[\text{C}_2\text{H}_6]} &= \frac{k_1[\text{H}_2][\text{CH}_3]e^{-E_M/RT}}{k_2[\text{CH}_3]^2 e^{-E_E/RT}} \\ &= k_3 e^{-11.4/RT}. \end{aligned}$$

From this equation we deduce

$$E_{(\text{CH}_3)} - E_M = -11.4 - E_E + 2E_{(\text{CH}_3)}.$$

As before, from the observed slope $\log [\text{CH}_4]/[\text{CO}]$ vs. $1/T$,

$$E(\text{CH}_3) - E_M = -6.4.$$

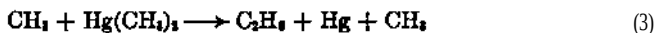
By addition,

$$2E_M - E_E = 17.8 \text{ kcal.}$$

This gives a minimum value for E_M when $E_E = 0$, in which case $EM = 8.9$ kcal., and $E(\text{CH}_3)$ becomes 2.5 kcal. This also will give the correct variation of ethane formation in presence of hydrogen with temperature. A positive value of EE would increase EM by $1/2 EE$ for $EE = 5$ kcal., the value of EM would be $8.9 + 2.5 = 11.4$ kcal., and for $E_E = 8$ kcal., $E_M = 12.9$ kcal."

It will be seen that this does not give any definite value for E_E . However, general indications are (see VI-27) that EM is about 9 kcal., which supports the idea that EE is quite small.

Cunningham and Taylor¹³² investigated the thermal and photochemical decomposition of mercury dimethyl alone and in the presence of hydrogen. The products of the decomposition in the absence of hydrogen are mainly methane and ethane. The ethane may arise entirely by recombination of methyls, but the increase in quantum yield with rising temperature suggests also



or some such process. A plot of log ethane production against $1/T$ yields an activation energy of 1.5 kcal. This may be due to (3), in which case (28a) has zero activation energy. In any case an upper limit to the activation energy of (28a) of 1.5 kcal. seems to be established. Cunningham and Taylor attribute at least part of this small activation energy to (28a) since it seems to occur less rapidly than the reaction



as indicated by the low quantum yield in the photolysis of methyl iodide due to the occurrence of the back reaction. In the photolysis of mercury dimethyl the quantum yield is nearly unity.

The work of Smith and Taylor¹³³ on the reaction of methyl radicals, from mercury dimethyl, with deuterium similarly supports the conclusion that (28a) has a low activation energy.

In a large number of investigations the formation of ethane in cases where methyl radicals are undoubtedly present points to the ready occurrence of (28a). Thus Sickman¹³⁴ in discussing the decomposition of ethylene oxide favors a three-body mechanism in which methyls recombine. This is however, purely speculative.

Helm and Mack¹³⁵ decomposed silicon tetramethyl in the temperature range 659° to 717°. The main products were carbon, hydrogen, and

¹³² J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.*, **6**, 359 (1938).

¹³³ J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

¹³⁴ D. V. Sickman, *J. Chem. Phys.*, **4**, 297 (1936).

¹³⁵ D. F. Helm and E. Mack, *J. Am. Chem. Soc.*, **59**, 60 (1937).

methane. At the high temperatures necessary for the decomposition it appears probable that the mechanism of the reaction is



followed by the pyrolysis of ethane. This is suggested by the fact that the products were almost quantitatively the same as those from the ethane pyrolysis at the same temperature. It is, however, possible that in place of (28a) we have



followed by the pyrolysis of ethylene.

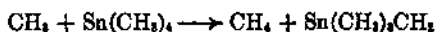
Waring and Horton^{135a} investigated the decomposition of tetramethyl tin. The reaction was of the first order over the temperature range 440° to 493°. The gaseous products consisted mainly of methane, with smaller amounts of ethylene and hydrogen. The rate was given by

$$k = 8.32 \times 10^{21} e^{-82400/RT} \text{ sec.}^{-1}.$$

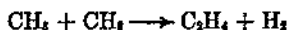
They interpret their results on the basis of a direct molecular rearrangement. The very high frequency factor combined with an unusually high activation energy strongly suggests compensating errors, and it appears almost certain that the reaction is complex. By analogy with other cases it seems highly probable that the initial step is



and that methane arises by reactions such as



or



followed by pyrolysis of ethylene.

Fletcher and Rollefson¹³⁶ interpret their results on the decomposition of ethyl ether on the basis of chain termination by (28a) in agreement with the Rice theory. They draw similar conclusions¹³⁷ for the ethylene oxide decomposition. They conclude in this case that the major recombination occurs at binary rather than at ternary collisions. Numerous other investigations point to similar conclusions about the ready occurrence of (28a).¹³⁸

^{135a} C. E. Waring and W. S. Horton, *J. Am. Chem. Soc.*, 67, 540 (1945).

¹³⁶ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2129 (1936).

¹³⁷ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2135 (1936).

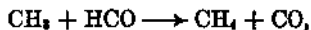
¹³⁸ E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research*, **B16**, 314 (1938); H. v. Hartel, *Trans. Faraday Soc.*, 30, 187 (1934); W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 466 (1940); W. West and L. Schlessinger, *J. Am. Chem. Soc.*, 60, 961 (1938); J. W. Linnett and H. W. Thompson, *Trans. Faraday Soc.*, 33, 501 (1937); H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, 33, 874 (1937); C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, 35, 898 (1939); S. W. Benson and G. S. Forbes, *J. Am. Chem. Soc.*, 65, 1399 (1943).

Davis, Jahn, and Burton¹³⁹ investigated the photolysis of azomethane, and made much more careful analyses than had previous workers. They found in every case an excess-of nitrogen, indicating condensable products. At room temperature the hydrocarbons formed were methane 7 per cent, ethane 90 per cent. At 220° they were methane 69 per cent, ethane 15 per cent, together with higher hydrocarbons, perhaps propane. They assume, and it appears well established, that the primary process is



The excess of nitrogen, etc., apparently indicates a marked interaction of methyls with azomethane (E not over 6 or 7 kcal.). They conclude that none of the ethane formed arises by (28a), that "methyl radicals do not combine readily at ordinary temperatures to form ethane," and that the ethane arises from the decomposition of more complex substances. This conclusion, however, should be accepted with great reserve, as H. S. Taylor points out.¹⁴⁰

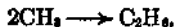
Burton, Taylor, and Davis¹⁴¹ similarly discuss the mechanism of the acetaldehyde photolysis. They conclude from an analysis of the mechanism that (28a) is not the chain-terminating step, and that it is slow compared with



which probably has an activation energy of 17 kcal.¹⁴² On this basis they assign the value $E_{28a} = 22$ kcal. In view of the complex nature of the acetaldehyde photolysis and the other evidence which points to a reasonably rapid rate for (28a), this conclusion does not appear to be on very reliable ground.

Gordon and H. A. Taylor¹⁴³ investigated the photolysis of methyl bromide. (See X-36.) There seems to be no doubt that the primary step is a split to methyl and a bromine atom, but ethane is not a product. They suggest that in general the frequent absence of ethane as a product in reactions where methyl is present is due to the fact that the activation energies of competing reactions are always low enough to swamp out the radical recombination.

On the whole the evidence certainly favors the fairly ready occurrence of the reaction



but the indications seem to point to some third body restrictions which result in a steric factor which! may be rather low. The main trouble in

¹³⁹ T. W. Davis, F. P. Jahn, and M. Burton, *J. Am. Chem. Soc.*, **60**, 10 (1938); M. Burton, T. W. Davis, and H. A. Taylor, *J. Am. Chem. Soc.*, **59**, 1038, 1989 (1937).

¹⁴⁰ H. S. Taylor, *J. Phys. Chem.*, **42**, 763 (1938).

¹⁴¹ M. Burton, H. A. Taylor, and T. W. Davis, *J. Chem. Phys.*, **7**, 1080 (1939); H. A. Taylor and M. Burton, *J. Chem. Phys.*, **7**, 675 (1939).

¹⁴² M. Burton, *J. Am. Chem. Soc.*, **60**, 212 (1938).

assessing the evidence is the possibility of surface effects being of major importance in some investigations.

The reverse of reaction (28b) has already been discussed, and appears to have an activation energy of ca. 5 kcal. Reaction (286) is endothermic to about 12 kcal., and hence should have an activation energy of about 17 kcal. This is high enough to make it unimportant compared with (28a). There seems to be no evidence for its occurrence.

Rice¹⁴⁴ suggests that reaction (28c) occurs readily. This is supported by the fact that there is considerable evidence for disproportionation in the analogous case of ethyl radicals. The reaction has been postulated by Faltings¹⁴⁵ in the mechanism of the photodecomposition of ethane. His mechanism, however, is almost certainly unsound.

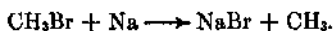
Paneth, Hofeditz, and Wunsch¹²³ found that appreciable amounts of ethylene were formed in the decomposition of lead tetramethyl, perhaps by the mechanism



However, the ethylene might possibly have arisen by



Bawn and Dunning¹⁴⁶ investigated the reaction of sodium atoms with methyl bromide at 350°,



Ethane was formed but no methane, which argues against the occurrence of (28d).



See section VI-27 for a discussion of the possible occurrence of this reaction.



This is the simplest example of an important type of reaction. Since it forms a C—C and breaks a C—H bond, the reaction will be endothermic to the extent of 10 to 15 kcal. As we have seen in section VI-9, the reverse reaction appears to have an activation energy of 30 kcal. or more. The activation energy of (29) must thus be > 40 kcal., and the reaction is

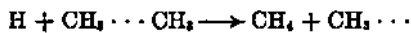
¹⁴³ A. Gordon and H. A. Taylor, *J. Am. Chem. Soc.*, 63, 3435 (1941).

¹⁴⁴ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

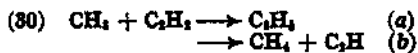
¹⁴⁵ K. Faltings, *Ber.*, 72B, 1207 (1939).

¹⁴⁶ C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, 36, 898 (1939).

therefore of no importance. In other words the argument against reactions of the type



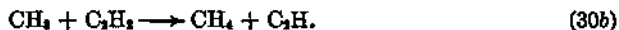
automatically rules out the reverse reactions



Rice and Sickman¹⁴⁷ found that the acetylene polymerization could be induced by methyl radicals from decomposing azomethane at 300°. The initial step might be



or



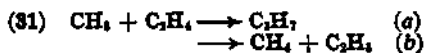
The former is, perhaps, the more likely.

Taylor and Jungers¹⁴⁸ found that the polymerization could be induced by radicals, presumably methyls, from the photodecomposition of acetone at 25°.

Rice and Rice¹⁴⁴ suggest that reaction (30a) has an activation energy in the range 2 to 10 kcal. In view of the very small activation energy of the companion reaction



either (30a), or (30b), or both, would appear to have a very low activation energy.



As discussed in Chapter IV, there is a great deal of evidence that the ethylene polymerization can be sensitized by methyl radicals, undoubtedly by reaction (31a) and others of the same type. All the evidence points to a low value for the activation energy of the reaction. From the temperature coefficient of the polymerization induced by methyl radicals from the photolysis of acetone Taylor and Jungers¹⁴⁸ conclude that the activation energy is not more than one or two kcal. From a qualitative theoretical discussion Rice and Teller¹⁴⁹ also conclude that reaction (31a) has a very low activation energy.

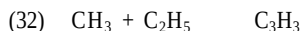
There is no conclusive evidence for the occurrence of reaction (31b). Taylor and Jungers in their investigation of the acetone sensitized polymerization of ethylene point out that some methane may be formed by

¹⁴⁷ O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, **4**, 608 (1936).

¹⁴⁸ H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937).

¹⁴⁹ F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

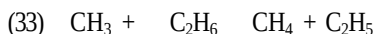
(316) at higher temperatures, but if so it is only in small amounts. Taylor and Smith¹⁵⁰ have discussed the reaction and compared it with the corresponding reactions of propylene and of saturated hydrocarbons. They conclude that the strong C—H bonds in ethylene are responsible for the relatively high activation energy. Taylor suggests¹⁵¹ that the activation energy is greater than 10 kcal.



As with the reaction



this reaction has been frequently postulated, but there is little real information concerning it. What evidence there is points strongly to its ready occurrence. In common with other recombination reactions, Rice¹⁴⁴ assumed an activation energy of 8 kcal., and a steric factor of 0.1. It appears certain that Rice's estimate is too high, and that the activation energy is very small.



Rice, in the absence of any experimental evidence, assigned an activation energy of 20 kcal. to this reaction in order to obtain agreement with free radical mechanisms. He later adopted the value of 17 kcal.¹⁴⁴

Rice and Sickman¹⁴⁷ obtained evidence of some decomposition of ethane at 300° induced by methyl radicals from decomposing azomethane.

Steacie and Phillips,¹⁵² in discussing the mechanism of the mercury photosensitized decomposition of ethane, assumed that reaction (33) was relatively slow, and that the activation energy was of the order of 10 kcal. or more.

Rice and Teller¹⁴⁹ conclude from a theoretical discussion that all reactions of the type



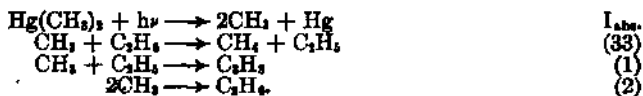
should have a relatively low activation energy.

The first direct investigation of the reaction was made by Smith and Taylor.¹¹⁵ Methyl radicals produced by the photodecomposition of mercury dimethyl were allowed to react with ethane in the temperature range 100° to 300°. They measured the methane formation, and from a log k_{CH_4} — 1/T plot obtained an activation energy of 8.3 kcal. They suggest as the mechanism of the reaction

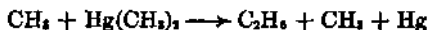
¹⁵⁰ H. S. Taylor and J. O. Smith, *J. Chem. Phys.*, 8, 543 (1940).

¹⁵¹ H. S. Taylor, *Ann. New York Acad. Sci.*, 41, 231 (1941).

¹⁵² E. W. R. Steacie and N. W. F. Phillips, *Can. J. Research*, B16, 303 (1938).



Reactions of the type



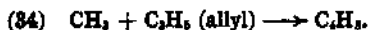
probably occur also, but do not affect the methyl radical concentration or the production of methane, and may therefore be neglected for our present purpose.

From the above sequence

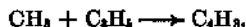
$$\frac{d[\text{CH}_3]}{dt} = \frac{k_{22}(2k_{23}[\text{C}_2\text{H}_6] + (4k_{22}[\text{C}_2\text{H}_6]^2 + 8k_2 I_{\text{abs.}})^{\frac{1}{2}})}{2k_3} [\text{C}_2\text{H}_6] = k_{22}[\text{C}_2\text{H}_6]A.$$

Since ethane is the main product in the low temperature range (see Cunningham and Taylor's work on the photodecomposition of mercury dimethyl alone),¹¹³ A is practically constant. Hence the slope of the $\log k_{\text{cm}} - 1/T$ curve gives a measure of the activation energy of reaction (33), viz., 8.3 kcal. At higher temperatures this simple relation will no longer hold, and the rate determining step will become the rate of formation of methyl radicals.

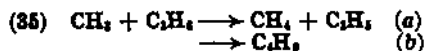
Eltenton¹⁵³ investigated the reaction of methyl radicals from decomposing lead tetramethyl with ethane, and followed the methyl radical concentration with a mass spectrometer. He concluded that the reaction of methyl radicals with ethane is slower than that with propylene, but faster than with ethylene.



The reactions of the allyl radical have been discussed to some extent by Taylor and Smith.¹⁶⁰ They point out that the resonance characteristics of the allyl radical result in a weak $\text{C}_3\text{H}_5\text{—H}$ bond in propylene. Hence in hydrocarbon systems the allyl radical would be expected to have a long life, and to disappear by a reaction such as



or by combination with itself to give diallyl. (See also footnote 154.)



Rice¹⁴⁴ in connection with free radical mechanisms estimated an activation energy of about 12 kcal. for the reaction



¹⁵³ G. C. Eltenton, *J. Chem. Phys.*, 10, 403 (1942).

¹⁵⁴ O. Beeck and R. F. Rust, *J. Chem. Phys.*, 9, 480 (1941).

Rice and Sickman¹⁴⁷ found that methyl radicals from the decomposition of azomethane caused some polymerization of propylene. This was merely stated and no details were given. It suggests that at temperatures in the neighbourhood of 300° the reaction



occurs to some extent: it appears, however, to be about 10 times slower than the corresponding reaction with ethylene.¹⁵⁵

Rice and Teller¹⁴⁹ have discussed the question of the occurrence of reactions of this type. They conclude that on the approach of a methyl radical to an olefin the shielding effect of the hydrogens is not nearly as pronounced as it is with paraffins, and hence the reactions with olefins will have a much lower activation energy. However, the replacement of the hydrogens in ethylene by other groups will increase the shielding effect again, thus explaining the much slower rate of reaction of methyls with propylene as compared with ethylene.

Taylor and Smith¹⁵⁰ investigated the reaction of methyl radicals, produced by the photolysis of mercury dimethyl, with propylene. Their data are summarized in Table XLVIII.

From a log k_{CH_4} — $1/T$ plot, the activation energy of methane production was found to be 3.1 kcal.: this is apparently the activation energy of the reaction

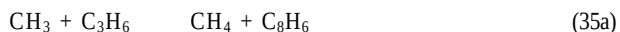
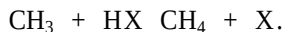


TABLE XLVIII. REACTION OF METHYL RADICALS WITH PROPYLENE

Partial pressure of $\text{Hg}(\text{CH}_3)_2 = 40$ mm. Partial pressure of $\text{C}_3\text{H}_6 = \text{ca. } 200$ mm.			
Temperature, °K	k_{CH_4}	$X \cdot 10^3$	Pressure decrease, expressed as cc. at N.T.P. per min.
383		8.83	124
430		14.82	214
480		19.25	605
539		28.6	—

This is the lowest activation energy found by Taylor and his collaborators for any reaction of the type



(The compounds studied were ethane, butane, iso-butane, neopentane, toluene, benzene, diphenyl methane, and hydrogen.) With ethylene, as previously discussed, the reaction analogous to (35a) is negligible compared with the reaction of type (35b). This indicates that it is the hydrogens of the methyl group in propylene which are reacting. From the point of view of reactions of this type, therefore, propylene is much more like ethane than

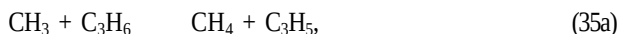
¹⁵⁶ D. V. Sickman, unpublished, quoted in footnote 149.

it is like ethylene, since it is the weaker C—H bonds on the methyl group which undergo reaction. Actually the C—H bonds in the methyl group in propylene appear to be weaker than those in ethane by $8.1 - 3.1 = 5$ kcal. This conclusion is in general agreement with the evidence from organic chemistry.

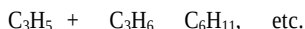
The data given above on the pressure decrease accompanying the reaction also indicate an efficient polymerization of propylene in the presence of methyl radicals. It is difficult to say whether this proceeds by



or by the formation of an allyl radical and methane,



followed by polymerization by reactions such as



Taylor and Smith compare the reactions of methyl radicals with ethane, ethylene, and propylene, as follows: "This double bond influence is most marked in the reaction with propylene where the decrease in observed activation energy over the primary bond in saturated hydrocarbons amounts to 5 kcal. It is obvious that in any free radical mechanism involving saturated hydrocarbons reaction of the radical with propylene would be faster than that with either primary, secondary, or tertiary C—H bonds in the saturated molecule. Such interaction would yield, as Rice and Polly¹⁵⁶ have pointed out, the allyl radical. The weakness of the allyl-H bond here indicated as compared with the C—H bonds in the saturated molecules implies a correspondingly decreased efficiency as a chain link in such chain decomposition processes. The radical would have longer life and would have greater opportunity to disappear by collision with itself or other radical to produce diallyl or a substituted propylene, respectively. The formation of this latter would have a net effect of breaking two radical chains and of producing an olefin of approximately equal efficiency with propylene as a chain breaking agent. The formation of diallyl would have the net effect of breaking one chain per propylene, the diallyl probably having a further efficiency as a chain breaker by reason of its C—H bonds on the carbon atoms in the beta position to the two double bonds.

"With ethylene such conditions do not immediately obtain. The strong C—H bonds in this compound imply a lesser reactivity with methyl radicals to form methane than with the saturated hydrocarbons. Association of ethylene and alkyl radicals generates a higher alkyl radical. It is not surprising, therefore, that Echols and Pease¹⁵⁷ found no inhibitory in-

¹⁵⁶ F. O. Rice and O. L. Polly, *J. Chem. Phys.*, 6, 273 (1938).

¹⁵⁷ L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, 61, 1024 (1939).

fluence of ethylene and a marked influence of propylene on the thermal decomposition of n-butane.

"The differences in activation energy between ethylene and propylene . . . may be associated with the resonance characteristics of the allyl radicals produced . . . by the withdrawal of a hydrogen atom. It has been estimated¹⁵⁸ that the resonance energy of the allyl radical amounts to 15.4 kcal. so that this energy would separate the potential energy surface of the radical-methane product from that which would obtain with a non-resonating radical-methane product from another hydrocarbon reaction as, for example, that between methyl and ethylene. A similar energy difference, due to resonance, of the activated complexes in the two reactions would account fully for the difference in methane formation observed.

"The interpretation of the experimental data with respect to the unsaturated . . . hydrocarbons on the basis of resonance energy of the activated complexes and the radicals produced rather than on the basis of bond strengths of the compounds studied raises the question as to whether the data on the reactivities of the primary, secondary, and tertiary C—H groupings in the saturated hydrocarbons might not be similarly interpreted. In these cases the radicals formed, *e.g.*, ethyl, butyl, isobutyl, are not ordinarily regarded as resonating structures. The differences in activation energies observed, amounting to 4 kcal. between ethane and isobutane are of a lower order of magnitude than those observed between ethylene and propylene. By attributing these differences of activation energy to differences of stability due to resonance effects between such radicals as ethyl and isobutyl, one could retain the Pauling principle of C—H bond energies practically identical in magnitude in the saturated hydrocarbons. The thermochemical data of Kistiakowsky and his co-workers do, however, suggest that differences in bond energies up to but not exceeding those found in our earlier work may exist in such systems.

"A more difficult problem is involved, however, in the application of resonance to the comparative rates of formation of methane from the interaction of methyls with ethane and ethylene. The greater reactivity of ethane would suggest that there was a much greater resonance in the activated complex ($\text{CH}_3\text{—C}_2\text{H}_6$) than in that of ($\text{CH}_3\text{—C}_2\text{H}_4$). It is not at once evident why this should be so. The alternative is that the C—H bond strength in ethylene is stronger than that in ethane. This conclusion is in accord with classical views in organic chemistry."

Beeck and Rust¹⁵⁴ investigated the polymerization of propylene sensitized by methyl radicals from the thermal decomposition of lead tetramethyl. They found that the rate was much slower than that with ethylene, in agreement with the results of Taylor and Smith.

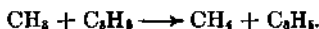
¹⁵⁸ J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, 35, 811 (1939).

Danby and Hinshelwood¹⁵⁹ investigated the polymerization of propylene photosensitized by acetaldehyde. (See IV-8.) The results were similar to those with ethylene (IV-2), except that here the rate of polymerization was smaller, and there was much more marked inhibition of the photolysis. Further, the rate of polymerization became independent of the olefin concentration at moderate propylene pressures. In other words the inhibition is so large that the radicals are practically all removed by the olefin. The aldehyde, therefore, acts merely as a source of radicals, the normal radical removing process being negligible by comparison with the new chain-ending step introduced by the olefin. If this is first order the rate will become independent of the olefin concentration. However, the mechanism is too complex to allow definite conclusions to be drawn other than that the reaction

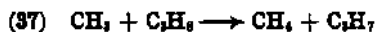


is rapid at 300°.

Eltenton¹⁶³ has investigated the reaction of methyl radicals with propylene by following the concentration of methyl and other radicals with a mass spectrometer. The methyl radicals were produced by the decomposition of lead tetramethyl. He concluded that methyl radicals react more readily with propylene than with ethane. This would indicate an activation energy for reaction (35a) of less than 8 kcal. He also succeeded in detecting the allyl radical in mixtures of methyl and propylene, thus confirming the occurrence of the reaction



As with (32), this reaction is often assumed but there is little definite information concerning it. Rice¹⁴⁴ again assumes an activation energy of 8 kcal., with a steric factor of 0.1.



Rice and Rice¹⁴⁴ suggested the following values for E_{37} :

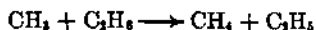


These values are unquestionably too high, but the difference in activation energy for the removal of a secondary as compared with a primary hydrogen is not far from recently determined experimental values.

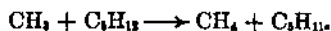
Rice and Sickman¹⁰⁴ obtained indirect evidence that methyl radicals from decomposing azomethane can cause some decomposition of propane.

¹⁵⁹ C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A179,169 (1941).

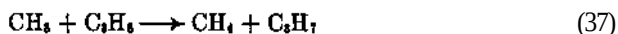
Smith and Taylor¹¹⁵ obtained an activation energy of 8.3 kcal. for the reactions



and

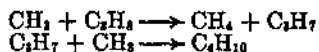


Apparently the reaction



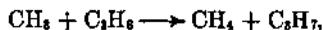
will have a similar activation energy.

Allen¹⁶⁰ investigated the reactions of methyl radicals, produced by the photolysis of acetone, with propane at temperatures from 254° to 337°. He concludes that in the presence of propane the main reactions of methyl radicals produced by the acetone photolysis are



On this basis he calculates that in a 2 to 1 propane-acetone mixture the fraction of the methyl radicals which react with propane rises from 0.125 at 254° to 0.250 at 337°.

The main products of the reaction were *n*- and iso-butane, and smaller amounts of pentane and probably hexane. The ratio of iso- to *n*-butane was approximately 2 to 1. On the assumption that both butanes arise by combination of methyl and propyl (or iso-propyl) radicals, and that the propyl radicals come from



this means that secondary hydrogens are removed twice as often as primary. Whence, allowing for the relative number of each in propane, the activation energy for the abstraction of a secondary hydrogen atom works out at 2.0 kcal. lower than that for a primary hydrogen. This agrees well with the value found by Smith and Taylor, and with the qualitative results of Steacie and Dewar on the mercury photosensitized reactions of propane.¹⁶¹



Danby and Hinshelwood¹⁶⁹ investigated the polymerization of *n*-butylene photosensitized by acetaldehyde. (See IV-8.) The results were similar to those with propylene (VI-35), and show that at 300° reaction (38) occurs readily.

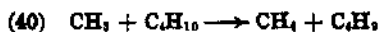
They conclude that alkyl radicals react about equally readily with ethylene, propylene, and butylene, but that the chain length of the induced polymerization diminishes with the higher olefins.

¹⁶⁰ A. O. Allen, *J. Am. Chem. Soc.*, 63, 708 (1941).

¹⁶¹ E. W. R. Steacie and D. J. Dewar, *J. Chem. Phys.*, 8, 571 (1940).

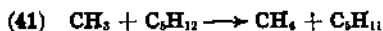


The situation is similar to that of reactions VI-32 and VI-36.

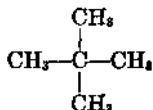


There is a great deal of evidence to show that methyl radicals can induce the decomposition of *n*- and iso-butane (see III-6), presumably by a mechanism including reaction (40).

Smith and Taylor¹¹⁵ investigated the reaction of methyl radicals produced by the photodecomposition of mercury dimethyl with *n*- and iso-butane. The mechanism postulated is similar to that previously discussed for ethane (VI-33). They found activation energies of 5.5 kcal. for *n*-butane, and of 4.2 kcal. for iso-butane.



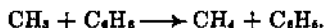
By the same method used with ethane and the butanes Smith and Taylor¹¹⁵ investigated the reaction of methyl radicals with neo-pentane,



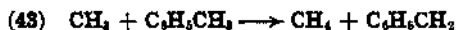
They obtained an activation energy of 8.3 kcal.



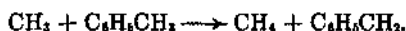
This reaction was investigated by Taylor and Smith¹⁵⁰ in a similar manner to that of ethane (VI-33). The methane formation was so small that they were unable to obtain a reliable estimate of the activation energy of the reaction



The activation energy is, however, very high by comparison with toluene, diphenyl methane, or ethane, and is greater than 10 kcal.¹⁵¹

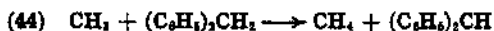


By the same method as that described in (VI-33) Taylor and Smith found an activation energy of 5.6 kcal. for the reaction



This value is about 2.5 kcal. lower than that for primary hydrogens in saturated paraffins. Taylor and Smith discuss the difference between benzene and toluene in a manner similar to that given above for ethylene and propylene (VI-35), and attribute the difference mainly to the resonance characteristics of the benzyl radical.

Jost and v. Muffling¹⁶² found that mercury dimethyl had no effect on the rate of decomposition of toluene at 690°. In view of the very high temperature used, however, this result is perhaps not conclusive.



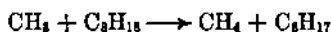
Taylor and Smith¹⁵⁰ investigated the reaction of methyl radicals, produced by the photolysis of mercury dimethyl, with diphenyl methane. Only two experiments were made. These indicated a methane production greater than that with propylene in the temperature range 478° to 538°. They conclude that reaction (44) has an activation energy less than 5.6 kcal. This points to a weakening of the C—H bonds in methane on the introduction of phenyl groups.

(46) CH_3 -H Higher Hydrocarbons

Jost and v. Muffling¹⁶² found that the decomposition of cyclohexane was accelerated by mercury dimethyl. Nitric oxide had no effect on the thermal decomposition of cyclohexane.

They also found that the decomposition of n-heptane at 498° was accelerated by mercury dimethyl.

Norrish¹⁶³ from experiments on the photolysis of methyl ethyl ether in iso-octane solution at 100° concluded that the reaction



has an activation energy of about 12.3 kcal.

Comparison of the Rates of Reaction of Methyl Radicals with Various Paraffins

As discussed in the previous sections, Smith and Taylor obtained the following results for the activation energies of the reactions of methyl radicals with paraffins:

$\text{CH}_3 + \text{C}_2\text{H}_6$	$E = 8.3 \text{ kcal.}$
$\text{CH}_3 + n\text{-C}_4\text{H}_{10}$	5.5
$\text{CH}_3 + \text{iso-C}_4\text{H}_{10}$	4.2
$\text{CH}_3 + \text{neo-C}_4\text{H}_{10}$	8.3

In discussing these results, they draw the following conclusions:

"That the activation energies for ethane and neo-pentane are the same indicates that the removal of primary hydrogens from hydrocarbons is, energetically, independent of the hydrocarbon. The ratio of 1.3 for the absolute rates in the two cases under similar conditions can be accounted for by the relative sizes of the two hydrocarbon molecules. The lower

¹⁶² W. Jost and L. v. Muffling, *Z. Elektrochem.*, 47, 766 (1941).

¹⁶³ R. G. W. Norrish, *Trans. Faraday Soc.*, 36, 897 (1939); C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1938, 1531.

activation energies with butane and iso-butane we ascribe to the greater reactivity of secondary and tertiary hydrogens. The value found for butane will be somewhat higher than the true value for secondary hydrogen since, at each temperature, some primary hydrogen may be reacting. The statistical factor of six primary to four secondary hydrogens favors the reaction of primary hydrogen, but this factor does not change with temperature and should not therefore affect the activation energy. In the case of iso-butane, with a large statistical factor of nine primary to one tertiary, conditions might be expected to favor primary hydrogen reaction, but the low activation energy found, 4.2 kcal., indicates large tertiary hydrogen reaction, favored by the larger spread in energy $(8.3 - 4.2) = 4.1$ kcal. as $A_2^?$ in the expression $e^{-\Delta E/RT}$ for the ratio of rates in the two cases of ethane and iso-butane.

" The activation energy differences here found of 2.8 and 4.1 kcal. between primary and secondary and primary and tertiary reactions compare favorably with the predictions of Rice,¹⁴⁴ 1.2 and 4.0 kcal. based on the decomposition of hydrocarbon vapors, an analysis of the products, and an interpretation of these in terms of assumed activation energies for the various intermediate steps. Our values, therefore, are contributory evidence in support of the chain mechanism of decomposition of saturated hydrocarbons, and supply reliable data for the activation energies of typical radical-molecule reactions.

" We believe that the differences in activation energies here under discussion are closely related to the bond energies in question. We are aware of the dangers attending such an identification of one with the other but we are confirmed in our belief by the data of Kistiakowsky and his co-workers¹⁶⁴ on the heats of hydrogenation of the substituted ethylenes. Mono-substituted ethylenes on hydrogenation change a double bond to a single C—C bond and form one primary and one secondary C—H bond. Other types of substitution give other combinations. If the Harvard data be analyzed on this basis, it is found that as many as seven independent thermal measurements for the energy difference, primary-secondary, yield the value 2.4 ± 0.25 kcal. and, for the primary-tertiary difference, three measurements yield 4.4 kcal. We believe this cumulative evidence warrants a confident modification of the first approximation in the estimates of C—H bond energies in hydrocarbons which assigns them all an equal value. We suggest, as a second approximation, bond energy differences of 2.5 and 4 kcal. between primary and secondary and primary and tertiary C—H bonds in saturated hydrocarbons."

Gordon and H. A. Taylor¹⁶⁵ suggest that the activation energies found by

¹⁶⁴ G. B. Kistiakowsky *et al.*, *J. Am. Chem. Soc.*, 58, 137 (1936), 59, 831 (1937), 60, 440 (1938), 61, 1873 (1939).

¹⁶⁵ A. Gordon and H. A. Taylor, *J. Am. Chem. Soc.*, 63, 3435 (1941).

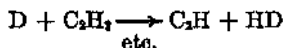
the method of photolysing mercury dimethyl in the presence of hydrocarbons are too low on account of excess energy carried over from the primary step in the photolysis. In view of the consistency of Smith and Taylor's work, and the agreement of their values with those of other methods, this criticism does not appear to be valid.



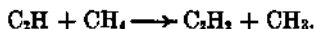
This reaction is perhaps involved in the mercury photosensitized reactions of acetylene.¹⁶⁶ (See IV-7.)



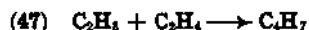
Stearie and Phillips⁷⁸ investigated the reaction of deuterium atoms produced by a discharge with mixtures of acetylene and methane. If, as appears probable, at least a part of the rapid exchange of acetylene goes by the mechanism



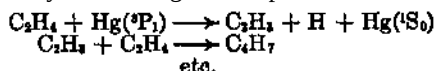
then in the presence of methane we might expect the occurrence of the reaction



This would lead to exchange of methane via methyl. Actually, no appreciable exchange of methane occurred. This points to a value of E_{46A} 8 kcal.

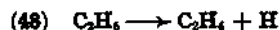


This reaction is probably involved in the mercury photosensitized polymerization of ethylene at higher temperatures,¹⁶⁷ viz.,

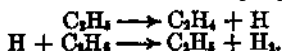


(For details see IV-4.)

A similar mechanism probably holds for the polymerization sensitized by 5^1P_1 cadmium atoms¹⁶⁸ and 4^1P_1 zinc atoms.¹⁶⁹



This reaction is one of the fundamental steps in the chain mechanism proposed by Rice and Herzfeld¹⁷⁰ for the thermal decomposition of ethane. (See III-5.) In this mechanism the chain-propagating steps are



¹⁶⁶ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, 12, 117 (1944).

¹⁶⁷ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, 10, 676 (1942).

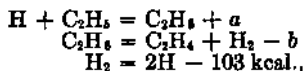
¹⁶⁸ E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, 10, 22 (1942).

¹⁶⁹ H. Habeeb, D. J. LeRoy, and E. W. R. Steacie, *J. Chem. Phys.*, 10, 261 (1942).

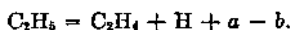
¹⁷⁰ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, 66, 284 (1934).

To obtain agreement with the experimentally measured activation energy of the overall reaction, they assumed an activation energy of 49 kcal. for reaction (48).^m The original scheme was later modified by Kiichler and Theile,¹⁷² and Rice and Herzfeld^m accept the modified mechanism and again assume 49 kcal. for the activation energy of reaction (48).

It is possible to estimate the activation energy of reaction (48) if we know the C—H bond strength in ethane, from the sequence



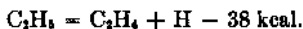
where a is the C—H bond strength in ethane, and b is the heat of hydrogenation of ethylene. Adding the above equations,



If we put

$$\begin{aligned} b &= 32 \text{ kcal.}^{174} \\ a &= 97 \text{ kcal.}, \end{aligned}$$

then



(See III-1.)

The energy of activation, EM is therefore equal to 38 kcal, plus the activation energy of the reverse reaction, which is probably in the range 0 to 5 kcal. Hence

$$E_{48} = 38 - 43 \text{ kcal.}$$

This is in fair agreement with Rice's assumptions, and in any event there appears to be no doubt that reaction (48) will only be of importance at elevated temperatures. Thus Paneth and Loleit^m found indications that the decomposition of ethyl radicals first became appreciable in the neighborhood of 600°.

Bawn¹⁷⁶ concludes from transition state considerations that EM is between 48 and 50 kcal. These calculations are of interest in so far as they confirm other estimates, although they are only to be relied upon as far as the order of magnitude is concerned.

Steacie and Cunningham¹⁷⁷ have investigated the mercury photosensitized decomposition of ethane at temperatures up to 475°. In this reaction the primary step is undoubtedly a split into C_2H_5 and H . They find no appreciable amount of ethylene in the reaction products even at 475°. This means that equilibrium in the reaction



¹⁷¹ See F. O. Rice, *J. Am. Chem. Soc.*, 56, 488 (1934).

¹⁷² L. Kiichler and H. Theile, *Z. physik. Chem.*, **B42**, 359 (1939).

¹⁷³ F. O. Rice and K. F. Herzfeld, *J. Chem. Phys.*, 7, 671 (1939).

¹⁷⁴ See F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances*, New York, 1936.

¹⁷⁵ F. Paneth and H. Loleit, *J. Chem. Soc.*, **1935**, 366.

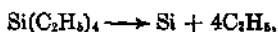
¹⁷⁶ C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 1536 (1935).

¹⁷⁷ E. W. R. Steacie and R. L. Cunningham, *J. Chem. Phys.*, 8, 800 (1940).

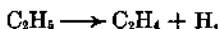
is still far over to the left at 475°. This is in general agreement with the estimates of the activation energies discussed above. Frost¹⁷⁸ calculates from Rice and Herzfeld's assumptions that the equilibrium at 900°K is given by

$$K_p = \frac{P_H \cdot P_{C_2H_4}}{P_{C_2H_6}} = 2 \times 10^{-4}.$$

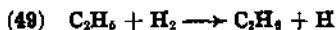
Waring^m investigated the thermal decomposition of silicon tetraethyl in the temperature range 560° to 600°. The initial products of the reaction were predominantly ethylene and hydrogen. There seems to be little doubt that the initial step is



and this is, therefore, evidence for the occurrence at 560° to 600° of the reaction

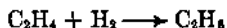


No appreciable butane was present. The reaction was not inhibited appreciably by small amounts of nitric oxide, and hence chains are apparently not involved.

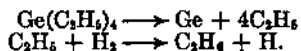


Leermakers¹⁸⁰ found no difference in the rate of pressure increase when tetraethyl lead was decomposed in the presence of hydrogen at 275°, and concluded that reaction (49) had an activation energy greater than 15 kcal. However, the mere determination of the rate of pressure increase is a rather uncertain criterion of reaction.

Geddes and Mack¹⁸¹ investigated the decomposition of germanium tetraethyl in the temperature range 420° to 450°, and found that the products consisted normally of about 30 per cent ethane, 30 per cent ethylene, and smaller amounts of methane, hydrogen, higher olefins, etc. In the presence of added hydrogen, however, the amount of ethane formed rose to ca. 50 per cent. Since the reaction



does not occur at an appreciable rate at these temperatures, this apparently indicates the occurrence of the reactions



The latter reaction seems, therefore, to occur readily above 400°.

¹⁷⁸ A. V. Frost, *J. Phys. Chem.* (U.S.S.R.), 8, 290 (1936).

¹⁷⁹ C. E. Waring, *Trans. Faraday Soc.*, 36, 1142 (1940).

¹⁸⁰ J. A. Leermakers, *J. Am. Chem. Soc.*, 55, 4508 (1933).

¹⁸¹ R. L. Geddes and E. Mack, *J. Am. Chem. Soc.*, 52, 4372 (1930).

Cramer¹⁸² investigated the decomposition of lead tetraethyl in benzene solution in the presence of hydrogen at high pressures in the temperature range 180° to 240°. The benzene was inert, and the products were mainly those of the disproportionation reaction

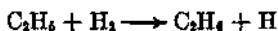


The presence of the hydrogen had no effect, and hence the reaction



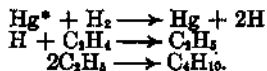
does not seem to occur to an appreciable extent. However, since the quantity of dissolved hydrogen would probably be quite small, this is not conclusive.

Moore and Taylor¹⁸³ investigated the photolysis of mercury diethyl and zinc diethyl both in the presence and in the absence of hydrogen. They found no appreciable change in the rate of decomposition in the presence of hydrogen up to 160°. This is the temperature at which reaction becomes perceptible between methyl radicals and hydrogen, and they, therefore, conclude that the activation energies of the two reactions are about the same, viz., about 9 kcal. This is not in agreement with Leermakers' result. The effect observed by Moore and Taylor at 160° is, however, very small (see Table XLIX), and perhaps their estimate of the activation energy is rather low. On the other hand it should be noted that there is a definite increase in ethane in the products in the presence of hydrogen even at 160°, and this supports the conclusion that the reaction

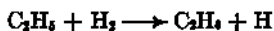


is occurring to an appreciable extent even at 160°.

In the mercury photosensitized hydrogenation of ethylene Jungers and Taylor¹⁸⁴ found that butane is almost the sole product at room temperature. This is undoubtedly formed by



The absence of appreciable quantities of ethane as a product shows that at room temperature the reaction



is slow, and they estimate an activation energy greater than 11 kcal.

¹⁸² P. L. Cramer, *J. Am. Chem. Soc.*, 56, 1234 (1934).

¹⁸³ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 396 (1940).

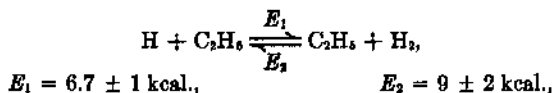
¹⁸⁴ J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, 6, 325 (1938).

TABLE XLIX. PHOTOLYSIS OF MERCURY DIETHYL (MOORE AND TAYLOR)

Temperature	Added H ₂ mm.	Initial pressure = 25 mm.					Rate, mm. per min.
		H ₂	Mole per cent of products		C ₄ H ₁₀	C ₄ H ₈	
100	0	1	21	33	37	8	1.25
	0	1	22	30	38	10	1.26
	0	1	21	30	41	7	0.96
	200	-	21	38	38	3	1.33
160	0	4	20	31	34	11	1.55
	0	2	22	30	37	9	1.52
	200	-	15	47	33	5	1.60
	200	-	—	—	—	—	1.98
200	0	1	20	41	30	9	1.89
	0	2	15	40	34	9	1.87
	0	1	21	36	33	9	1.89
	200	-	16	51	30	3	2.47
	200	-	16	56	23	5	2.03
	200	-	9	50	38	3	2.38
250	0	1	20	42	28	9	2.26
	0	1	19	37	34	9	2.43
	0	2	19	37	33	9	2.35
	700	-	1	90	9	0	—
	200	-	8	64	23	5	4.06
	200	-	9	60	27	4	4.22
	200	-	8	61	24	7	3.94
	100	-	12	56	25	7	2.63
	50	-	14	48	33	5	2.90

The C—H bond strength in ethane

If we accept for the values of the activation energies of the opposing reactions



we have

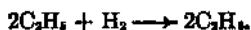


and hence we obtain for the C—H bond strength in ethane a value of $102.5 - 2.3 = 100.2 \pm 3 \text{ kcal.}$ This agrees within the limits of error with modern estimates which put the C—H bond strength in ethane at about 97 kcal.

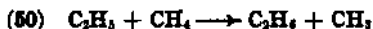
By analogy with the case of methane, it is possible that the Q—H bond strength in ethane might be lower than the value indicated above, if the mechanism of the disappearance of ethyl radicals were not



but rather



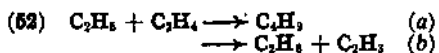
The arguments for and against such a mechanism are virtually identical with those in the case of methane (see VI-27), and there appears to be no doubt that the value of 97 kcal. for the C—H bond strength in ethane is now well established. (See III-1).



Rice¹⁴⁴ on the basis of assumed mechanisms for hydrocarbon decompositions hfts suggested a value of 22 kcal. for *Em*.



Joris and Jungers¹⁸⁶ investigated the polymerization of acetylene photosensitized by ethyl iodide. The actual reaction occurring is unknown, but the first step is undoubtedly due to ethyl radicals and is probably an association such as (51). The rate of polymerization was about half that of ethylene under comparable conditions.

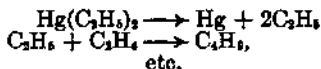


As pointed out in section IV-2, reactions of this type were first suggested by Taylor and his co-workers. Taylor and Bates¹⁸⁶ investigated the mercury photosensitized reactions of ethylene, and assumed that reactions such as



played a prominent part in the mechanism.

The same general mechanism was also postulated by Taylor and Jones^m who investigated the decomposition of mercury diethyl and lead tetraethyl in the presence of hydrogen and ethylene at 250° to 300°. They found that the main result was polymerization of the ethylene. This indicates that the mechanism is



As discussed in detail in section IV-2 many other investigations have shown that the ethylene polymerization is sensitized by ethyl radicals,¹⁸⁸ un-

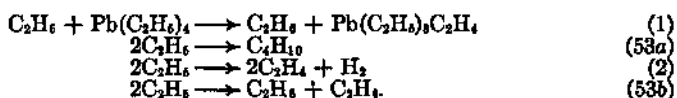
¹⁸⁶ G. G. Joris and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 47,135 (1938); J. C. Jungers and G. G. Joris, *Bull. Soc. Chim. Belg.*, 60, 61 (1941).

¹⁸⁶ H. S. Taylor and J. R. Bates, *Proc. Nat. Acad. Set.* (Washington), 12, 714 (1926).

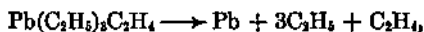
¹⁸⁷ H. S. Taylor and W. H. Jones, *J. Am. Chem. Soc.*, 52, 1111 (1930).

¹⁸⁸ P. L. Cramer, *J. Am. Chem. Soc.*, 56,1234 (1934); H. S. Taylor and H. J. Emeleus, *J. Am. Chem. Soc.*, 53, 562 (1931); G. G. Joris and J. C. Jungers, *Trans. Faraday Soc.*, 33, 1353 (1937); O. Beeck and F. F. Rust, *J. Chem. Phys.*, 9, 480 (1941); C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A179, 169 (1941); R. v. Tassel, *Natuurw. Tijdschr.*, 20, 83 (1938).

Meinert¹⁹¹ also investigated the thermal decomposition of tetraethyl lead, in the liquid state as well as in the gas, and by both static and flow methods. In the liquid state at 220° the products were almost entirely ethane and ethylene. He concludes that this is not due to simple disproportionation, but that in the liquid state the whole process is too complicated to disentangle. In the gaseous state he postulates 4 reactions to explain his results in the range 300° to 425°,



He concludes that reaction (1) is of prime importance at high pressures and low temperatures, *i.e.*, when the concentration of tetraethyl lead is high and that of ethyl is low. Under these circumstances the amount of ethane formed was very high (up to four times as great as that of ethylene). Meinert offers no explanation as to what happens to the tetraethyl lead after it has lost its hydrogen. If, as might perhaps be expected, it decomposes by



this gives no explanation of the fact that the ethane formed is greater than the ethylene. Meinert also found that the percentage of ethane in the products increased on packing the reaction vessel, and he therefore concludes that (1) is a wall reaction.

In flow experiments at both low and high pressures butane was always an important product, amounting to about 1/3 of the gaseous products. This indicates the importance of reaction (53a). Considerable hydrogen is formed in flow experiments, especially at higher temperatures, which points to the occurrence of (2), or of the sequence



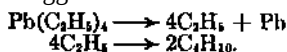
He concludes that the disproportionation reaction (53b) occurs only to a smjttl extent, since most of the ethane can be accounted for by (1), and the ethylene by (2). However, reaction (2) appears to be very unlikely, and if ethylene is not formed by disproportionation it almost certainly arises by (3) and (4).

Cramer¹⁸² investigated the thermal decomposition of tetraethyl lead in solution in benzene at high pressures. He found ethane and olefins as the predominant products, and assumed that the main reaction is disproportionation.

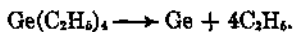
Leermakers¹⁸⁰ also investigated the decomposition of tetraethyl lead at 245° to 275° by the static method, the reaction being followed only by the

¹⁹¹R. N. Meinert, *J. Am. Chem. Soc.*, 65, 979 (1933).

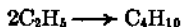
pressure change, and not by analysis. However, the final pressure was twice the initial, which suggests that the main reactions were



An investigation of the decomposition of germanium tetraethyl was made by Geddes and Mack,¹⁸¹ in the temperature range 420° to 450°. There appears to be little doubt that the primary step is

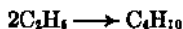


They reported H_2 , CH_4 , C_2H_6 , C_3H_8 , C_2H_4 , and higher olefins as products, the main ones being C_2H_6 and C_2H_4 , which again points to a predominance of the disproportionation reaction. No butane was reported. However, the "propane" reported was merely estimated from the carbon content of the saturated hydrocarbons as determined by combustion, and it was undoubtedly mainly butane. Assuming this, the results indicate that the reaction



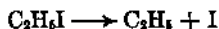
is occurring to an extent only about 1J3 to 1J4 that of the disproportionation.

In general the evidence regarding the occurrence of (53a) versus (53b) is very fragmentary and comes from a variety of sources. Thus Frey and Hepp¹⁹² investigated the pyrolysis of di-n-butyl and di-sec-butyl mercury at 490°, and found comparatively small amounts of ethane in the products and considerable butane. They conclude therefore that the reaction



is considerably faster than the disproportionation. In a number of photochemical and other reactions in which ethyl radicals are undoubtedly present butane is a product but no olefins are formed,¹⁹³ and this also argues against the disproportionation reaction.

Job and Emschwiller¹⁹⁴ investigated the photodecomposition of ethyl iodide, presumably at room temperature and in the liquid phase. The products were, in per cent, $\text{C}_2\text{H}_4 - 53$, $\text{C}_2\text{H}_6 - 36$, $\text{C}_4\text{H}_{10} \div 6$, $\text{H}_2 - 5$. This suggests that the primary step is



and that the predominant secondary reaction is disproportionation. Similar results were obtained by West and Schlessinger¹⁹⁵ who investigated the photolysis of liquid ethyl iodide at room temperature and found only ethane and ethylene as products.

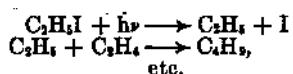
¹⁹² F. E. Frey and H. J. Hepp, *J. Am. Chem. Soc.*, 56, 3357 (1933).

¹⁹³ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 6, 179 (1938); *Can. J. Research*, B16,303 (1938); E. W. R. Steacie and R. Potvin, *J. Chem. Phys.*, 7,782 (1939).

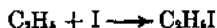
¹⁹⁴ A. Job and G. Emschwiller, *Compt. Rend.*, 179, 52 (1924).

¹⁹⁵ W. West and L. Schlessinger, *J. Am. Chem. Soc.*, 60, 961 (1938).

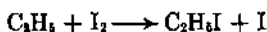
Joris and Jungers¹⁹⁶ investigated the polymerization of ethylene photosensitized by ethyl iodide. There is little doubt that the main reaction is



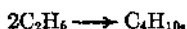
The reverse reaction



and the reaction



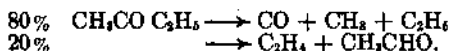
are rapid, and must be much faster than



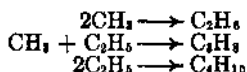
This may be due to a moderate activation energy for (53a), or more likely to a lower steric factor.

Garrison and Burton¹⁹⁷ account for the production of butane in the photolysis of propionaldehyde by reaction (53a), but suggest that it occurs on the wall, or by a three body process. There does not appear to be much experimental support for this suggestion. (See V-4 for details.)

Norrish and Appleyard¹⁹⁸ investigated the photolysis of methyl ethyl ketone at about 80°. The products indicate that the primary step occurs by



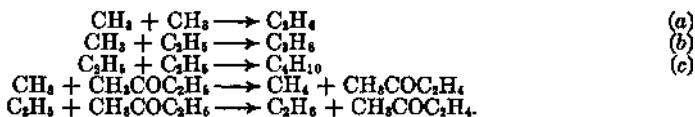
The saturated hydrocarbons formed consisted of roughly equal amounts of ethane, propane, and butane. This suggests that the three recombination reactions,



occur at approximately equal rates. However, the methods of gas analysis used were not reliable enough to allow much confidence in this result.

In a recent paper Moore and Taylor¹⁹⁹ point out that on the basis of probability we would expect ethane, propane, and butane to be formed in the ratio 1:2:1, if steric factors, etc., have no influence. Using more refined methods of gas analysis they re-investigated the matter. The products found are given in Table L.

The mechanism of hydrocarbon formation in the reaction is presumably



¹⁹⁶ G. G. Joris and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 47, 146 (1938).

¹⁹⁷ W. M. Garrison and M. Burton, *J. Chem. Phys.*, 10, 730 (1942).

¹⁹⁸ R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 1934, 874.

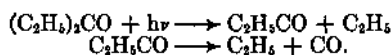
¹⁹⁹ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 466 (1940).

TABLE L. PRODUCTS OF THE PHOTOLYSIS OF METHYL ETHYL KETONE
(MOORE AND TAYLOR)

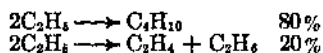
Temperature	90	110	155	200
H ₂	0.4	0.1	0.3	0.0
CO	47.5	49.0	47.0	48.5
CH ₄	3.4	4.4	9.0	18.0
C ₂ H ₄	2.2	0.5	1.7	3.0
C ₂ H ₆	11.5	13.0	14.5	12.5
C ₃ H ₈	19.1	20.0	18.6	11.0
C ₄ H ₁₀	13.2	13.0	9.0	7.0
C ₄ H ₈	1.5	—	0.0	—

At the lower temperatures the hydrocarbons probably arise by the combination of radicals. At 110° the ratio of the numbers of collisions of types *a:b:c* is roughly 1.00:1.74:0.83, while the observed formation of ethane, propane, and butane are in the ratio 1.00:1.54:1.00.

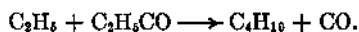
The photolysis of diethyl ketone was investigated by Noyes and Ells²⁰⁰ at room temperature. They found 80% butane, and 10% each of ethane and ethylene. The mechanism of the reaction is almost certainly



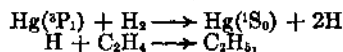
Hence on the basis of the products formed



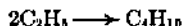
The only dubious point in this argument is the possibility of butane being formed to some extent by the reaction



Jungers and Taylor²⁰¹ investigated the mercury photosensitized hydrogenation of ethylene at room temperature much more thoroughly than had previous workers. They found that in clean vessels butane was the predominant product, not ethane. They conclude that the mechanism is



and that



is much faster than the disproportionation reaction. In reaction vessels which were not flamed out between runs a film of polymer (CH_n), formed on the walls, and under these circumstances much methane was formed.

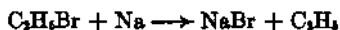
Similar results were obtained by Moore and Taylor,²⁰² who investigated the mercury photosensitized hydrogenation of ethylene at room temperature, and found the products to contain 84% butane, 14% ethane, and 2% methane.

²⁰⁰ V. R. Ells and W. A. Noyes, *J. Am. Chem. Soc.*, **61**, 2492 (1939).

²⁰¹ J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, **6**, 325 (1938).

²⁰² W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 504 (1940).

Bawn and Dunning²⁰³ by the dilute flame technique investigated the reaction of ethyl bromide and of ethyl chloride with sodium vapor at 350° Butane was found to be the sole product, *i.e.*, the reaction



appears to be followed only by combination of ethyls to butane.

The most reliable information on the question of recombination vs. disproportionation probably comes from the work of Moore and Taylor¹⁸⁸ on the photolysis of diethyl zinc and diethyl mercury. In the case of diethyl zinc, the products were approximately 10% hydrogen, 31% ethylene, 28% ethane, 20% butane, and 10% butene at room temperature. At 250° they were 2% hydrogen, 15% ethylene, 35% ethane, 38% butane, and 11% butene. At high temperatures in the presence of added hydrogen butane decreased somewhat and ethane increased. No significant amounts of methane were formed.

With mercury diethyl, the approximate products were

At 45°	H ₂ 1%,	C ₂ H ₄ 25%,	C ₂ H ₆ 29%,	C ₄ H ₁₀ 38%,	C ₄ H ₈ 7%.
At 250°	H ₂ 1%,	C ₂ H ₄ 20%,	C ₂ H ₆ 42%,	C ₄ H ₁₀ 28%,	C ₄ H ₈ 9%.

The main difference between these results and those with diethyl zinc is the smaller amount of hydrogen and greater ethane.

In the presence of hydrogen, ethane formation increases greatly especially at higher temperatures and high hydrogen concentrations. Ethane formation was also increased by increasing the mercury diethyl pressure, or by decreasing the light intensity.

TABLE LI. PRODUCTS FORMED FROM ETHYL RADICALS

Source of ethyls	Temp.	Products, mole per cent					
		H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₄ H ₁₀	C ₄ H ₈
EtBr + Na, EtCl + Na (Bawn and Dunning)	350	0	0	0	0	100	0
Et ₂ CO photolysis (Noyes and Ells)	30	0	0	10	10	80	0
Hg photosensitized hydro- genation of C ₂ H ₄	25		4		16	80	0
Mercury diethyl photolysis	45	2	0	25	29	38	7
Zinc diethyl photolysis	45	10	0	25	22	34	9
Lead tetraethyl pyrolysis (Meinert)	150	1	0	38	46	14	2
Ethyl iodide photolysis in presence of Hg	100	1	0	29	43	15	12
Ethyl iodide photolysis (West and Schlesinger)	25	0	0	50	50	0	0

Moore and Taylor summarize the products formed by ethyl radicals from various sources in Table LI. It will be noticed that the products vary from

²⁰³ C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, 35, 898 (1939).

100 per cent butane to 100 per cent of (ethane + ethylene). Moore and Taylor discuss the question as follows:

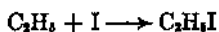
"If the disproportionation of two ethyl radicals to ethane and ethylene occurs bimolecularly in the gas phase, the activation energy, E , in order to account for the results of Bawn and Dunning must be at least 4 kcal. greater than that for the combination of the radicals. It is possible, however, that some of the butane formation observed by Bawn and Dunning occurs through the intermediacy of sodium ethyl at the walls of the reaction vessel. Although we do not believe that disproportionation is an important process at the low temperatures of the present investigations, it may be of much greater significance at the higher temperatures prevailing in the pyrolyses of the hydrocarbons.

"The large formation of ethane and ethylene observed in the photolysis of ethyl iodide, the considerable formation from the metal alkyls, and the small quantity formed from diethyl ketone must all be ascribed to reactions of the type

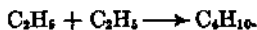


The activation energy for this reaction will be at most two to three kcal. greater than that for combination of ethyls to form butane. The ethane-ethylene fraction from mercury diethyl increases with increase in pressure of the alkyl and decrease in light intensity, which is to be expected if it depends on a reaction such as (5), while butane is formed by the combination of two ethyl radicals.

"The most important of the factors responsible for the large variation in products between, *e.g.*, ethyl iodide and diethyl ketone as a source of ethyl radicals is the correspondingly large variation in the ethyl radical concentrations from these compounds. An ethyl radical will combine with an iodine atom much more efficiently than with another ethyl or with a propionyl radical. This is because of the greater probability of formation of the activated state in a reaction involving an atom and a radical as compared with a reaction between two complex radicals. Thus Bawn¹⁷⁶ has estimated that the steric factor for



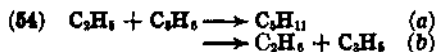
is unity, compared with a value of around 10^{-4} for



Since the formation of butane depends on the square of the ethyl radical concentration, while the reaction equivalent to disproportionation depends only on the first power, any decrease in the radical concentration will favor the formation of ethane and ethylene.

"However, even when a large proportion of the iodine atoms are removed during the photolysis of ethyl iodide by the addition of mercury vapor to

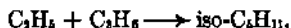
the system, the butane formation is still small (around 20 per cent), and factors other than the variation in radical concentration must also be considered to explain the variation in products between diethyl ketone, the metal ethyls, and ethyl iodide. One may reasonably expect slight differences in the energy of activation of (5) due to the influence of the different C—X bonds on the adjacent C—H bonds, and such small differences in activation energy may lead to considerable differences in the composition of the products."



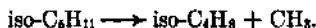
Beeck and Rust¹⁵⁴ investigated the polymerization of propylene sensitized by ethyl radicals from the thermal decomposition of lead tetraethyl. A flow system was used at 400°. They found that from 0.3 to 0.6 mole of propylene reacted per mole of radicals from lead tetraethyl. The rate is thus about 3 to 4 times slower than the rate of polymerization of ethylene under similar conditions. This is similar to the result with methyl radicals (*q.v.*), and is presumably due to the formation of allyl radicals by



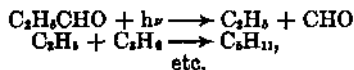
These have a long life and ultimately disappear by recombination, thus breaking the polymerization chain. The results are thus in complete agreement with the findings of Taylor and Smith. (See VI-35.) They also found indications of the reaction



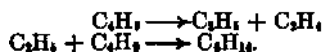
since they attributed the formation of *iso*-C₄H₁₀ to the reaction



Danby and Hinshelwood¹⁵⁹ investigated the polymerization of propylene photosensitized by propionic aldehyde at 300°. The reaction presumably occurred by a mechanism similar to the one discussed above, *viz.*,

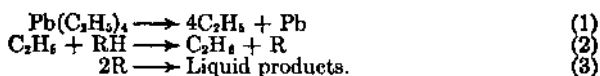


Frey and Hepp¹⁹² investigated the decomposition of di-*n*-butyl mercury by a flow method at 490°. Considerable hexane was formed, presumably by the reactions



(56) C_2H_5 + Other Hydrocarbons**Paraffins**

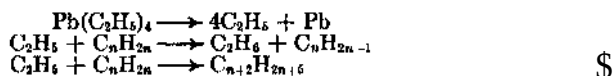
Cramer²⁰⁴ investigated the decomposition of tetraethyl lead dissolved in liquid paraffins at ca. 200° and high pressures. The main reactions appeared to be



He found that n-heptane, 2,2,3-tri-Me-butane, 2,2,4-tri-Me-pentane, n-decane, and cyclohexane all reacted in this way. The extent of reaction (2) appeared to be proportional to the number of secondary and tertiary hydrogens in the molecule, *i.e.*, the secondary and tertiary C—H bonds appear to be weaker than the primary.

Olefins

Cramer also investigated liquid olefins at 220° to 235° in a similar way. The main reactions occurring appeared to be



i.e., the radical can either abstract a hydrogen atom from the olefin, or else add on to form a higher alkyl radical. The results for a number of olefins are given in Table L II.

TABLE L II

Olefin	% reaction of olefin, <i>i.e.</i> , occurrence of (5)	% conversion of ethyl to ethane, <i>i.e.</i> , occurrence of (4)
1-hexene	53	47.1
2,3-di-Me-1-butene	50	34.5
2,3-di-Me-2-butene	28	70.4
3,3-di-Me-1-butene	58	18.0
1-heptene	65	45.8
2,3,3-tri-Me-1-butene	48	23.2
Di-iso-butylene	42	44.3
cyclohexene	32	62.9

A few general conclusions may be drawn:

(a) with the alpha-olefins reaction (4) occurs to a very slight extent provided that there are few secondary or tertiary hydrogens.

(b) with the normal olefins both reactions occur.

(c) 2,3-di-Me-2-butene appears to be relatively unsuceptible to reaction (5). This is in accord with its relatively low heat of hydrogenation.²⁰⁵

(d) cyclohexene undergoes reaction (4) readily.

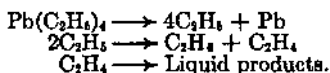
²⁰⁴ P. L. Cramer, *J. Am. Chem. Soc.*, 60, 1406 (1938).

²⁰⁵ J. B. Conant and G. B. Kistiakowsky, *Chem. Reviews*, 20, 181 (1937).

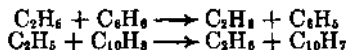
The results are rather rough and it is difficult to draw detailed conclusions. They are, however, in general accord with the work of Smith and Taylor. (See VI-35.)

Aromatic Compounds

Cramer also investigated benzene and naphthalene in a similar way. He found that about 43 per cent of the ethyl radicals from the lead tetraethyl were converted to ethane, but the benzene and naphthalene were unaffected. The reactions occurring are apparently:



The possible reactions

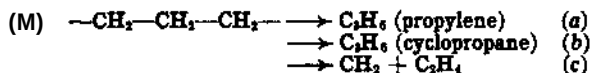


do not occur and must, therefore, have relatively high activation energies. This agrees with the generally accepted idea that the C—H bonds in aromatic nuclei are unusually strong. This is contrary to the statement of Hey and Waters²⁰⁶ that no known solvent is inert as far as the action of free radicals is concerned.

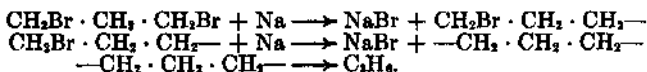
In the case of tetrahydronaphthalene and decahydronaphthalene, about 80 per cent of the ethyl radicals were converted to ethane showing that the C—H bonds on the hydrogenated carbon atoms are relatively weak. In addition, considerable amounts of the hydrocarbons disappeared by the formation of higher condensation products.



Reaction (57) is perhaps involved in the polymerization of propylene induced by methyl radicals from the photolysis of mercury dimethyl.¹⁶⁰ (See IV-8 for details.)



Using the diffusion flame technique Bawn and Hunter²⁰⁷ investigated the reaction of sodium atoms with $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$ at 382° . The products of the reaction were entirely cyclopropane and propylene, and they suggest that these arise by

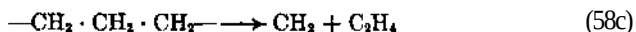


²⁰⁶ D. H. Hey and W. A. Waters, *Chem. Reviews*, 21, 169 (1937).

²⁰⁷ C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, 34, 608 (1938).

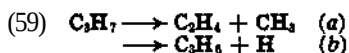
It was found that the ratio of propylene to cyclopropane in the products was decreased by increasing the pressure of the carrier gas, or by decreasing the pressure of tri-methylene bromide. It thus appears that propylene must be formed from the biradical by a wall reaction, while cyclopropane is formed homogeneously.

They conclude by the transition state method, by comparison with the propyl radical, that the activation energy of the reaction



is about 30 kcal.

Rice and Rice¹⁴⁴ estimate from free radical mechanisms an activation energy of about 5 to 10 kcal. for the reaction



Early attempts to prepare and detect the propyl radical were unsuccessful and this led to the conclusion that it had a very short life. Thus Paneth and Lautsch²⁰⁸ decomposed tetra-n-propyl lead at about 400°. The method was identical with that used by Paneth and Hofeditz²⁰⁹ to detect the methyl and ethyl radicals. Paneth and Lautsch attempted to identify the products of the decomposition by means of lead, zinc, and antimony mirrors. The only identifiable organo-metallic compounds were methyl compounds (bis-dimethyl antimony and dimethyl zinc). They therefore concluded that any propyl radicals formed decomposed rapidly to yield methyls by



Paneth and Loleit²¹⁰ had observed that ethyl decomposes at around 600°. They therefore concluded that the propyl radical might be stable at lower temperatures, and Paneth and Lautsch²¹¹ attempted to decompose tetra-n-propyl lead at lower temperatures by using lead and copper catalysts, and by high-frequency discharges. These attempts were unsuccessful.

Rice²¹² attempted to carry the propyl radicals in a current of ethylene in order to shift the equilibrium



over to the left, and thus inhibit the decomposition of the propyl radical. However, he obtained evidence only of the presence of methyl, and he concluded that all alkyl radicals higher than ethyl are unstable and decompose

²⁰⁸ F. Paneth and W. Lautsch, *Ber.*, **64**, 2708 (1931).

²⁰⁹ F. Paneth and W. Hofeditz, *Ber.*, **62**, 1335 (1929).

²¹⁰ F. Paneth and H. Loleit, *J. Chem. Soc.*, **1935**, 366.

²¹¹ F. Paneth and W. Lautsch, *J. Chem. Soc.*, **1936**, 380.

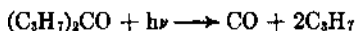
²¹² F. O. Rice, *Tram. Faraday Soc.*, **30**, 152 (1934).

rapidly at temperatures above 450°. Rice and Rice¹⁴⁴ estimated that the activation energy of reaction (59a) was about 25 kcal.

However, some conflicting evidence in this respect was obtained by Rice and Evering.²¹³ They decomposed azoisopropane in the presence of acetone in the temperature range 450° to 550°, using the usual Rice technique, and measuring the lives of the radicals produced by means of standard mirrors. It was found that the radical concentration fell off with distance from the furnace in a manner identical with that of methyl radicals from tetramethyl lead, except that at distances greater than 20 cm. the concentration fell off more slowly. This indicated the presence of a radical with a life *greater* than that of methyl, and suggests that the propyl radical is involved.

Bamford and Norrish²¹⁴ obtained hexane as a product of the photodecomposition of di-n-propyl ketone, and they concluded that the propyl radical was involved, and was stable at ordinary temperatures.

The first convincing demonstration of the existence of the n-propyl radical was made by Pearson and Purcell,²¹⁵ who streamed di-n-propyl ketone at about 2 mm. pressure through a quartz tube and irradiated it with light from a hot mercury arc. Under these circumstances it might be expected that the reaction



would occur. They detected active fragments at distances up to 35 cm. from the irradiated zone by their reaction with metallic mirrors, and found reaction with arsenic, antimony, tellurium, mercury, and lead. The product from the reaction with mercury reacted with mercuric bromide, to form n-propyl mercuric bromide which was definitely identified. The presence of the n-propyl radical was thus established. At room temperature in a silica tube 8 mm. in diameter they found a half-life of 2.3×10^{-3} sec. as compared with 3.3×10^{-3} and 5.3×10^{-3} sec. for ethyl and methyl under the same conditions. In a somewhat wider tube (11.2 mm.) Glazebrook and Pearson²¹⁶ obtained a half-life of 4.0×10^{-3} sec.

It thus appears that the n-propyl radical is stable at room temperature, but decomposes at high temperatures, and is thus not detectable in the products of thermal decomposition reactions at high temperatures.

Bawn,²¹⁷ from transition state calculations, concluded that the reaction



was endothermic to from 9 to 36 kcal., and had an activation energy of 24 to 39 kcal. This would make the propyl radical stable at room tempera-

²¹³ F. O. Rice and B. L. Evering, *J. Am. Chem. Soc.*, **55**, 3898 (1933).

²¹⁴ C. H. Bamford and R. G. W. Norrish, *Chem. and Ind.*, 54, 488 (1935); *J. Chem. Soc.*, **1935**, 1504.

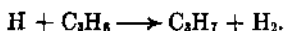
²¹⁵ T. G. Pearson and R. H. Purcell, *Nature*, **136**, 221 (1935); *J. Chem. Soc.*, **1936**, 253.

²¹⁶ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1936**, 1777.

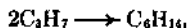
²¹⁷ C. E. H. Bawn, *Trans. Faraday Soc.*, **34**, 598 (1938).

ture, but unstable at temperatures not much higher than room temperature, in agreement with experimental findings.

Further information concerning the stability of the propyl radical comes from the work of Steacie and Parlee²¹⁸ on the reaction of hydrogen atoms with propane. There is no doubt that the primary step is

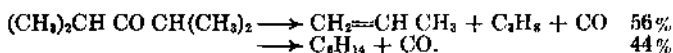


From the products of the reaction it appears that the propyl radicals thus formed are decomposing noticeably at temperatures above 170°. However, in the mercury photosensitized reactions of propane²¹⁹ at high pressures (see VI-62), the products of the reaction were almost exclusively hydrogen and hexane at temperatures up to 320°. This indicates that propyl radicals disappear exclusively by the reaction



and that dissociation of the propyl radical is inappreciable even at 320°. On the other hand,²²⁰ in the cadmium photosensitized reactions of propane at 310°, methane, butanes, and pentanes are also formed, and this suggests the ready occurrence of reaction (59a) at 310°. The evidence from photosensitization experiments is thus conflicting.

Glazebrook and Pearson²¹⁶ investigated the photolysis of di-isopropyl ketone in a manner similar to that of Pearson and Purcell with di-n-propyl ketone. They found radicals with a half-life of ca. 4.4×10^{-3} sec. at room temperature. However, the products found were n-propyl mercuric halides, rather than iso-propyl derivatives. Bamford and Norrish²²¹ concluded that the decomposition proceeded by



The hydrocarbon C_6H_{14} consisted mainly of di-isopropyl. Hence it may be concluded that the iso-propyl radical is formed in Glazebrook and Pearson's work, and that the isomerization occurs on combining with mercury, or on forming the alkyl mercuric halide. The iso-propyl radical thus appears to be very slightly more stable than the n-propyl radical.

Rice¹⁴⁴ suggests that the iso-propyl radical is much more stable than n-propyl, and suggests an activation energy about 20 kcal. higher for its decomposition.

In an investigation of the reaction of methyl radicals, produced by the photolysis of acetone, with propane at temperatures from 254° to 337°,

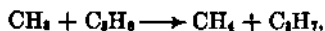
²¹⁸ E. W. R. Steacie and N. A. D. Parlee, *Trans. Faraday Soc.*, 35, 854 (1939); *Can. Research*, **B17**, 371 (1939).

²¹⁹ E. W. R. Steacie and D. J. Pewart, *J. Chern. Phys.*, 8, 571 (1940).

²²⁰ E. W. R. Steacie, D. J. LeRoy, and R. Potvin, *J. Chem. Phys.*, 9, 306 (1941).

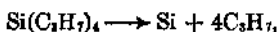
²²¹ C. H. Bamford and R. G. W. Norrish, quoted from (216).

Allen²²² found that no olefinic products were produced. The primary reaction is certainly



and hence the propyl and iso-propyl radicals appear to be reasonably stable at temperatures up to 337°.

Reaction (59&) is considerably more endothermic than (59a), and it would not be expected to be important. About the only evidence for its occurrence is the work of Waring²²³ who investigated the decomposition of silicon tetrapropyl in the temperature range 530° to 550°. The initial products were predominantly propylene, with lesser amounts of ethylene and some hydrogen. The primary step is presumably



and the presence of propylene suggests that the main secondary reaction at these temperatures is



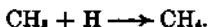
He accounts for the presence of ethylene by the reaction



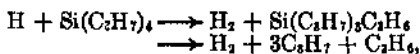
It seems extremely unlikely that such a reaction, involving two hydrogen atoms, should occur, and the obvious explanation of the presence of ethylene is



This explains the presence of methane, and the smaller amount of hydrogen present as compared with propylene can be accounted for by the reaction



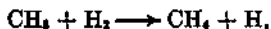
Reactions such as



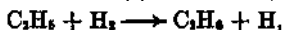
probably occur as well. Small amounts of nitric oxide were found to have no effect on the rate of reaction, so chains apparently do not participate.



No direct information is available on this reaction. However, since Cunningham and Taylor¹¹³ and Smith and Taylor¹¹⁶ found an activation energy of about 9 kcal. for the reaction



and Moore and Taylor¹⁸³ found approximately the same value for



the activation energy of

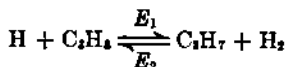


is perhaps about the same.

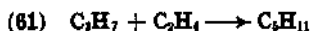
²²² A. O. Allen, *J. Am. Chem. Soc.*, 63, 708 (1941).

²²³ C. E. Waring, *Trans. Faraday Soc.*, 36, 1142 (1940).

If in the reaction

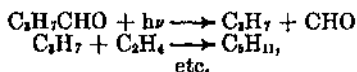


we take $E_1 = 10$ kcal. and $E_2 = 9$ kcal., we get for the C—H bond strength in propane approximately 103.5 kcal. This is definitely high, and it may be that E_1 is really somewhat lower than 10 kcal. and has a low steric factor. In view of the uncertainties of the discharge tube method, it appears probable that Steacie and Parlee's results (see VI-12 and VI-16) are not incompatible with $E_1 = 7$ kcal., and a steric factor of the order of 0.001. It is also possible that E_2 is higher than 9 kcal.

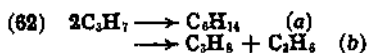
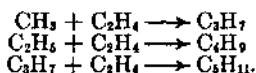


Jungers and Yeddanapalli²²⁴ showed that the ethylene polymerization could be sensitized by the photolysis of *n*- and iso-propyl iodides, presumably by means of the above reaction.

Danby and Hinshelwood¹⁵⁹ investigated the polymerization of ethylene photosensitized by butyric aldehyde at 300°, *i.e.*,



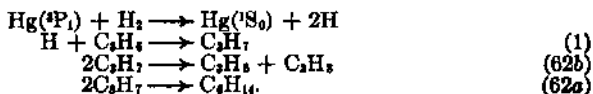
They conclude that there is little difference in the rates of the reactions



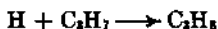
Moore and Taylor²²⁵ investigated the mercury photosensitized hydrogenation of propylene. The products were

Substance	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}
Per cent	2	1	26	5	2	64	—

The mechanism appears to be



The reaction



is left out of consideration since reaction (1) is so rapid that the hydrogen atom concentration will be kept down to a very low value. Hence, from

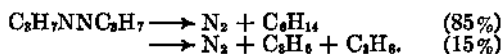
²²⁴ J. C. Jungers and L. M. Yeddanapalli, *Trans. Faraday Soc.*, 36, 483 (1940).

²²⁵ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 504 (1940).

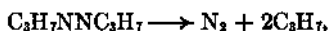
the products, it appears that the recombination reaction (62a) is faster than the disproportionation (626).

They point out that much more disproportionation occurs here than is the case with ethyl radicals. Thus in the mercury photosensitized hydrogenation of ethylene we have²²⁶ as products 2 per cent CEU, 14 per cent C₂H₆, and 84 per cent C₄H₁₀. They suggest that this might be due to the radicals in this case being mainly iso-propyl rather than n-propyl. In this connection it may be noted that Norrish²²⁷ found that propane and propylene were produced in large amounts in the photolysis of di-iso-propyl ketone, but not in the photolysis of di-n-propyl ketone.

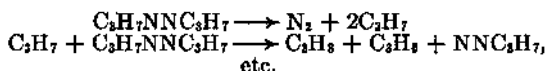
In the thermal decomposition of azo-iso-propane Ramsperger²²⁸ found that the overall reaction could be represented by



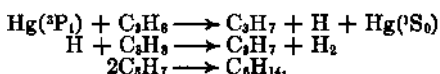
If we assume that the first step is in every case



this means that recombination of iso-propyl radicals occurs about 6 times as readily as disproportionation in the temperature range 250° to 290°. However, there is the definite possibility of



Steacie and Dewar²¹⁹ investigated the mercury photosensitized reactions of propane. The products were almost exclusively hydrogen and hexane, the latter being formed unquestionably by the reactions



Similar results were obtained with the cadmium photosensitized reaction.²²⁰ Similarly Bamford and Norrish²²⁹ found hexane as the main product of the photolysis of di-normal propyl ketone at room temperature, and attributed it to radical recombination.

In order to explain the pyrolysis of n-propyl iodide (see XI-17) Schumacher²³⁰ suggests a mechanism involving the reaction



This is consistent with the experimental results if $E_{626} \sim 20$ kcal., and the steric factor is about 0.05.

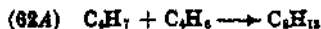
²²⁶ H. S. Taylor and J. C. Jungers, *J. Chem. Phys.*, 6, 325 (1938).

²²⁷ R. G. W. Norrish, quoted from footnote 225.

²²⁸ H. C. Ramsperger, *J. Am. Chem. Soc.*, 60, 714 (1928).

²²⁹ C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1935, 1504.

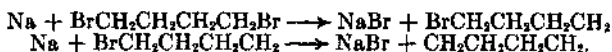
²³⁰ H. J. Schumacher, *Chemische Gasreaktionen*, Leipzig, 1938.



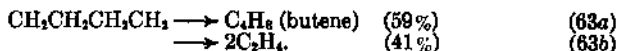
This reaction is probably involved in the mercury photosensitized polymerization and hydrogenation of butadiene.²³⁰ (See IV-9.)



Bawn and Milsted⁹⁶ investigated by the dilute flame method the reaction of excess sodium vapor with tetramethylene dibromide. There is no doubt that the primary steps are



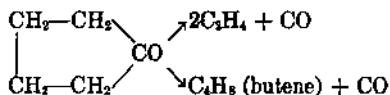
The final products corresponded to



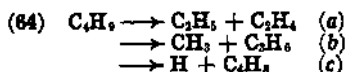
They calculate by the transition state method that

$$E_{63a} \sim 15 \text{ kcal.}$$

Experiments by Bamford and Norrish²³¹ on the photodecomposition of cyclopentanone gave as products approximately the amounts corresponding to the equal occurrence of the reactions

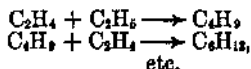


They suggested that the initial step was the formation of the tetramethylene radical and carbon monoxide, and that it subsequently either rearranged to butene or decomposed to ethylene. Their results are thus almost exactly equivalent to those of Bawn and Milsted.



The indications are that the butyl radical is less stable than propyl, just as propyl is less stable than ethyl. Paneth and Lautsch²³² decomposed lead tetra-iso-butyl. They were unable, however, to detect any radicals other than methyl, and hence concluded that the iso-butyl radical was relatively unstable.

However, evidence from the mercury photosensitized polymerization of ethylene (see IV-4) seems to indicate that the reaction proceeds, at least in part, by



²³⁰* H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, 12, 484 (1944).

²³¹ C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1938, 1521.

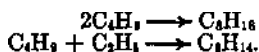
²³² F. Paneth and W. Lautsch, *Ber.*, 64, 2702 (1931).

Hence the butyl radical would appear to possess a fair stability at room temperature.

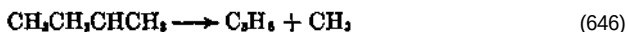
Frey and Hepp¹⁹² decomposed di-n-butyl mercury, and di-sec-butyl mercury by passing the compounds through a hot tube at low pressures at 490°. From di-n-butyl mercury a variety of products were obtained, but the predominant ones were C₂H₄ and C₄H₁₀, indicating that about 3/4 of the n-butyl radicals decomposed by



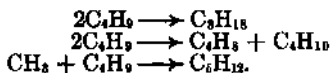
Other reactions of importance appeared to be



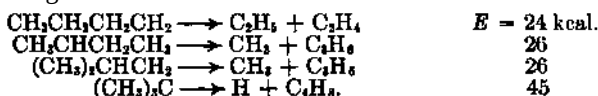
In the case of di-sec-butyl mercury, the principal products were C₃H₆, C₄H₈, n-C₄H₁₀, n-C₅H₁₂, and C₈H₁₈. This suggests about 10 per cent decomposition by



the other products arising by



Rice and his co-workers were unable to detect butyl radicals in the decomposition of organic compounds.²¹² He arbitrarily assigns¹⁴⁴ the following activation energies



Some indirect evidence regarding the stability of the butyl radical is obtainable from the work of Steacie and Brown⁵⁸ on the reaction of hydrogen atoms with butane. From the products formed they concluded that there were indications that the reaction



was occurring at temperatures above 100°.

Beeck and Rust²³³ also conclude that butyl radicals decompose only by a C—C split, and never by splitting off an H-atom. This is in agreement with the general evidence from other work, and in any case the latter process would be expected to be much more endothermic.



Frey and Hepp¹⁹² decomposed di-n-butyl mercury and di-sec-butyl mercury at low pressures and 490° in a flow system. In both cases CsHis was

²⁸⁸ O. Beeck and F. F. Rust, *J. Chem. Phys.*, 9, 480 (1941).

one of the products. They suggest that this arises by the obvious reaction



In any case, by analogy with other recombination reactions, this reaction would be expected to occur readily.

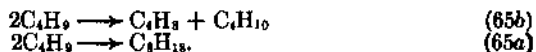
Moore and Taylor²²⁵ investigated the mercury photosensitized hydrogenation of butene. The products were

Substance	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}
Per cent	3	1	1	29	—	—	66

The first steps in the reaction are obviously



The main secondary reactions then are



It appears, therefore, that the recombination reaction is somewhat faster than the disproportionation. (There is also the possibility of the butane arising by $\text{H} + \text{C}_4\text{H}_9 \longrightarrow \text{C}_4\text{H}_{10}$, which they ignore, probably justly since the butene will keep the hydrogen atom concentration down to a very low value.)

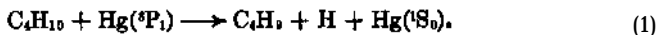
They point out that much more disproportionation occurs here than is the case with ethyl radicals, and suggest that this might be due to the radicals in this case being mainly iso-butyl rather than n-butyl.

Octanes are among the main products of the mercury photosensitized reactions of n-butane²³⁴ and of iso-butane.^{234a} It appears certain that they arise by (65a). (See VI-66 for details.)



The mercury photosensitized decomposition of n-butane has been investigated over a range of temperatures by Hay and Winkler.²³⁴ The products are almost exclusively hydrogen, octanes, and dodecanes at all temperatures studied, as shown in Table LIII.

There seems to be no doubt that, analogous to the other paraffins, the primary step is



The octanes then obviously arise by



and hydrogen atoms will presumably disappear by



²³⁴ A. W. Hay and C. A. Winkler, *Can. J. Research*, B21, 149 (1943).

^{234a} B. deB. Darwent and C. A. Winkler, *J. Phys. Chem.*, 49,150 (1945).

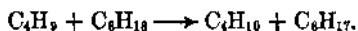
TABLE LIII. MERCURY PHOTSENSITIZED REACTION OF n-BUTANE

Temperature	ϕ_{H_1}	H_2	Products, moles $\times 10^*$		CWHM
			CH_4	C_3H_8	
100	0.19	1.06	—	0.350	0.529
	0.19	1.11	—	0.351	0.518
	0.19	1.09	—	0.342	0.50p
175	0.25	1.44	—	0.386	0.641
	0.26	1.46	—	0.394	0.653
250	0.29	1.65	0.01	0.939	0.737
	0.28	1.61	0.01	0.951	0.741
	0.29	1.89	0.04	1.01	0.694
	0.30	1.90	0.04	1.01	0.759

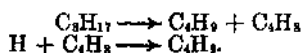
Dodecanes can arise by



The octyl radicals will be produced from octane by reactions analogous to (1) and (3). The large amount of dodecanes relative to octanes, especially at lower temperatures, suggests also the occurrence of the reaction

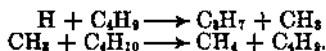


At high temperatures, the relative decrease in dodecanes is explainable by

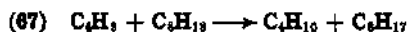


The mercury photosensitized reaction of iso-butane has been investigated by Darwent and Winkler,^{234a} and is very similar to the reaction of n-butane. Over the temperature and pressure range investigated, 80° to 250°, and 6 to 60 cm., the products were mainly H_2 , C_8H_{18} and $C_{12}H_{26}$. Small amounts of methane and heptane were also formed. The nature of the products and the reaction rate were independent of the pressure of iso-butane and of the presence of hydrogen. The mechanism is undoubtedly similar to that of n-butane, the main steps being (1), (2), (3), and (66).

Methane production is probably the result of the sequence



At higher temperatures decomposition of the propyl radical probably occurs also.



The occurrence of this reaction in the mercury photosensitized reactions of n-butane and of iso-butane has been suggested.^{234,234a} (See VI-66 for details.)

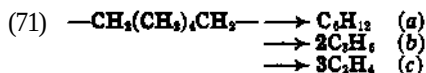
The yield of radicals was very small, most of them combining to diphenyl by reaction (70).

Diphenyl is also a product of the thermal²³⁷ and photochemical²³⁸ decomposition of lead tetraphenyl, probably by reaction (70).

Krassina²³⁹ investigated the photolysis of benzene in the region X1850-X2200 and suggests that the main secondary reaction is (70). The occurrence of (70) has also been suggested in the mercury photosensitized reactions of benzene.²⁴⁰ Wilson and Noyes,²⁴¹ however, were unable to detect diphenyl in the photolysis of benzene, and doubt the formation of phenyl radicals in the reaction.

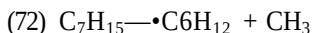


Since dibenzyl is a product of the thermal decomposition of dibenzyl tin at low pressures,²¹¹ EnA is presumably small.

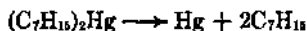


Bawn and Milsted⁹⁶ investigated the reaction of sodium atoms with hexamethylene dibromide. On the assumption that the primary step involved the formation of the hexamethylene biradical the products corresponded to a trace of (71b) and (71c), and almost all cyclohexane and hexenes (71a).

Similar conclusions were drawn by Bamford and Norrish²³¹ from experiments on the photolysis of cycloheptanone.

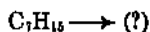


Rice and Polly²⁴² obtained cyclohexane as a product of the decomposition of diheptyl mercury at 350°. They conclude that this is formed by



followed by (72).

Stauff and Schumacher²⁴³ assume the reaction



as a step in the mechanism of the photochlorination of heptane, and suggest that $E_{72} \sim 0$. (For details see IX-41.)

²³⁷ M. F. Dull and J. H. Simons, *J. Am. Chem. Soc.*, **66**, 3898, 4328 (1933).

²³⁸ P. A. Leighton and R. A. Mortensen, *J. Am. Chem. Soc.*, **68**, 448 (1936).

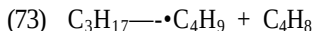
²³⁹ G. I. Krassina, *Acta Physicochimica* (U.R.S.S.), **10**, 189 (1939); see also N. Prileshajeva, *Acta Physicochimica* (U.R.S.S.), **10**, 193 (1939).

²⁴⁰ G. S. Forbes and J. E. Cline, *J. Am. Chem. Soc.*, **63**, 1713 (1941).

²⁴¹ J. E. Wilson and W. A. Noyes, *J. Am. Chem. Soc.*, **63**, 3025 (1941).

²⁴² F. O. Rice and O. L. Polly, *Ind. Eng. Chem.*, **27**, 915 (1935).

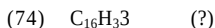
²⁴³ J. Stauff and H. J. Schumacher, *Z. Elektrochem.*, **48**, 271 (1942).



Hay and Winkler²³⁴ found dodecanes as products of the mercury photosensitized reactions of n-butane. These were almost certainly formed by the reaction



At higher temperatures (250°) the amount of dodecanes relative to octanes fell off. They ascribe this to the decomposition of the octyl radical by reaction (73). (For details see section VI-66.)



Stauff²⁴⁴ suggests reaction (74) with an activation energy of ~ 0 as a chain ending step in the photochlorination of hexadecane. (For details see IX-46.)

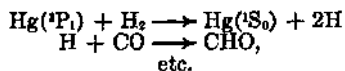
²⁴⁴ J. Stauff, *Z. Elektrochem.*, 48, 550 (1942).

Chapter VII

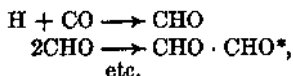
Systems Containing Oxygen

(1) $\text{H} + \text{CO} \longrightarrow \text{CHO}$

The reaction of hydrogen and carbon monoxide photosensitized by mercury proceeds with a quantum yield of about 1 at room temperature.¹ The products are formaldehyde, polymerized substances, etc.,² and the mechanism obviously seems to be



This indicates a relatively low activation energy for reaction (1). Frankenburger³ investigated the mercury photosensitized reaction more thoroughly, and found a quantum yield of about 1. Formaldehyde and glyoxal were detected among the products. He suggests the mechanism



Geib and Harteck⁴ produced hydrogen atoms by the discharge tube method, and investigated their reaction with carbon monoxide at low temperatures. No noticeable reaction occurred. This might be due to (a) an appreciable activation energy for (1), or (b) the rapid destruction of CHO by hydrogen atoms.

The reaction of hydrogen atoms, produced by mercury photosensitization, with CO, was also investigated by Farkas and Sachsse.⁶ The reaction was followed by measuring the drop in hydrogen atom concentration in the presence of carbon monoxide by means of the para-ortho hydrogen conversion. On the assumption that the reaction occurs by a three-body mechanism,



their results lead to the conclusion that at room temperature 1 three-body collision in 3700 is effective. This probably arises from a combination of an

¹ M. Barak and H. S. Taylor, *Trans. Faraday Soc.*, 28, 569 (1932).

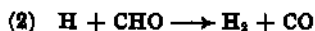
² H. S. Taylor and A. L. Marshall, *J. Phys. Chem.*, 29, 1140 (1925).

³ W. Frankenburger, *Z. Elektrochem.*, 36, 757 (1930); W. Frankenburger and R. Zell, *Z. physik. Chem.*, B2, 395 (1929).

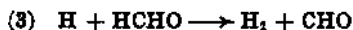
⁴ K. H. Geib and P. Harteck, *Ber.*, 66, 1815 (1933).

⁶ L. Farkas and H. Sachsse, *Z. physik. Chem.*, B27, 111 (1934).

appreciable, but not large activation energy and a relatively small steric factor.

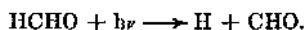


This reaction has been postulated as a step in photochemical and thermal mechanisms, although there is little direct evidence for it. Thus it has been assumed in the pyrolysis of benzaldehyde,⁶ and in the photolysis of acetaldehyde.⁷ It has also been suggested as one alternative explanation of the results of Geib and Harteck⁴ on the reaction of H-atoms with CO. (See VII-1.) Gorin⁸ in connection with an investigation of the photolysis of formaldehyde in the presence of iodine, has suggested that $E_2 \sim 5$ kcal. (See V-2.)

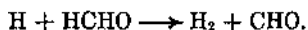


This reaction is an important step in the mechanism of the formaldehyde photolysis. (See V-2 for details.)

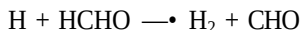
Akeroyd and Norrish⁹ investigated the photolysis of formaldehyde at higher temperatures. The quantum yield was found to increase strongly with increasing temperature, and in view of the chain characteristics of the reaction it appears certain that the primary step is



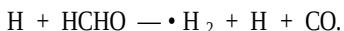
From the temperature coefficient of the reaction they obtained an activation energy of 16.2 kcal., which they suggest is the activation energy of the reaction



The reaction was investigated directly by the discharge tube method by Geib,¹⁰ who concluded that the activation energy was smaller than 5 kcal. Geib suggests that there are two primary steps



and



However, it seems more likely that the results can be explained by the first reaction together with



In the absence of a detailed description of Geib's work it is not possible to suggest an explanation of the discrepancy between his results and those of Akeroyd and Norrish.

⁶ J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A175**, 131 (1940).

⁷ R. F. Barrow, T. G. Pearson, and R. H. Purcell, *Trans. Faraday Soc.*, **35**, 880 (1939).

⁸ E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

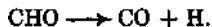
⁹ E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 890.

¹⁰ K. H. Geib, *Ergeb. exakt. Naturwiss.*, **15**, 44 (1936).

Gorin ⁸ (see V-2) suggests that the reaction occurring is



At high temperatures, however, there is little difference between this and (3) followed by



(4) $\text{H} + \text{HCOOH} \longrightarrow (?)$

Urey and Lavin ¹¹ investigated the reaction of formic acid with hydrogen atoms produced by the discharge tube method. They found that the acid catalysed the recombination of H-atoms, and that formaldehyde was formed. The reaction was also investigated by Geib, ¹⁰ who found it to be complicated and at least partly heterogeneous, the products being CO, CO₂, and water. The activation energy was in the neighbourhood of 7-8 kcal. The mechanism is doubtful.

Burton ¹² investigated the photolysis of formic acid with an apparatus of the Pearson type. Antimony mirrors were not removed by the products of the photolysis, and hence hydrogen atoms were not present. In the case of acetic acid (VII-8) H-atoms are detectable. He, therefore, used acetic-formic acid mixtures as a check on whether H-atoms were formed but were removed by a very fast reaction with formic acid. The result was that a mixture of 4 acetic to 1 formic acid removed mirrors about 4 times more slowly than pure acetic acid. This indicates that hydrogen atoms react rapidly with formic acid, in agreement with the results of Geib by the Wood-Bonhoeffer method. The rate, however, is much too low to account for the failure to observe mirror removal with formic acid, and it follows, therefore, that H-atoms are not formed in its photolysis.

(5) $\text{H} + \text{CH}_3\text{OH} \longrightarrow (?)$

Geib ¹⁰ investigated the reaction of hydrogen atoms produced by the discharge tube method with methyl alcohol. The products were water, CO, and CH₄. Chemiluminescence also occurred, the C—H and C—C bands being emitted, and there appeared to be evidence of a catalytic recombination of hydrogen atoms in the presence of methyl alcohol. The data are too scanty to permit any conclusions regarding the mechanism. The activation energy of the primary step must be ≤ 10 kcal.

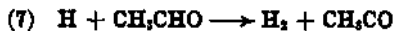
(6) $\text{H} + \text{CH}_3\text{COO} \longrightarrow \text{CH}_4 + \text{CO}_2$

Burton ¹³ has suggested this reaction with a low activation energy as a step in the photolysis of acetic acid vapor. (See VII-8.)

¹¹ H. C. Urey and G. I. Lavin, *J. Am. Chem. Soc.*, 51, 3286 (1929).

¹² M. Burton, *J. Am. Chem. Soc.*, 58, 1655 (1936).

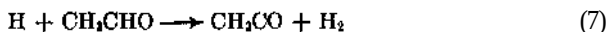
¹³ M. Burton, *J. Am. Chem. Soc.*, 58, 692, 1645 (1936).



There is little direct information about this reaction. Urey and Lavin¹¹ attempted to investigate it by the discharge tube method and found that polymerization of acetaldehyde occurred, apparently to paraldehyde. This, however, was probably merely due to heat. A few experiments by Steacie¹⁴ indicate that virtually no reaction occurs at room temperature, corresponding to an activation energy of not less than ca. 10 kcal.

The reaction is a step in the mechanism suggested by Rice and Herzfeld for the thermal decomposition of acetaldehyde. (See III—10.) It does not appear in the final rate expression, however, and hence no estimate of its activation energy is necessary as far as the mechanism is concerned.

Patat and Sachsse¹⁵ investigated the acetaldehyde decomposition by the para-ortho hydrogen method. The hydrogen atom concentration was found to be about 3 powers of 10 lower than that predicted by the mechanism. Letort¹⁶ has discussed the possible free-radical mechanisms in detail, and concludes that it is possible to reconcile Patat and Sachsse's results with the Rice-Herzfeld scheme provided that, among other things, the activation energy of the reaction

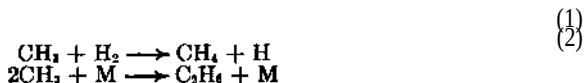


lies between 0 and 14 kcal.

Leermakers¹⁷ investigated the photolysis of acetaldehyde and proposed a Rice-Herzfeld type of mechanism which includes reaction (7). Patat¹⁸ investigated the stationary H-atom concentration during the photolysis by the para-ortho hydrogen method. He adopts Leermakers' mechanism, and concludes that

$$k = \frac{k_1}{k_7 k_2^{1/2}}$$

where reactions (1) and (2) are



and

$$[\text{H}] = k \sqrt{I_{\text{abs}}} \sqrt{[\text{H}_2]} / [\text{CH}_3\text{CHO}]$$

The experimental activation energy was 1.9 kcal., hence

$$E_1 - E_7 - \frac{1}{2}E_2 = 1.9 \text{ kcal.}$$

Assuming $E_2 \approx 0$,

$$E_1 - E_7 \approx 1.9 \text{ kcal.}$$

¹⁴ E. W. R. Steacie, unpublished.

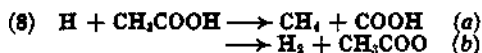
¹⁵ F. Patat and H. Sachsse, *Z. physik. Chem.*, **B31**, 105 (1935); H. Sachsse, *Z. Elektr. Chem.*, **41**, 493 (1935); F. Patat, *Z. physik. Chem.*, **B32**, 294 (1936).

¹⁶ M. Letort, *Thesis*, Paris, 1937.

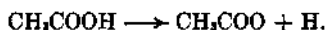
¹⁷ J. A. Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934).

¹⁸ F. Patat, *Z. physik. Chem.*, **B32**, 274 (1936).

Patat attempts in a rather inconclusive way to evaluate E_1 and E_7 separately (see V-3), and concludes that if the steric factor of reaction (7) is 0.1, $E_7 \leq 7.2$ kcal., and $E_1 \leq 9$ kcal. The upper value of 9 kcal. is in agreement with general evidence concerning reaction (1), but 7.2 kcal. seems rather low for reaction (7).



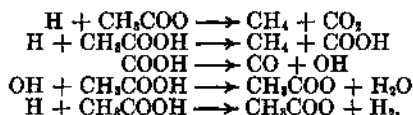
The quantum yield of the photolysis of acetic acid vapor is approximately 1.¹⁹ The reaction has been investigated by the Paneth method by Burton.²⁰ Using the guard-ring method he concluded that H-atoms are formed but no methyl radicals. The number of mirror-active particles was less than 1/10 that with acetone under the same conditions. Since no methyl radicals are produced, CH_3CO cannot be formed either, as it would yield methyl by dissociation. The primary process must, therefore, be



The reaction



is also ruled out by the absence of methyl radicals. This agrees with Rice's assignment of 40-70 kcal. for the activation energy of this reaction. Burton suggests secondary reactions such as



The rate of decay of H-atoms with distance from the irradiated zone corresponded to an activation energy of about 7.3 — 10.3 kcal. for the reaction of H-atoms with acetic acid, and he suggests that the reaction to which this applies is (8a), and that the activation energy of (8b) is about 1.8 kcal. higher, since the yield of hydrogen is much less than that of carbon monoxide.

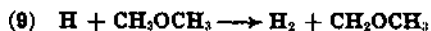
However, he points out that there is another possible mechanism involving double molecules of acetic acid. If this holds, then it is probable that the experimentally found activation energy of 7.3 — 10.3 kcal. corresponds to (86) rather than to (8a).

Clusius and Schanzer^{20a} have investigated the photolysis of solutions of acetic acid in D_2O . They conclude that the reaction proceeds by a free radical mechanism which does involve methyl radicals. It is, of course, possible that the mechanism in the liquid phase is quite different from that of the vapor.

¹⁹ L. Farkas and O. H. Wansborough-Jones, *Z. physik. Chem.*, **B18**, 124 (1932).

²⁰ M. Burton, *J. Am. Chem. Soc.*, **58**, 692, 1645 (1936).

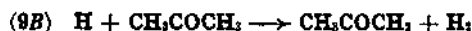
^{20a} K. Clusius and W. Schanzer, *Ber.*, **76B**, 1795 (1942). (Seen in abstract only.)



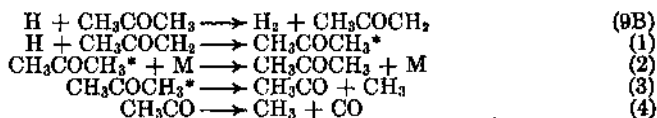
In connection with a postulated chain mechanism for the thermal decomposition of dimethyl ether Rice and Herzfeld²¹ have suggested an activation energy of 10 — 15 kcal. for reaction (9).



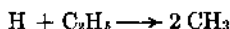
This reaction, of the atomic cracking type, has been postulated as a step in the mechanism of the reaction of hydrogen atoms with acetone. (See VII-9B.)



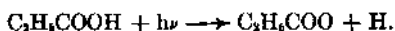
The reaction of hydrogen atoms, produced by the discharge-tube method, with acetone has been investigated by Harris and Steacie.^{21a} The sole reaction products were methane and carbon monoxide. With deuterium atoms, the resulting methane was almost completely exchanged, while the remaining acetone was only slightly deuterized. They suggest the mechanism



The measured activation energy is 9 kcal., which is presumably to be ascribed to (9B). Rice's early estimate of 8 kcal. is in good agreement with the experimental value. It may be noted that reactions (1) and (3) together constitute the equivalent of 'atomic cracking' reactions such as



Henkin and Burton²² have investigated the photolysis of propionic acid vapor. The reaction is similar to that of acetic acid in that by the guard-mirror method H-atoms can be detected but no alkyl radicals. They conclude, therefore, that the primary process is

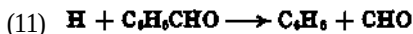


From the rate of decay of H-atoms with distance from the irradiated zone they conclude that the activation energy of reaction (10) is between 7.7 and 9.2 kcal., assuming a steric factor of unity.

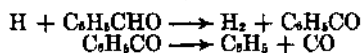
²¹ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, 56, 284 (1934).

^{21a} G. M. Harris and E. W. R. Steacie, *J. Chem. Phys.*, in press.

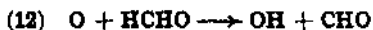
²² H. Henkin and M. Burton, *J. Am. Chem. Soc.*, 60, 831 (1938).



This reaction has been assumed as a step in the chain mechanism for the thermal decomposition of benzaldehyde.²³ The reactions

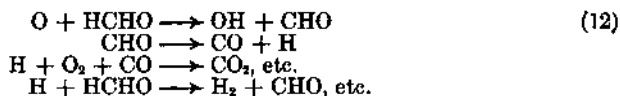


would, however, seem more likely by analogy with other aldehydes. (See 111-12.)

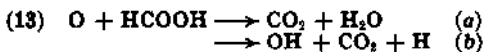
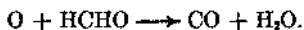


Geib and Vaidya²⁴ have investigated the luminescence produced when oxygen atoms are mixed with formaldehyde vapor. The luminescence was very weak, and only the hydroxyl bands at 3064Å could be identified.

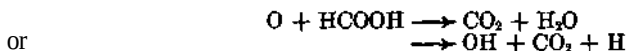
Geib¹⁰ investigated the reaction of oxygen atoms produced by the discharge tube method with formaldehyde vapor at room temperature. The products were about 40 per cent CO, 40 per cent H₂, and 20 per cent CO₂. He suggests the mechanism



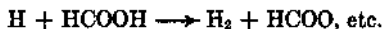
No estimates of activation energies are given, but from the fact that the reaction proceeds readily at room temperature it may be concluded that *E*₁₂ is not greater than 8 kcal. Geib²⁶ has discussed the mechanism of the reaction from the point of view of Rice and Teller's principle of least motion, and concludes that this favors reaction (12) as the primary step rather than the possible reaction



Geib¹⁰ has investigated the reaction of oxygen atoms produced by the discharge tube method with formic acid vapor. The main product was carbon dioxide (up to 90 per cent), and a trace of carbon monoxide and some hydrogen were also formed. He suggests that the primary reaction is



with an activation energy of 6 to 7 kcal. This is followed by reactions such as

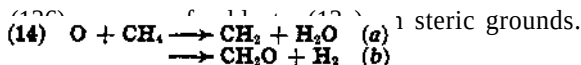
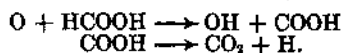


²³ J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 237 (1942), **A175**, 131 (1940).

²⁴ K. H. Geib and W. M. Vaidya, *Proc. Roy. Soc. (London)*, **A178**, 351 (1941); K. H. Geib, *Z. Elektrochem.*, **47**, 275 (1941).

²⁶ K. H. Geib, *Z. Elektrochem.*, **47**, 761 (1941).

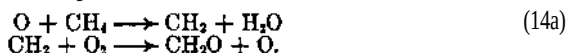
Reaction (136) might, of course, occur in stages



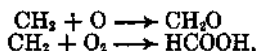
Kistiakowsky and Millington²⁶ investigated the reaction of photochemically produced oxygen atoms (in ³P and ¹D states) with methane. The collision yield was less than 10⁻⁵, and probably less than 10⁻⁶ at room temperature. The activation energy of the reaction is thus greater than 6 kcal.

Harteck and Kopsch²⁷ produced oxygen atoms by the discharge tube method and found practically no reaction with methane. In a later paper²⁸ the same authors reported the results in more detail. About 1 per cent of methane reacted at room temperature, and about 6 per cent at 190°. Water and carbon dioxide were formed in the ratio of 2 : 1. This corresponds to an activation energy of about 7 kcal.¹⁰ Geib and Harteck²⁹ also found that O atoms reacted negligibly with methane at room temperature.

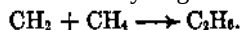
Steacie and Parlee³⁰ investigated the reaction by the discharge tube method from 30° to 330°. The products of the reaction were carbon monoxide, carbon dioxide, and water. Ethane was not formed. The activation energy was found to be 8.1 kcal. in agreement with Harteck and Kopsch's results. In connection with the theory of hydrocarbon oxidation Norrish³¹ has suggested that the chain steps in the oxidation of methane are



Steacie and Parlee suggest that the reaction occurring in their investigation is perhaps (14a), and that this is rate-controlling and thus has an activation energy of about 8 kcal. The secondary reactions are then perhaps



followed by the oxidation of formaldehyde and formic acid. The absence of ethane is then due to the relatively high activation energy of the reaction



The reaction has also been investigated by the discharge-tube method by Kuschnerov and Schechter,³² who found that formaldehyde constituted

²⁶ G. B. Kistiakowsky and P. E. Millington, *Z. physik. Chem.*, **B13**, 155 (1931).

²⁷ P. Harteck and U. Kopsch, *Z. Elektrochem.*, **36**, 714 (1930).

²⁸ P. Harteck and U. Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

²⁹ K. H. Geib and P. Harteck, *Z. physik. Chem.*, **A170**, 1 (1934).

³⁰ E. W. R. Steacie and N. A. D. Parlee, *Can. J. Research*, **B16**, 203 (1938).

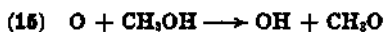
³¹ R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A150**, 36 (1935).

³² M. Kuschnerov and A. Schechter, *Compt. Rend. Acad. Sci. (U.R.S.S.)*, **32**, 560 (1941).

about 50 per cent of the gaseous products. They suggest that this is formed directly by the reaction

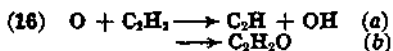


and that this is followed by further oxidation of formaldehyde, ultimately giving carbon dioxide and water as found by previous workers.



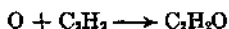
Harteck and Kopsch²⁸ found that oxygen atoms produced by the Wood-Bonhoeffer method reacted completely with methyl alcohol under the normal experimental conditions at room temperature. Luminescence occurred and the hydroxyl bands were emitted. The products were CO_2 , H_2O , CO , and H_2 . They suggest that the primary reaction is (15). From the collision yield the activation energy appears to be ≤ 4 kcal.

Geib and Vaidya²⁴ investigated the luminescence when oxygen atoms are mixed with methyl alcohol. Both OH and CH bands were detected.



Harteck and Kopsch²⁸ found instantaneous reaction between acetylene and oxygen atoms produced by the discharge tube method, *i.e.*, the activation energy is not greater than 4 kcal. The main products were H_2O , CO_2 , CO , and H_2 . The primary reaction would appear to be either 16(a) or (b).

Geib and Harteck⁴ found that an addition product was formed when oxygen atoms reacted with acetylene at -183° . The empirical formula of the product was $\text{C}_2\text{H}_2\text{O}_2$. Since the reaction occurs at liquid air temperature, it suggests that the reactions



and



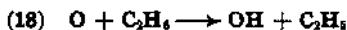
have practically zero activation energy, but they probably are surface-catalysed under Geib and Harteck's conditions.

Geib and Vaidya²⁴ have investigated the luminescence which accompanies the reaction. CC, CH, OH, and CHO bands were observed.

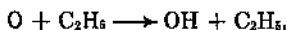


Geib and Harteck⁴ found that an addition product was formed when oxygen atoms were mixed with ethylene at -183° . The activation energy of reaction (17), which probably occurs at the wall, thus appears to be practically zero.

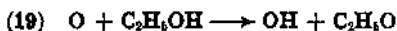
Geib and Vaidya²⁴ have investigated the luminescence which accompanies the reaction of oxygen atoms with ethylene. CC, CH, OH, and CHO bands were detected.



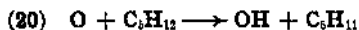
Harteck and Kopsch²⁸ investigated the reaction of oxygen atoms, produced by the discharge tube method, with ethane at room temperature. From 2 to 5 per cent reaction occurred under the normal experimental conditions, corresponding to an activation energy of about 7 kcal. Hydroxyl bands were emitted as luminescence, and the main products were CO₂ and H₂O. The reaction occurring is perhaps



but this is by no means established.



The reaction was investigated by Harteck and Kopsch.²⁸ The results were practically identical with those for methyl alcohol. (See VII-15.) The activation energy thus appears to be ≤ 4 kcal.

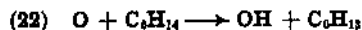


This reaction was investigated by the discharge tube method by Harteck and Kopsch.²⁸ From 10 to 25 per cent reaction occurred, corresponding to an activation energy of about 5 kcal. The reaction occurring may perhaps be (20).

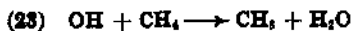


Harteck and Kopsch²⁸ found instantaneous reaction between benzene vapor and oxygen atoms produced by the discharge tube method. The activation energy of the reaction is thus ≤ 4 kcal. OH, CH, and CC bands were emitted as luminescence, and the main products were H₂O, CO₂, H₂, and CO. The primary reaction is perhaps (21a).

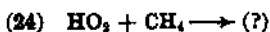
Geib and Harteck⁴ found that addition products were formed when oxygen atoms were mixed with benzene at low temperatures. This suggests an activation energy of approximately zero for reaction (21b) but it is probably a wall reaction under these conditions. The luminescence has been further investigated by Geib and Vaidya.²⁴



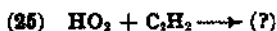
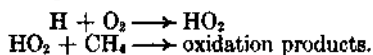
The reaction has been investigated by Harteck and Kopsch.²⁸ By the discharge tube method, under the usual experimental conditions, 10 to 25 per cent reaction occurred at room temperature, corresponding to an activation energy of about 5 kcal. The main products were CO₂ and H₂O, and OH bands were emitted as luminescence. The reaction occurring is perhaps (22).



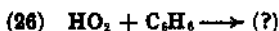
Van Tiggelen³³ investigated the acetone photosensitized oxidation of methane, and concluded that reaction (23) occurred with an activation energy of 8.5 kcal. (See VII-40.)



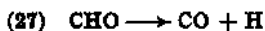
Geib and Harteck²⁹ found that while hydrogen and oxygen atoms both react negligibly with methane at room temperature, hydrogen atoms when added to a mixture of methane and oxygen cause rapid oxidation of methane even at -183° . This is probably due to the reactions



As with methane, hydrogen atoms when added to a mixture of acetylene and oxygen cause rapid oxidation of acetylene.²⁹ (See VII-24.)



Results with benzene are similar to those with methane and acetylene.²⁹ (See VII-24 and 25.)



The formyl radical has been assumed to occur in many reaction mechanisms, and there seems to be no doubt that it does so. There is no definite spectroscopic evidence for its existence, although Vaidya³⁴ has suggested that bands observed in the spectrum of burning ethylene may be due to it. It also seems certain that it possesses moderate stability. Estimates of the activation energy of reaction (27) are bound up with the mechanism of the photolyses of formaldehyde and acetaldehyde. These have already been discussed in detail. (See V-2 and 3.)

In early photochemical work it was assumed³⁵ that formyl would decompose instantaneously, *i.e.*, with no activation energy. Rice, however, in connection with free radical mechanisms, assumed a fair stability for the radical,³⁶ and suggested an activation energy of 30 ± 10 kcal. for reaction (27).

Burton³⁷ has reviewed the evidence concerning the participation of formyl in photochemical processes and concludes that formyl is stable up

⁸³ A. van Tiggelen, *Ann. mines Belg.*, 43, 117 (1942). (Seen in abstract only.)

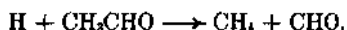
³⁴ W. M. Vaidya, *Proc. Roy. Soc. (London)*, A147, 513 (1934).

⁸⁸ R. G. W. Norrish, *Trans. Faraday Soc.*, 30, 107 (1934).

⁸⁶ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

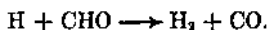
⁸⁷ M. Burton, *J. Phys. Chem.*, 41, 322 (1937); *J. Am. Chem. Soc.*, 60, 212 (1938).

to at least 100°. He bases his argument on the following facts. He points out that his experiments¹² on the acetaldehyde photolysis by the guard-mirror method indicate that methyl radicals are formed in the photolysis, but not hydrogen atoms. Bates has suggested that hydrogen atoms might be formed and disappear by a very rapid reaction with acetaldehyde, such as



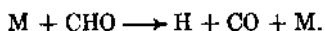
It seems certain, however, that the reaction of H-atoms with acetaldehyde is not sufficiently fast for this explanation to hold, and it may, therefore, be assumed that hydrogen atoms are not formed in the reaction to an appreciable extent. Formyl radicals are undoubtedly formed in the reaction, and they must, therefore, have sufficient stability to disappear by reactions other than decomposition at temperatures up to 100°.

It has also been suggested³⁸ that hydrogen atoms might be formed in the acetaldehyde photolysis and then be cleaned up by the reaction

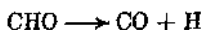


Even this explanation, however, would require a moderate stability for the formyl radical.

Style and Summers³⁹ found that the photolysis of formaldehyde at temperatures above 100° is accelerated by hydrogen and nitrogen. The temperature coefficient of the reaction corresponds to an activation energy of 12 kcal. They suggest that this is due to the reaction



Bawn⁴⁰ has estimated theoretically that the activation energy of the reaction

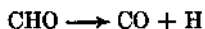


is 19.5 kcal. The estimate is based on the assumption that the strength of the C—H bond in CHO is 80 kcal., and that the reaction



is exothermic to the extent of 80 kcal.

Gorin⁴¹ has investigated the photolysis of acetaldehyde in the presence of iodine. His work has been discussed in detail in Section V-3. Hydrogen atoms and methyl radicals were "fixed" by reaction with iodine, and the production of HI and CH₃I is thus a measure of their formation. Since one formyl is produced for each methyl in the primary step, the ratio HI/CH₃I gives a measure of the extent to which the reaction



⁸⁸ R. F. Barrow, T. G. Pearson, and R. H. Purcell, *Trans. Faraday Soc.*, 35, 880 (1939).

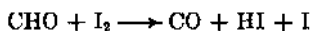
³⁹ D. W. G. Style and Summers, *Trans. Faraday Soc.*, 36, 899 (1939).

⁴⁰ C. E. H. Bawn, *Trans. Faraday Soc.*, 35, 899 (1939).

⁴¹ E. Gorin, *Acta Physicochimica* (U.R.S.S.), 9, 681 (1938); *J. Chem. Phys.*, 7, 256 (1939).

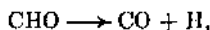
has occurred. From the temperature coefficient of the ratio **HI/CH₃I** he calculates an activation energy of 26 ± 2 kcal. for the decomposition of the formyl radical.

Gorin's work has been repeated in more detail by Blacet and his co-workers.⁴² Their results differ considerably from those of Gorin. They suggest that the reaction



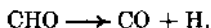
may be of importance. If this is so, Gorin's estimate of the activation energy of the decomposition of the formyl radical becomes unreliable.

Gorin⁴³ has also investigated the photolysis of formaldehyde in the presence of iodine. His results do not permit an estimate of the activation energy of the reaction

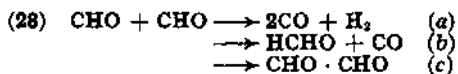


but are not inconsistent with a value of 26 kcal.

On the basis of experiments on the photolysis of acetaldehyde with intermittent light Haden and Rice⁴⁴ arrive at a value of 7.8 kcal. for the activation energy of a first-order chain-ending step at the wall. (See V-3 for details.) They suggest that the value applies to the reaction



The fact that the activation energy is lower for a wall reaction than for the gas phase decomposition is, of course, not surprising. There is, however, considerable doubt regarding the chain-breaking step to which this value applies, and it is quite probable that the reaction concerned is not VII-27



This reaction has frequently been postulated as a chain-ending step in the photolysis of aldehydes, the mechanisms of which are discussed in detail in sections V-2 to 4. Reaction (28a) has been suggested in the photolysis of formaldehyde,⁴⁵ acetaldehyde,⁴⁶ and propionaldehyde.^{47,49} Reaction (28b) has been suggested in the photolysis of formaldehyde,⁴³ acetaldehyde,^{41,48} and propionaldehyde,⁴⁹ and its occurrence is supported by the detection of formaldehyde as a product of the acetaldehyde photolysis.^{41, 48, 50} Reac-

⁴² F. E. Blacet and J. D. Holdman, *J. Am. Chem. Soc.*, 64, 889 (1942); F. E. Blacet and D. E. Loeffler, *J. Am. Chem. Soc.*, 64, 893 (1942).

⁴³ E. Gorin, *J. Chem. Phys.*, 7, 256 (1939).

⁴⁴ W. L. Haden and O. K. Rice, *J. Chem. Phys.*, 10, 445 (1942).

⁴⁶ M. Burton, *J. Am. Chem. Soc.*, 58, 1645 (1936).

⁴⁷ P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, 55, 1766 (1933).

⁴⁸ P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, 54, 3165 (1932).

⁴⁹ E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, 1936, 890.

⁵⁰ W. M. Garrison and M. Burton, *J. Chem. Phys.*, 10, 730 (1942).

⁵¹ F. E. Blacet and W. J. Blaedel, *J. Am. Chem. Soc.*, 62, 3374 (1940).

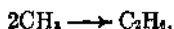
tion (28c) has been postulated in the mechanism of the photolyses of formaldehyde⁴⁵ and acetaldehyde,⁴⁸ and in the reaction of H-atoms with CO. (See VII-1.) If the reaction is really a chain-ending step, it must have a low activation energy.

Garrison and Burton⁴⁹ suggest that reactions (28a) and (28&) occur at the wall, but there seems to be no real evidence to support this.

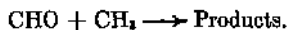
(29) $\text{CHO} + \text{CH}_3 \longrightarrow \text{CH}_4 + \text{CO}$

This reaction was assumed as a step in the mechanism of the photochemical decomposition of acetaldehyde by Leermakers,¹⁷ and by Leighton and Blacet.⁴⁶ (See V-3.) Leermakers assumed $E_{29} = 8$ kcal. Akeroyd and Norrish⁹ in connection with the mechanism of the acetaldehyde photolysis assumed $E_w = 0$.

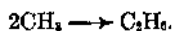
On the basis of a calculation by the semi-empirical method, Gorin⁴¹ concludes that the activation energy of the reaction is small, and that the velocity constant is three to four times greater than that of the reaction



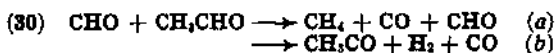
Haden and Rice⁴⁴ conclude from experiments on the photolysis of acetaldehyde in intermittent light (see V-3) that the activation energy of the chain-ending step is ≤ 2.6 kcal. They suggest that the reaction to which this value applies is



The products might be $\text{CEU} + \text{CO}$ or CH_3CHO . It is, however, possible that chains end by the recombination of methyls rather than by a reaction of formyl with methyl. If this is so the value of ≤ 2.6 kcal. does not apply to (29), but applies to



A detailed discussion of the thermal and photochemical reaction mechanisms for acetaldehyde has been given by Burton, Taylor, and Davis.⁸¹ They conclude by a lengthy argument that $E_{29} \geq 17$ kcal. However, in a later note⁵² they point out that the paper contains an arithmetical error which vitiates the argument.



This reaction has frequently been assumed as a chain-carrying step in the thermal and photochemical decomposition of acetaldehyde.

For the thermal reaction (30a) was assumed by Leermakers,¹⁷ and (30b) was assumed by Burton, Taylor, and Davis⁵¹ for both the thermal and photochemical reactions. For the photo-reaction at high temperatures

⁵¹ M. Burton, H. A. Taylor, and T. W. Davis, *J. Chem. Phys.*, 7, 1080 (1939).

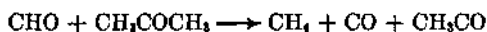
⁵² M. Burton, H. A. Taylor, and T. W. Davis, *J. Chem. Phys.*, 10, 146 (1942).

Leermakers¹⁷ suggested a chain mechanism which included reaction (30). Assuming $E_{so_a} \sim 15$ kcal., in agreement with the estimates of Rice for reactions of this type, the mechanism gave results in good agreement with experiment, and he concludes that $230_0 \cong 10$ kcal.

Akeroyd and Norrish⁴⁸ investigated the photolysis of mixtures of acetone and acetaldehyde. It was found that there was no inhibition by acetone of chain propagation in acetaldehyde; however, acetaldehyde did not sensitize the decomposition of acetone. They conclude that this is evidence against the occurrence of reaction (30a), since if



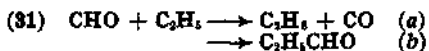
occurs, we would expect the analogous reaction



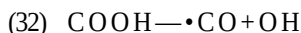
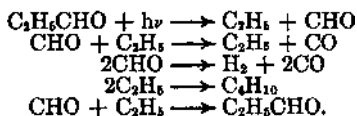
to occur, and this would lead to a methyl radical sensitized decomposition of acetone.

Reaction (30a) has also been suggested as a step in the photolysis by Haden and Rice.⁴¹ On the basis of experiments with intermittent light they arrive at a value of 11.3 kcal. for E_{w_a} . This value should, however, be taken with considerable reserve, since it is by no means certain that (30a) is the chain-carrying step in the photolysis as they assume. (See V-3.)

Reaction (306) has been suggested as a chain-carrying step in the photolysis at low temperatures by Blacet and his co-workers.⁵³ (See V-3.)

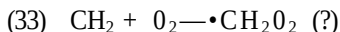


Both tKese reactions have been suggested as steps in the mechanism of the photolysis of propionaldehyde,⁴⁷ viz.,



Rice³⁶ suggested an activation energy of from 10 to 25 kcal. for this reaction. It has been suggested as a step in the photolysis of acetic acid by Burton.¹³ (See VII-8.)

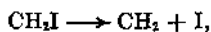
¹⁷ F. E. Blacet and D. Volman, *J. Am. Chem. Soc.*, 60, 1243 (1938); F. E. Blacet and W. J. Blaedel, *J. Am. Chem. Soc.*, 62, 3374 (1940); F. E. Blacet and J. D. Heldman, *J. Am. Chem. Soc.*, 64, 889 (1942); F. E. Blacet and D. E. Loeffler, *J. Am. Chem. Soc.*, **64**, 893 (1942).



The photo-oxidation of methylene iodide has been investigated by Gregory and Style.⁵⁴ The products were, among others, iodine, HCHO , HCOOH , and ethylene glycol, and the quantum yield of iodine production was 1.45. They conclude that the primary process is either



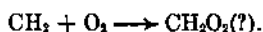
followed by



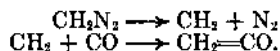
or else



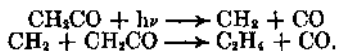
The overall activation energy is 1.9 kcal., which they ascribe to the reaction



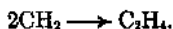
Staudinger and Kupfer⁵⁵ decomposed diazomethane thermally in the presence of carbon monoxide and found that ketene was formed. They suggested that this occurred by



The photolysis of ketene was investigated by Norrish, Crone, and Saltmarsh,⁵⁶ who concluded from the band spectrum that absorption was by the carbonyl group. (See V-11.) The products were quantitatively carbon monoxide and ethylene. They suggested the mechanism



However, a more detailed investigation by Ross and Kistiakowsky⁵⁷ makes it fairly certain that the secondary step is not reaction (35) but



Pearson, Purcell, and Saigh⁵⁸ investigated the thermal and photochemical decomposition of ketene and diazomethane, using the mirror removal method. (See II-6.) Methylene radicals were detected, and their rate of decay was investigated by means of standard mirrors. With ketene in an

⁵⁴ R. A. Gregory and D. W. G. Style, *Trans. Faraday Soc.*, 32, 724 (1936).

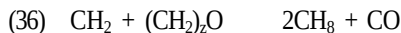
⁵⁶ H. Staudinger and O. Kupfer, *Ber.*, 45, 508 (1912).

⁵⁷ R. G. W. Norrish, H. G. Crone, and O. D. Saltmarsh, *J. Chem. Soc.*, **1933**, 1533.

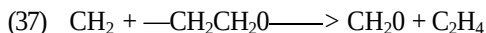
⁵⁸ W. F. Ross and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 56, 1112 (1934).

⁵⁸ T. G. Pearson, R. H. Purcell, and G. S. Saigh, *J. Chem. Soc.*, **1938**, 409.

11 mm. tube at a pressure of 0.15 mm. they found no appreciable decay in travelling 81 cm., corresponding to a time of 0.05jsec. On the other hand, if the radicals were prepared from diazomethane only about 1 per cent of the molecules decomposed contributed to mirror removal. It thus appears that although methylene reacts readily with diazomethane, it has a very long life in the presence of ketene. Reaction (35) must, therefore, have a relatively high activation energy.



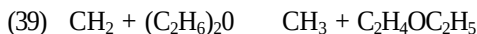
Methyl radicals are undoubtedly produced in the thermal decomposition of ethylene oxide. It is difficult to see how this occurs unless they are formed by a reaction of methylene with ethylene oxide, and reaction (36) has been postulated as a step in the mechanism of the ethylene oxide decomposition by Fletcher and Rollefson.⁵⁹ (See IV-16.)



This reaction, with an activation energy of 8 kcal., has been suggested as a step in the mechanism of the thermal decomposition of dioxane by Kuchler and Lambert.⁶⁰ The mechanism is highly speculative. The evidence is strong, however, for the occurrence of radicals other than alkyl, since the reaction is not sensitized by methyl radicals although it is strongly inhibited by nitric oxide. (See III-9.)



This reaction, with an activation energy of 23 kcal., has also been suggested as a step in the pyrolysis of dioxane.⁶⁰ (See III-9.)

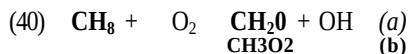


Rice and Glasebrook⁶¹ investigated the decomposition of diazomethane by their usual technique. Diazomethane with ether as a carrier was passed through a heated tube and then over mirrors. At lower temperatures methylene radicals were detected but no methyl, while at temperatures higher than 600° only methyl radicals were found. They conclude that the disappearance of methylene and appearance of methyl at higher temperatures is due to reaction with ether and is satisfactorily explained provided that reaction (39) has an activation energy of about 15 ± 5 kcal.

⁶⁰ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 68, 2135 (1936); C. J. M. Fletcher, *J. Am. Chem. Soc.*, 58, 534 (1936).

⁶⁰ L. Kuchler and J. D. Lambert, *Z. physik. Chem.*, B37, 285 (1937).

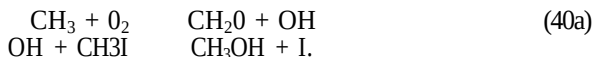
⁶¹ F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, 56, 4329. (1933), 56, 2381 (1934).



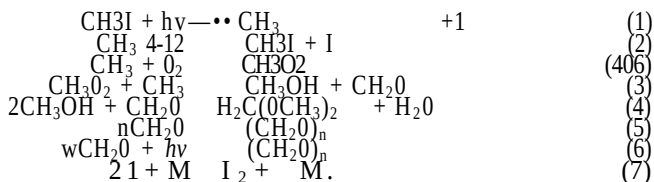
The photo-oxidation of methyl iodide has been investigated by Bates and Spence.⁶² The reaction is much faster than the concurrent decomposition. The products were iodine, paraformaldehyde, methylal and water, roughly as represented by the equation



The rate is proportional to the light intensity. The reaction is complex, but they suggest that the main steps are those which occur in the decomposition, together with



Blaedel, Ogg, and Leighton⁶³ were unable to detect the hydroxyl radical by absorption spectroscopy in the photo-oxidation of gaseous methyl iodide. If we accept Bates' mechanism above, and assume for reasons not stated that the last reaction has a high activation energy, then a high steady state concentration of hydroxyl would be expected. Since they were unable to detect hydroxyl its concentration must have been below 3×10^{-4} mm., and they rule out the mechanism of Bates and Spence and suggest instead



This yields an expression identical with that found experimentally by Bates and Spence. From this they get

$$E_{40b} - E_2 = 3.6 \text{ kcal.},$$

and since E_2 is small $E_{40b} \sim 3 \text{ kcal.}$ However, the mechanism can hardly be said to be established.

Van Tiggelen³³ has investigated the acetone photosensitized oxidation of methane at temperatures from 160° to 350° . From the mechanism postulated he derives the value $E_m = 1.5 + 0.5 \text{ kcal.}^*$

It should be noted that reaction (40a) violates the Rice-Teller principle, and on this ground (406) is to be preferred.

* The paper was not available, and no further details are given in the abstract.

⁶² J. R. Bates and R. Spence, *J. Am. Chem. Soc.*, 53, 1689 (1931); 53, 381 (1931); *Trans. Faraday Soc.*, 27, 468 (1941). See also G. Emschwiller, *Compt. Rend.*, **198**, 1151, 464 (1934), **199**, 854 (1934), **206**, 746 (1938), **207**, 1201 (1938); *Bull. Soc. Chim.*, 6, 551, 561 (1939).

⁶³ W. J. Blaedel, R. A. Ogg, and P. A. Leighton, *J. Am. Chem. Soc.*, 64, 2499, 2500 (1942).



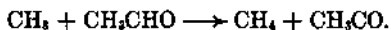
Faltings⁶⁴ found that some acetone is formed when an ethane-carbon monoxide mixture is irradiated with light in the Schumann region. This suggests the occurrence of reaction (41).



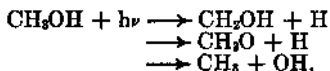
Fletcher and Rollefson⁶⁵ have shown that formaldehyde formed as an intermediate step in the decomposition of dimethyl ether at 504° decomposes 15 times faster than would be expected from its normal rate of decomposition alone. Since the decomposition of dimethyl ether appears to involve methyl radicals, it seems certain that the result is due to a methyl radical sensitized decomposition of formaldehyde, possibly by (42). (See IV-12 for details.)



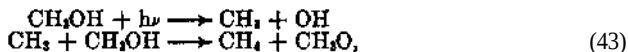
The decomposition of methyl alcohol is sensitized to some extent at 465° by radicals from the decomposition of ethylene oxide,⁶⁶ possibly by a reaction such as (43). It is not sensitized, however, by radicals from the photolysis of acetaldehyde,⁶⁷ probably because reaction (43) is slower than



Patat⁶⁸ has investigated the photodecomposition of methyl alcohol in the region from 1800 to 2000Å (methyl alcohol is transparent to longer wave lengths). The quantum yield is approximately unity at room temperature, so that chains are not involved. The mechanism is obscure. The primary process might involve radicals by



Patat rules out the latter reaction because formaldehyde is a product. However, CH_3O could be formed by the sequence



and if a free radical mechanism holds formaldehyde must presumably arise from CH_3O no matter what the primary step may be. In any event, in the case of ethyl alcohol no H-atoms are detectable in the photolysis and the process is probably a direct molecular split. By analogy, this appears to be the most likely mechanism for the methyl alcohol photolysis also.

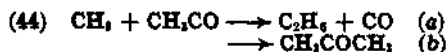
⁶⁴ K. Faltings, *Ber.*, **72B**, 1207 (1939).

⁶⁶ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2129 (1936).

⁶⁷ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2135 (1936).

⁶⁷ J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A159**, 32 (1937).

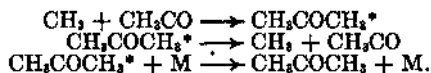
⁶⁸ F. Patat, *Z. Elektrochem.*, **41**, 494 (1935).



The reaction of methyl and acetyl radicals has frequently been suggested as a step in the photolysis of acetone (see V-6): opinions vary, however, as to the relative importance of reactions (44a)⁶⁹⁻⁷³ and (44b).^{70,73-77} Reaction (44a) has also been suggested as a step in the photolysis of diacetyl.⁷⁸

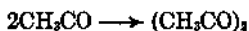
The main evidence for the occurrence of (44b) is the fact that the total quantum yield of the photolysis is low, and this suggests recombination.⁷⁶

Spence and Wild⁷⁰ suggest that reaction (44b) occurs by the sequence

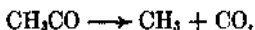


This is, of course, merely equivalent to suggesting a low steric factor for the bimolecular reaction.

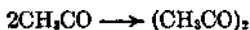
At higher temperatures diacetyl is no longer a product of the acetone photolysis, and this is undoubtedly due to the disappearance of acetyl radicals so rapidly that the reaction



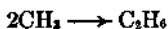
no longer occurs to an appreciable extent. It has usually been assumed that this is caused by the reaction



Gorin, however,⁷¹ on the grounds that acetyl iodide is still formed at higher temperatures when acetone is photolysed in the presence of iodine, estimates a minimum activation energy of 17 kcal. for the decomposition of the acetyl radical. He therefore suggests that acetyl radicals disappear not by decomposition, but by reaction (44a). The argument is by no means compelling, since a very rapid reaction of acetyl with iodine would also explain the facts. Herr and Noyes⁷⁶ conclude, contrary to Gorin, that reaction (44a) is not important in the acetone photolysis, since its inclusion in the mechanism along with



and



⁶⁹ R. Spence and W. Wild, *J. Chem. Soc.*, **1937**, 352, *Nature*, **138**, 206 (1936).

⁷⁰ R. Spence and W. Wild, *J. Chem. Soc.*, **1941**, 590.

⁷¹ E. Gorin, *Acta Physicochimica* (U.S.S.R.), **8**, 513 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

⁷² A. O. Allen, *J. Am. Chem. Soc.*, **63**, 708 (1941).

⁷³ K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

⁷⁴ J. A. Leermakers, *J. Am. Chem. Soc.*, **56**, 1899 (1934).

⁷⁶ H. S. Taylor and C. Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

⁷⁸ D. S. Herr and W. A. Noyes, *J. Am. Chem. Soc.*, **62**, 2052 (1940).

⁷⁷ J. J. Howland and W. A. Noyes, *J. Am. Chem. Soc.*, **63**, 3404 (1941).

⁷⁸ J. G. Roof and F. E. Blacet, *J. Am. Chem. Soc.*, **63**, 1126 (1941).

would make the quantum yield and the $\text{C}_2\text{H}_6/\text{CO}$ ratio independent of pressure and of light intensity, which is not the case. The reactions might, however, play some part at higher pressures where wall effects are relatively unimportant.

Burton, Taylor, and Davis⁵¹ have estimated $E_{44a} \sim 5.8$ kcal., on the basis of a review of the mechanism of the acetaldehyde photolysis. This discussion was later withdrawn on account of arithmetical errors.⁵² Saunders and Taylor⁷³ have discussed the mechanism of the acetone photolysis. They suggest that both (44a) and (44b) occur. They assume $E_{44b} \sim 8$ kcal., and estimate the value of E_{ua} on the basis of the following argument. The activation energy of the Walden inversion in methane was shown by Eyring⁷⁹ to be 37 kcal. The C—C bond strength in acetyl is ca. 18 kcal. The C—H bond strength in methane is ca. 95 kcal. They assume that E_{ua} will be equal to the activation energy of the Walden inversion in methane diminished in the ratio of the strengths of the bonds being broken in the two reactions, i.e.,

$$E_{44a} \sim \frac{18}{95} \times 37 \sim 7 \text{ kcal.}$$

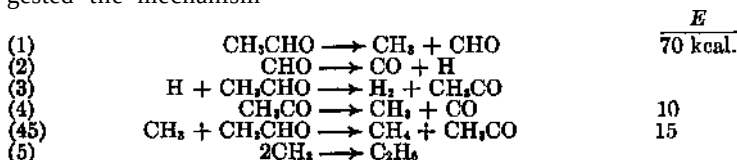
It seems very doubtful if this calculation has much meaning, although the value obtained is reasonable.

The occurrence of (44b) in the acetaldehyde photolysis has been suggested by Woolgar and Allmand⁸⁰ (see V-3), and its occurrence in the methyl butyl ketone photolysis has been suggested by Wilson and Noyes.⁸¹ There is, however, no real evidence for this.

(45) $\text{CH}_3 + \text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CH}_3\text{CO}$

This reaction is undoubtedly involved in the mechanism of the photolysis of acetaldehyde, and is probably involved in the thermal decomposition as well. (See 111-10 and V-3.)

For the thermal decomposition of acetaldehyde Rice and Herzfeld²¹ suggested the mechanism



The activation energies, including the value of 15 kcal. for EM, were frankly assigned⁸² to make the mechanism agree with experiment.

Qualitative evidence that reaction (45) occurs readily comes from numer-

⁷⁹ E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, 7, 633 (1939).

⁸⁰ C. W. Woolgar and A. J. Allmand, *Trans. Faraday Soc.*, 39, 219 (1943).

⁸¹ J. E. Wilson and W. A. Noyes, *J. Am. Chem. Soc.*, 66, 1547 (1943).

⁸² See F. O. Rice, *J. Am. Chem. Soc.*, 66, 488 (1934).

ous experiments which have shown that the acetaldehyde decomposition can be sensitized by methyl radicals. A variety of sources of methyl radicals have been used for this purpose including the pyrolysis of azomethane,⁸³ ethylene oxide,⁵⁹ and diacetyl,⁸⁴ and the photolysis of azomethane.⁸⁵

As we have seen there is some doubt about the importance of the role of free radicals in the thermal decomposition, and hence it is difficult to know how much weight may be attached to estimates of E_u which are based on free radical mechanisms. Letort⁸⁶ has reviewed the evidence and concludes that the Rice-Herzfeld scheme is compatible with the experimental data provided that, among other things, E_u lies within the limits 9 to 26 kcal.

Burton, Taylor, and Davis⁵¹ arrived at a value of 16.9 kcal. for E_u on the basis of a discussion of the mechanism of the acetaldehyde decomposition which was later withdrawn on account of errors.⁵²

Leermakers¹⁷ investigated the photolysis of acetaldehyde at high temperatures. He concludes that his results are consistent with the Rice-Herzfeld mechanism with a value of 15 kcal. for E_u as assumed by Rice.

The high temperature photolysis was also investigated by Akeroyd and Norrish.⁹ They obtained a value of 9.8 kcal. for the overall activation energy of the reaction, in excellent agreement with the value of 10 kcal. found by Leermakers. They conclude that this is the activation energy of reaction (45). Actually the rate expression for the Leermakers-Rice-Herzfeld mechanism also involves the rate constant of the chain-ending reaction involving radical recombination. Hence in reality

$$E_{\text{overall}} = E_{45} - E_{\text{recombination}}.$$

Thus Akeroyd and Norrish are tacitly assuming the radical recombination reaction to have zero activation energy. This may not be quite true, and hence Akeroyd and Norrish's value of 9.8 kcal. is a minimum value. Allen and Sickman⁸³ investigated the azomethane induced thermal decomposition of acetaldehyde. Their results lead to a value of 13.8 ± 2 kcal. for $E_{45} - E_{\text{recombination}}$, and hence to a minimum value of 11.8 kcal. for E_{45} . Grahame and Rollefson have discussed these results⁸⁷ and suggest that Allen and Sickman's value is too high on account of erroneous assumptions regarding the pyrolysis of azomethane. It seems to the writer, however, that the limits of error are large enough to reconcile Allen and Sickman's results with those of Leermakers and of Akeroyd and Norrish.

Grahame and Rollefson⁸⁷ made a very thorough investigation of the

⁸³ A. O. Allen and D. V. Sickman, *J. Am. Chem. Soc.*, 56, 2031 (1934); D. V. Sickman and A. O. Allen, *J. Am. Chem. Soc.*, 56, 1251 (1934).

⁸⁴ F. O. Rice and W. D. Walters, *J. Am. Chem. Soc.*, 63, 1701 (1941).

⁸⁵ F. E. Blacet and A. Taurog, *J. Am. Chem. Soc.*, 61, 3024 (1939).

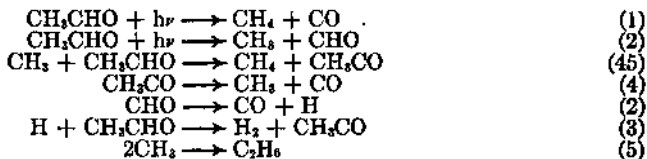
⁸⁶ M. Letort, *Thesis*, Paris, 1937.

⁸⁷ D. C. Grahame and G. K. Rollefson, *J. Chem. Phys.*, 8, 98 (1940).

high temperature photolysis of acetaldehyde, and obtained a rate law similar to that of Leermakers', viz.,

$$\phi_{\text{decomp.}} = k' + k[\text{CH}_3\text{CHO}]\text{I}_{\text{abs.}}^{-\frac{1}{2}}.$$

In all cases except where Φ was very small, i.e., at low temperatures, k' was negligible. A plot of $\log k$ against $\sqrt{I}$ gave a straight line with a slope corresponding to an activation energy of 8.6 kcal. They adopt a mechanism similar to that of Rice and Herzfeld, viz.,



By the usual steady-state method this leads to

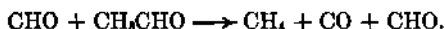
$$E_{\text{overall}} = E_{45} - \frac{1}{2}E_5.$$

Hence

$$E_{45} = 8.6 + \frac{1}{2}E_5 \text{ kcal.}$$

If E_5 is assumed to be approximately zero, this agrees well with previous estimates of E_{45} .

Haden and Rice^{88,89} from the results of an investigation of the photolysis of acetaldehyde with intermittent light conclude that the activation energy of the chain-carrying step is between 10 and 11.3 kcal., in good agreement with previous estimates. They conclude that the chain-carrying step is not (45), but rather the reaction



The mechanism is discussed in detail in V-3, and it appears to the writer that the chain-carrying step is much more likely to be (45).

The occurrence of reaction (45) as a step in the mechanism of the photolysis of acetaldehyde has also been suggested by numerous other workers.⁹⁰



The only evidence for a reaction of this kind is the fact that the decomposition of methyl formate at 460° is sensitized by methyl radicals from the photolysis of acetaldehyde.⁹¹

⁸⁸ W. L. Haden and O. K. Rice, *J. Chem. Phys.*, 10, 445 (1942).

⁸⁹ W. L. Haden, E. P. H. Meibohm, and O. K. Rice, *J. Chem. Phys.*, 8, 998 (1940).

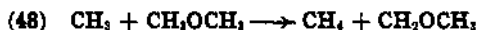
See also R. G. W. Norrish, *J. Chem. Phys.*, 9, 377 (1941).

⁹⁰ See Section V-3.

⁹¹ J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A169, 32 (1937).



This reaction has been suggested by Rice and Herzfeld²¹ as a step in the chain mechanism for the decomposition of dimethyl ether. They assign it an activation energy of 8 kcal.

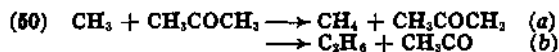


Rice and Herzfeld²¹ have suggested a chain mechanism for the thermal decomposition of dimethyl ether which includes this reaction with an activation energy of 15 kcal. (See III—7.) Evidence for its occurrence is the fact that the dimethyl ether decomposition can be induced by methyl radicals⁷⁴ from the photolysis of acetone. The results of the induced reaction are compatible with the Rice-Herzfeld mechanism and with a value of E_{48} of 15 kcal.



This reaction has been suggested as a step in the Rice-Herzfeld mechanism²¹ for the acetone decomposition. They assign it an activation energy of 8 kcal. It has also been suggested as an explanation of the production of methyl ethyl ketone in the photolysis of acetone.^{51, 72, 73, 74} In this connection Saunders and Taylor⁷³ also assign the reaction an activation energy of 8 kcal. Allen⁷² suggests that reaction (49) occurs heterogeneously.

Reaction (49) has also been suggested as a possible step in the photolysis of methyl butyl ketone.⁸¹



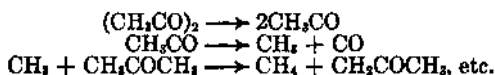
Reaction (50a) has been suggested as a step in the mechanism of the thermal decomposition of acetone by Rice and Herzfeld,²¹ who assigned it an activation energy of 15 kcal. Free radical chains cannot be set up readily in acetone, but there is evidence that free radicals can react with acetone in, the temperature range 350° to 450°. ^{59, 92} (See 111-14.) This indicates a moderate activation energy for reaction (50a). Thus Rice, Rodowskas, and Lewis⁹² decomposed dimethyl mercury in the presence of acetone in the temperature range 350° to 400°. Little decomposition of acetone occurred, but acetonyl acetone was formed in amounts corresponding to that of the dimethyl mercury. Hence although chain processes do not occur, methyl radicals evidently react with acetone,



⁹² F. O. Rice, E. L. Rodowskas, and W. R. Lewis, *J. Am. Chem. Soc.*, 56, 2497 (1934).

At lower temperatures methyl radicals apparently do not attack acetone, and reaction (50a) must, therefore, possess an appreciable activation energy.

At higher temperatures it appears to be possible to set up free radical chains in acetone. Thus at 526° Rice and Walters⁹³ found that chains could be set up by radicals from decomposing diacetyl, apparently by



For the photolysis of acetone at high temperatures Leermakers'⁷⁴ results are consistent with the Rice-Herzfeld mechanism, provided that reaction (50a) is assumed to have a moderate activation energy, say 20 kcal. A somewhat similar mechanism for the photolysis has been adopted by Spence and Wild.⁶⁹

Taylor and Rosenblum⁷⁵ investigated the high temperature photolysis in the presence of hydrogen, and the high temperature photolysis was also investigated by Allen.⁷² The overall activation energy of methane production was found to be 8.6 and 7.1 kcal. respectively in the two investigations. It seems probable that methane arises by a mechanism involving reaction (50a), and that the activation energy of this reaction is thus not large. The situation is too complex, however, to permit a direct evaluation of E_{50a} .

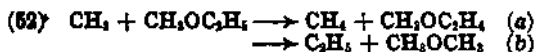
Saunders and Taylor⁷³ investigated the photolysis of acetone in the presence of mercury. They suggest a mechanism involving reaction (50a), and assign an activation energy of 16 kcal. to the reaction by analogy with the results of Haden, Meibohm, and Rice⁸⁸ on the reaction



Spence and Wild⁶⁹ point out that reaction (506) must be relatively unimportant since otherwise it would give rise to chains in the acetone photolysis.



This reaction has been suggested as a step in the thermal decomposition of ethyl ether.⁹⁴



The reactions of methyl ethyl ether are very similar to those of dimethyl ether and give rise to a similar Rice-Herzfeld mechanism, involving the reaction

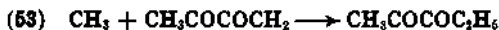
⁹³ F. O. Rice and W. D. Walters, *J. Am. Chem. Soc.*, **63**, 1701 (1941).

⁹⁴ J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 237 (1942).



The fact that methyl radicals react readily with methyl ethyl ether is shown by an investigation of Rice, Walters, and Ruoff⁹⁵ who found that the ether decomposition could be induced by the thermal decomposition of azomethane at 299°. The facts appear to be consistent with Rice's estimate of an activation energy of about 15 kcal. for reaction (52a).

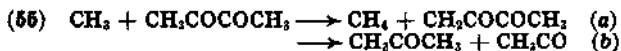
The possible reaction (52b) does not occur appreciably since Rice, Walters, and Ruoff found that dimethyl ether was not a product of the azomethane sensitized decomposition of methyl ethyl ether.



Rice and Walters⁹⁶ investigated the thermal decomposition of diacetyl. They suggest a typical Rice mechanism for the reaction, which includes reaction (53) as a chain ending step.



The fact that the decomposition of divinyl ether is induced by azomethane at 330° is evidence for the occurrence of (54) with a relatively low activation energy.⁹⁷



It has been suggested^{75, 80, 98} that the low quantum yield of the acetone photolysis might be due to the reformation of acetone from diacetyl by (55b). This, however, is ruled out by the work of Herr, Matheson, and Walters⁹⁹ who investigated the photolysis of acetone in the presence of deuterio-diacetyl. If (55b) occurred, it would be expected that some of the ethane formed in the photolysis would be deuterized, but this was not found to be the case at temperatures at which diacetyl is important in the acetone photolysis. They concluded that the occurrence of (55a) is much more probable, and suggested an activation energy for it of about 13 kcal. The occurrence of (55a) as a step in the pyrolysis of diacetyl has been suggested by Rice and Walters.⁹⁶ They point out that (55b) is unlikely to be of importance for the reasons given by Rice and Teller¹⁰⁰ for many analogous cases. (See, *e.g.*, VI-9.)

⁹⁵ F. O. Rice, W. D. Walters, and P. M. Ruoff, *J. Chem. Phys.*, 8, 259 (1940).

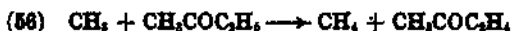
⁹⁶ F. O. Rice and W. D. Walters, *J. Chem. Phys.*, 7, 1015 (1939).

⁹⁷ F. P. Jahn, unpublished work, quoted by H. A. Taylor, *J. Chem. Phys.*, 4, 116 (1936).

⁹⁸ H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, 33, 1353 (1938).

⁹⁹ D. S. Herr, M. S. Matheson, and W. D. Walters, *J. Am. Chem. Soc.*, 63, 1464 (1941).

¹⁰⁰ F. O. Rice and E. Teller, *J. Chem. Phys.*, 6, 489 (1938).

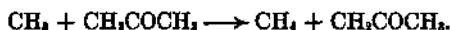


Rice³⁶ has suggested a chain mechanism for the thermal decomposition of methyl ethyl ketone analogous to that for acetone. This includes reaction (56) with an activation energy of about 15 kcal.

Moore and Taylor¹⁰¹ investigated the photolysis of methyl ethyl ketone. Methane formation was found to rise decidedly with increasing temperature, indicating an appreciable activation energy for reaction (56). They point out that methane is much more easily produced here than is the case with acetone, and hence reaction (56) must have a lower activation energy than



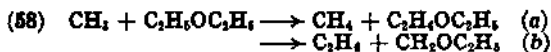
or



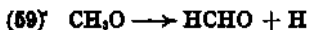
Saunders and Taylor⁷³ therefore suggest that $E_{56} < 16$ kcal.



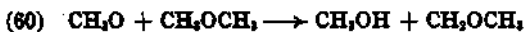
This reaction may be a step in the thermal decomposition of vinyl ethyl ether.¹⁰²



The fact that the ethyl ether decomposition can be induced by methyl radicals^{59,93} suggests the occurrence of (58a). Smith and Hinshelwood⁹⁴ have suggested the occurrence of (58b) as a step in the thermal decomposition of diethyl ether. This seems very unlikely, however, for the reasons given by Rice and Teller¹⁰⁰ in analogous cases. (See VI-9.)



This reaction, with an activation energy of from 20 to 45 kcal. has been suggested by Rice and Herzfeld²¹ as a step in the chain mechanism for the thermal decomposition of dimethyl ether.



Rice and Herzfeld²¹ have also suggested reaction (60) as a step in the dimethyl ether decomposition. They assign it an activation energy of 15 to 25 kcal.

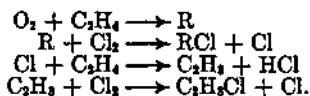


In view of the fact^{102a} that oxygen catalyses the thermal chlorination of ethylene at high temperatures, and that the reaction occurring is substitution, it appears probable that the mechanism is (see IX-32):

¹⁰¹ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 466 (1940).

¹⁰² S. N. Wang and C. A. Winkler, *Can. J. Research*, **21B**, 97 (1943).

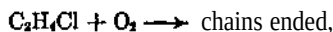
^{102a} F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, **5**, 472 (1940).



In order that this mechanism can hold, it is necessary that the reaction



be relatively slow compared with, say

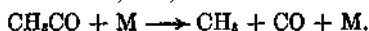


since oxygen inhibits strongly most chlorination reactions.

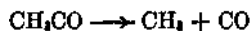
(61) $\text{CH}_3\text{CO} \longrightarrow \text{CH}_3 + \text{CO}$

Rice and Herzfeld²¹ assumed that reaction (61) was a step in the mechanism of the thermal decomposition of acetaldehyde and acetone, and assigned to it an activation energy of 10 kcal. The reaction has been almost universally assumed to be a step in the photolysis of acetaldehyde,^{9, 17, 37, 88, 103, 104} acetone,^{35, 69-72, 74, 76, 106-108} and diacetyl.^{78, 108}

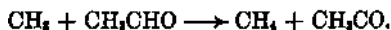
In the photolysis of acetaldehyde Blacet and Blaedel¹⁰³ showed that diacetyl was a product. The amount of diacetyl fell off with rising temperature, and only about 1J12 as much was formed at 102° as at 25°. This indicates an activation energy in the range 10 to 20 kcal. for reaction (61) if it is assumed that the decomposition of the acetyl radical with rising temperature is responsible for the decrease in diacetyl production. Blacet and his collaborators⁵³ suggest as have others^{69,73} that the disappearance of acetyl is a bimolecular reaction, i.e.,



Blacet and Loeffler⁵³ found that at temperatures from 100° to 150° the quantum yield increased rapidly, the apparent activation energy of the overall chain process being 9.6 kcal. This agrees well with previous values (Rollefson and Grahame¹⁰⁴ 8.3 kcal., Leermakers¹⁷ 10 kcal., Akeroyd and Norrish⁹ 9.8 kcal.). The previous workers' values were obtained at higher temperatures where the reaction



would be very rapid, and hence they considered the overall activation energy to be attributable to the reaction



¹⁰³ F. E. Blacet and D. Volman, *J. Am. Chem. Soc.*, **60**, 1243 (1938); F. E. Blacet and W. J. Blaedel, *J. Am. Chem. Soc.*, **62**, 3374 (1940).

¹⁰⁴ D. C. Grahame and G. K. Rollefson, *J. Chem. Phys.*, **8**, 98 (1940).

¹⁰⁵ R. G. W. Norrish, *J. Chem. Soc.*, **1934**, 874, 1456.

¹⁰⁶ H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, **1937**, 567.

¹⁰⁷ M. H. Feldman, J. E. Ricci, and M. Burton, *J. Chem. Phys.*, **10**, 618 (1942).

¹⁰⁸ H. W. Anderson and G. K. Rollefson, *J. Am. Chem. Soc.*, **63**, 816 (1941).

Since their work was done at relatively low temperatures, Blacet and Blaedel suggest that the slow step and the one to which the activation energy of 9.6 kcal. applies is the decomposition of the acetyl radical by reaction (61).

Most of our information on reaction (61) comes from work on the photolysis of acetone. Diacetyl was first identified as a product of the photolysis by Barak and Style,¹⁰⁹ and since then it has been shown by many workers that diacetyl is a product at low temperatures but not at high, and this may definitely be considered to be due to the decomposition of acetyl at higher temperatures. Thus Glazebrook and Pearson¹⁰⁶ found diacetyl at room temperature, but none at temperatures above 60°. In the presence of tellurium at room temperature diacetyl formation was also prevented. By the Paneth technique they concluded that in quartz vessels the acetyl radical has a life much shorter (by a factor of more than 10) than that of alkyl radicals under the same experimental conditions. The absence of diacetyl when the walls of the vessel were coated with tellurium suggests that diacetyl formation is a wall reaction. If this is so, the average acetyl radical at room temperature survives about 100 collisions with other molecules under the given experimental conditions before reaching the walls.

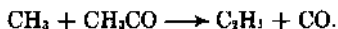
Spence and Wild⁶⁹ confirmed the production of diacetyl in the photolysis at temperatures below 60°, but not above. Further evidence for the decomposition of acetyl was the fact that the $C_2H_6:CO$ ratio in the products decreased at higher temperatures, obviously because of increased CO production by reaction (61). Decrease in diacetyl formation with rising temperature together with increased CO production was also observed by Anderson and Rollefson.¹⁰⁹

Feldman, Ricci, and Burton¹⁰⁷ investigated the production of free radicals in the acetone photolysis at 45° by the following method. A long heavy lead mirror was deposited in a tube: radicals reacting with it formed lead alkyls, and the lead in these was estimated by a micro-method. It was found that if a second mirror was deposited further down the tube more lead alkyl was formed. This is presumably due to the fact that while all the methyl radicals are picked up by the first mirror, acetyl radicals are not. These decompose on their way down the tube, and the methyls formed are caught by the second mirror. If the photolysis is carried out at 100°, however, no additional pick-up of lead occurs at the second mirror. This furnishes proof of the previously accepted fact that the acetyl radical is relatively stable at 45°, but is almost completely decomposed at 100°.

Gorin⁷¹ investigated the photolysis of acetone-iodine mixtures. At low temperatures very little CO was formed in the presence of iodine. Apparently, therefore, almost all the acetyl radicals formed in the primary step have been "fixed" by the iodine, and little decomposition of acetyl has

¹⁰⁹ M. Barak and D. W. G. Style, *Nature*, **135**, 307 (1935).

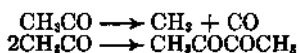
occurred. This points to a fairly high stability for acetyl. At higher temperatures CO production increased rapidly as would be expected if there is a competition between decomposition of the acetyl radical and the formation of acetyl iodide. However, a considerable amount of acetyl iodide is formed even at 130°, the highest temperature used, and this points to a very considerable stability for acetyl. Gorin estimates a minimum value of 17 kcal. for the activation energy of reaction (61), and concludes that the disappearance of diacetyl in the normal photolysis of acetone must be largely due to



In similar experiments Benson and Forbes¹¹⁰ found that a plot of $\log \frac{\text{diacetyl}}{\text{CO}}$ against $1/T$ corresponded to an activation energy of 15 ± 2 kcal. Correcting this for the small increase in CO with increasing temperature gives 16 ± 2 kcal. which they ascribe to reaction (61). They suggest that the reaction is heterogeneous.

Herr and Noyes⁷⁶ have given a detailed discussion of the mechanism of the acetone photolysis. (See V-6.) They suggest that in part acetyl decomposes owing to energy carried over from the primary step. Some, however, must decompose in the normal way since the quantum yield of decomposition and of carbon monoxide formation both increase with increasing temperature. In view of the rapid increase in CO and decrease in diacetyl with rising temperature E_{61} must be high, and they conclude that it has a value of approximately 18 kcal., in good agreement with Gorin's value. Bawn⁴⁰ from transition state calculations concludes that the activation energy of reaction (61) is 16 kcal.

Anderson and Rollefson¹⁰⁸ investigated the photolysis of acetone, diacetyl, and of acetyl bromide. ϕ_{CO} in every case reached a final value at high temperatures, but with diacetyl and acetyl bromide this is less than unity. They conclude, therefore, that while acetyl is unstable it yet has a life sufficiently long that some acetyl radicals are able to enter into other reactions even at higher temperatures. In some of their experiments an excess of nitrogen was added, but this produced no appreciable effect. They conclude, therefore, that the reactions

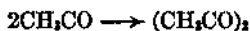


must both occur homogeneously or both heterogeneously. They favor the latter. However, the nitrogen pressure employed was only of the order of 25 mm. and the data are scanty, so that this conclusion does not rest on very convincing evidence. Howland and Noyes¹¹¹ to verify this conclu-

¹¹⁰ S. W. Benson and G. S. Forbes, *J. Am. Chem. Soc.*, 65, 1399 (1943).

¹¹¹ J. J. Howland and W. A. Noyes, *J. Am. Chem. Soc.*, 63, 3404 (1941).

sion, photolysed acetone in the presence of high pressures of carbon dioxide. They found that ϕ_{CO} was increased considerably at low intensities, but only slightly at high by the presence of the foreign gas. They conclude that (61) is homogeneous and

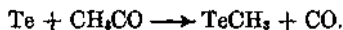


is heterogeneous, but that at high intensities the latter reaction occurs homogeneously as well.



There is much evidence that diacetyl is a product of the photolysis of acetaldehyde¹⁰³ and of acetone.^{69,106,108,109,110} There is no question that this is formed by reaction (62).

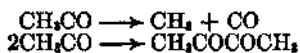
As pointed out in the preceding section Glazebrook and Pearson¹⁰⁶ found that in the photolysis of acetone diacetyl formation was prevented by coating the walls of the reaction vessel with tellurium, probably because of some reaction such as



The fact that a wall coating can prevent diacetyl formation suggests that reaction (62) is heterogeneous.

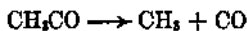
Herr and Noyes⁷⁶ have given a comprehensive discussion of the mechanism of the acetone photolysis. (See V-6.) They found that the $C_2H_6JCO^*$ ratio increased as the pressure was lowered at constant intensity. This suggests that diacetyl is formed by the diffusion of acetyl to the walls. However, since there was some increase in C_2H_6JCO with intensity at constant pressure, there appears to be some homogeneous recombination of acetyl as well. This appears, however, to be only a small fraction of the whole.

Anderson and Rollefson¹⁰⁸ investigated the photolysis of diacetyl. In some of their experiments nitrogen was added, but it produced no appreciable effect. They conclude, therefore, that the two main fates of the acetyl radical

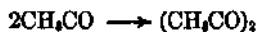


must both occur homogeneously or both heterogeneously. The quantity of nitrogen added was quite small, and the results are not very certain.

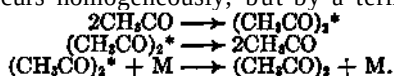
Howland and Noyes¹¹¹ used very high pressures of carbon dioxide as an inert gas in a similar investigation with acetone. They point out that on the basis of Herr and Noyes mechanism the presence of an inert gas should decrease the ratio C_2H_6JCO and increase ϕ_{CO} if the reaction



is homogeneous and



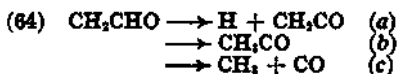
is heterogeneous. This was found to be the case at low light intensities. At high intensities, however, ϕ_{CO} increased only very slightly, and they conclude that at high intensities, reaction (62) proceeds homogeneously as well. Spence and Wild,⁶⁹ who used much higher light intensities, suggest that the reaction occurs homogeneously, but by a termolecular mechanism



Reaction (62) has also been suggested as a step in the mechanism of the photolysis of methyl butyl ketone.⁸¹



This reaction has been suggested as one of the steps in the mechanism of the acetone photolysis by Saunders and Taylor.⁷³



Rice and Rice³⁶ have suggested that

$$\begin{aligned} E_{\text{sta}} &= 60 \text{ to } 80 \text{ kcal.} \\ E_{\text{stab}} &\approx 15 \text{ to } 30 \text{ kcal.} \end{aligned}$$

Taylor and Burton¹¹² have suggested (64c) as a step in the thermal decomposition of acetaldehyde.



The photo-oxidation of ethyl iodide was briefly investigated by Jones and Bates.¹¹³ The products are complex and little can be said about the mechanism, except that it possibly involves reaction (65) with a low activation energy.



The decomposition of acetaldehyde is sensitized by ethyl radicals from the pyrolysis of diethyl ether,¹¹⁴ ethyl bromide,¹¹⁵ and ethyl iodide.¹¹⁵ The primary step is presumably reaction (66).



Mitchell and Hinshelwood⁹¹ investigated the propionaldehyde photolysis at high temperatures. An overall activation energy of 6.5 kcal. was found.

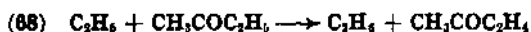
¹¹² H. A. Taylor and M. Burton, *J. Chem. Phys.*, 7, 675 (1939).

¹¹³ L. T. Jones and J. R. Bates, *J. Am. Chem. Soc.*, 56, 2285 (1934).

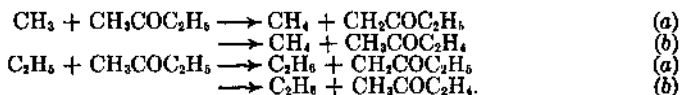
¹¹⁴ C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2129 (1936); M. W. Travers and C. G. Silcocks, *Nature*, 139, 1018 (1937).

¹¹⁵ J. G. Roof and F. Daniels, *J. Am. Chem. Soc.*, 62, 2912 (1940).

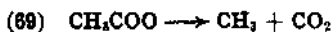
If it is assumed that (67) is the chain-carrying step, and that the activation energy of the chain-terminating step is zero, then this value corresponds to the activation energy of reaction (67). There is no real evidence for this assumption, other than analogy with the acetaldehyde photolysis.



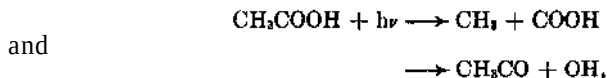
Moore and Taylor¹¹⁶ found that the products of the photolysis of methyl ethyl ketone at 90° were CO, and C₂H₆, C₃H₈, and C₄H₁₀ in approximately the ratio to be expected from random recombination of methyl and ethyl radicals. A small amount of methane and unsaturated hydrocarbons was also formed. At higher temperatures, around 200°, methane increased strongly and propane and butane fell off. Ethane, however, did not fall off appreciably. This indicates that while at lower temperatures radical recombination is the main fate of the radicals formed in the primary step, at higher temperatures methane and ethane are formed by reaction of methyl and ethyl radicals with the ketone, *i.e.*,



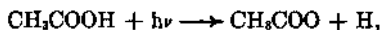
Since methane is more easily produced from methyl ethyl ketone than from acetone, they conclude that the radical attacks the ethyl group in the ketone rather than the methyl, and hence the reactions marked (b) occur in preference to (a).



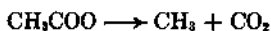
Burton¹³ has investigated the photolysis of acetic acid vapor by the Paneth method. By the guard-mirror technique he concluded that H-atoms were formed, but no methyl radicals. This rules out the primary steps



since the latter would lead to methyl radicals by the dissociation of acetyl. The primary step must, therefore, be



and since no methyl radicals are detectable, the reaction

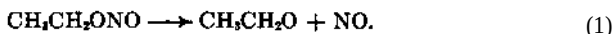


is also ruled out, and must, therefore, have a high activation energy. (See also VII-8.) This agrees with Rice's assignment³⁶ of $E_{69} = 40\text{--}70$ kcal.

¹¹⁶ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, 8, 466 (1940).

(70) $\text{CH}_3\text{CH}_2\text{O} \longrightarrow \text{CH}_3 + \text{HCHO}$

Steacie and Shaw¹¹⁷ investigated the thermal decomposition of ethyl nitrite (see III—18), and concluded that the primary step, as with other nitrites, is



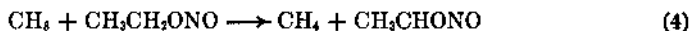
A similar conclusion was reached by Rice and Rodowskas¹¹⁸ who investigated the reaction by the Paneth technique. They suggested that the secondary reactions were



At low pressures, however, it would also be expected that the reactions



and



would occur, leading to the formation of formaldehyde and methane as products. No indications of such a change in mechanism were obtained by Steacie and Katz,¹¹⁹ who investigated the reaction down to a pressure of 10^{-2} mm.

From the fact that reaction (70) apparently does not come into play until quite low pressures are reached, Rice and Rodowskas conclude that $E_0 - E_2 \sim 16$ kcal., and they suggest that plausible values are

$$\begin{aligned} E_2 &= 12 - 18 \text{ kcal.} \\ E_0 &= 28 - 34 \text{ kcal.} \end{aligned}$$

(71) $\text{CH}_3\text{OCH}_3 \longrightarrow \text{CH}_3 + \text{HCHO}$

This reaction was suggested by Rice and Herzfeld²¹ as a step in the chain mechanism for the pyrolysis of dimethyl ether, with an activation energy of 38 kcal.

Leermakers⁷⁴ investigated the acetone photosensitized decomposition of dimethyl ether, and concluded that his results were well fitted by the Rice-Herzfeld mechanism provided that, among other assumptions, $E_{71} \sim 36$ kcal. (See III-7.)

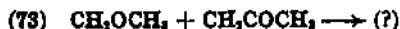
(72) $\text{CH}_3\text{OCH}_3 + \text{CH}_3\text{OCH}_3 \longrightarrow (\text{CH}_3\text{OCH}_2)_2$

This reaction, with an activation energy of 8 kcal., has been assumed by Rice and Herzfeld²¹ as a step in the chain mechanism for the thermal decomposition of dimethyl ether. (See III—7.)

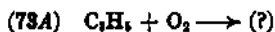
¹¹⁷ E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.*, 2, 345 (1934).

¹¹⁸ F. O. Rice and E. L. Rodowskas, *J. Am. Chem. Soc.*, 57, 350 (1935).

¹¹⁹ E. W. R. Steacie and S. Katz, *J. Chem. Phys.*, 5, 125 (1937).



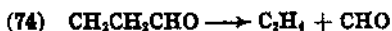
This reaction has been assumed by Leermakers⁷⁴ to be a step in the mechanism of the acetone photosensitized decomposition of dimethyl ether. (See III—7.) The mechanism gives agreement with experiment provided that, among other assumptions, $E_{73} \sim 10$ kcal.



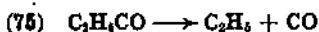
The fact that oxygen catalyses the thermal chlorination of propylene at high temperatures, rather than inhibiting it^{102a} suggests that this reaction is relatively slow. (For further details see the analogous case of



discussed in VII-60A.)



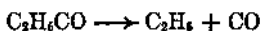
This reaction has been suggested as a step in the thermal decomposition of propionaldehyde. (See III—11.) Rice³⁶ assigns the reaction an activation energy of 25 kcal.



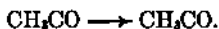
Ells and Noyes¹²⁰ have compared the photolyses of acetone, methyl ethyl ketone, and diethyl ketone. The quantum yield of CO formation rises strongly on going up the series from acetone to diethyl ketone. Thus with light of wave length around 3000A, ϕ_{CO} had the values

CH_3COCH_3	0.095
$\text{CH}_3\text{COC}_2\text{H}_5$	0.12
$\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$	1.04

Since the low yield for acetone is largely due to the formation of diacetyl rather than the decomposition of acetyl to form CO, this points to

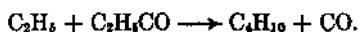


occurring much more readily than



Since the latter reaction has an activation energy of ca. 17 kcal., reaction (75) must have a small activation energy. (See V-8.)

It is possible to explain the results not on the basis of the ease of decomposition of $\text{C}_2\text{H}_5\text{CO}$, but rather by the ready occurrence of the reaction

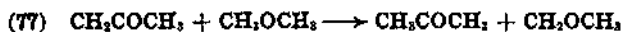


However, this does not seem as plausible, and in any case $\text{C}_2\text{H}_5\text{CO}$ would be expected to be less stable than CH_3CO .

¹²⁰ V. R. Ells and W. A. Noyes, *J. Am. Chem. Soc.*, 61, 2492 (1939), 60, 2031 (1938).



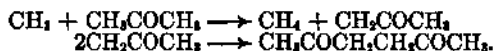
This reaction, with an activation energy of 48 kcal., was suggested by Rice and Herzfeld as a step in the mechanism for the thermal decomposition of acetone.²¹ (See III—14.) It has also been assumed in the high temperature photolysis of acetone,⁷⁴ and in the diacetyl sensitized decomposition of acetone.⁹³ Rice, Rodowskas, and Lewis⁹² found that acetonyl acetone was a product of the reaction of methyl radicals with acetone at temperatures up to 400°. This indicates that the acetonyl radical is stable at these temperatures, and supports the assignment of a high activation energy to (76).



Leermakers⁷⁴ has suggested reaction (77) as a step in the mechanism of the acetone photosensitized decomposition of dimethyl ether. The mechanism agrees with experiment when, among other assumptions, E_{77} is given a value of 20 kcal. (See III-7.)



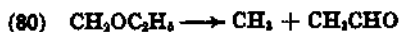
Rice, Rodowskas, and Lewis⁹² decomposed dimethyl mercury in the presence of acetone in the temperature range 350° to 400°. Acetonyl acetone was formed in amounts corresponding to that of dimethyl mercury. It seems certain that this is formed by the sequence



Reaction (78) has also been assumed as a step in the photodecomposition of acetone at high temperatures.^{73,74}



The overall activation energy of the photolysis of n-butyraldehyde is 5.6 kcal.¹²¹ The photolysis at high temperatures follows a rate law similar to that of acetaldehyde, and the mechanisms are, therefore, probably similar. (See V-5.) There is thus some probability that $E_{79} = 5.6$ kcal.



Hobbs¹²² has investigated the inhibition by nitric oxide of the thermal decomposition of diethyl ether. (See III—8.) He explains his results by

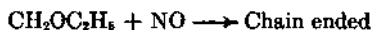
¹²¹ P. A. Leighton, L. D. Levanas, F. E. Blacet, and R. D. Rowe, *J. Am. Chem. Soc.*, **59**, 1843 (1937)

¹²² J. E. Hobbs, *Proc. Roy. Soc. (London)*, **A167**, 456 (1938); see also J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 237 (1942); J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A162**, 357 (1937).

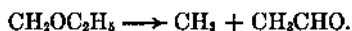
means of a mechanism analogous to that of Rice and Herzfeld.²¹ The inhibition was found to be independent of the ether pressure, in contrast to other cases such as that of ethane. Hobbs concludes, therefore, that there must be a competition between the reaction



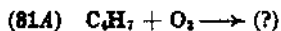
and a first-order reaction which would continue the chain, and he suggests that the competing reactions are:



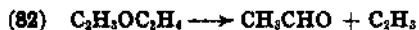
and



This has been suggested as a step in the thermal decomposition of diacetyl by Rice and Walters⁹⁶ in order to account for the production of ketene in the reaction. (See V-7.)



This reaction is probably relatively slow.^{102a} (See the analogous case of $C_2H_3 + O_2$ (?) discussed in VII-6OA.)

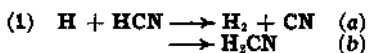


This reaction may be involved in the thermal decomposition of vinyl ethyl ether.¹⁰²

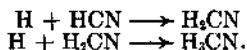
Chapter VIII

Systems Containing Nitrogen

Information on the reactions of nitrogen compounds is, with one or two exceptions, decidedly scanty, and in most cases even the evidence for the occurrence of a reaction rests on rather dubious ground.



Geib and Harteck¹ investigated the reaction of hydrogen atoms, produced by the discharge-tube method, with HCN at liquid air temperatures. A solid product was obtained with the empirical formula H₃CN. This was unstable at temperatures above — 60°. It appears almost certain that this is formed by successive addition of H-atoms, *i.e.*,

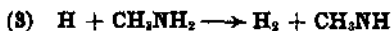


Robertson and Pease² have investigated the thermal reaction between hydrogen and cyanogen at temperatures around 625°. The results are well fitted by a mechanism of the type given by Bodenstein and Lind for the hydrogen-bromine reaction, involving reaction (1a).

The mechanism does not lead to a value for E_{1a} , but to explain the inhibition of the reaction by HCN it must be moderately low. (See VIII-16 for details.)



This has been suggested as a step in the reaction of hydrogen atoms with azomethane³ (see VIII-5 and VIII-8), and with methyl amine (see VIII-3.)



This reaction has been suggested on the basis of very little evidence as a step in the thermal⁴ and photochemical⁵ decomposition of methyl amine.

¹ K. H. Geib and P. Harteck, *Ber.*, 66, 1815 (1933).

² N. C. Robertson and R. N. Pease, *J. Am. Chem. Soc.*, 64, 1880 (1942).

³ H. Henkin and H. A. Taylor, *J. Chem. Phys.*, 8, 1 (1940).

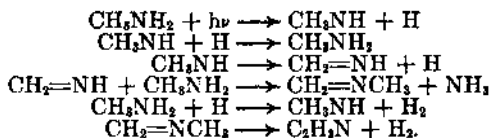
⁴ H. J. Emeleus and L. J. Jolley, *J. Chem. Soc.*, 1936, 929.

⁵ H. J. Emeleus and H. S. Taylor, *J. Am. Chem. Soc.*, 63, 3370 (1931).

Geib and Harteck¹ found no evidence of the formation of an addition product when hydrogen atoms, produced by the discharge tube method, were mixed with methyl amine-at liquid air temperature.

In a recent paper^{6a} Wetmore and Taylor investigated the reaction at 100° by the discharge tube method. Considerable ammonia and small amounts of methane were formed. The results were purely qualitative, but it appears probable that reaction (3) is the primary process, with an activation energy ≤ 10 kcal.

The same authors also investigated the photolysis of methyl amine, and suggested the mechanism

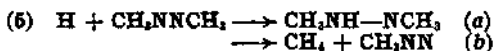


This is highly speculative.

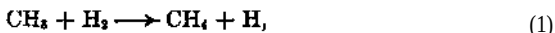
(4) $\text{H} + (\text{CN})_2 \longrightarrow \text{HCN} + \text{CN}$

Geib and Harteck¹ found that an addition product was formed from H-atoms and cyanogen at liquid air temperature.

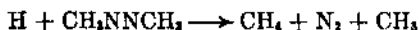
Robertson and Pease² investigated the reaction of hydrogen with cyanogen, as discussed in VIII-16. A steady-state treatment of the results does not lead to a direct evaluation of E_4 . It must, however, be very small in order that (4) can serve as a chain-carrying step. This would be expected also by analogy with the reactions of H-atoms with the halogens.



Patat⁶ investigated the photolysis of azomethane at 265° in the presence of para-hydrogen. From the effect of temperature on the overall reaction he concludes that hydrogen atoms are produced by the reaction



and that these react with azomethane by a reaction which is essentially (5b),



with an activation energy of 5.1 kcal.

The reaction of hydrogen atoms produced by the discharge tube method with azomethane was investigated by Henkin and Taylor.³ At room temperature the sole product of the reaction was dimethyl hydrazine. The reaction was very rapid, so that the overall activation energy cannot be greater

^{5a} O. C. Wetmore and H. A. Taylor, *J. Chem. Phys.*, 12, 61 (1944).

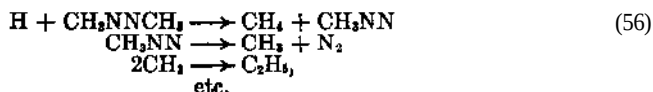
⁶ F. Patat, *Nach. Ges. Wiss. Göttingen*, II, 6, 77 (1936).

than 3-4 kcal. Since two hydrogen atoms are required to hydrogenate one molecule of azomethane, and since the H-atom concentration was much less than that of azomethane, they conclude that the reaction has chain characteristics, *i.e.*,

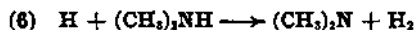


They suggest that reaction (5a) has an activation energy of approximately zero, and that the overall activation energy of 3-4 kcal. is that of reaction (2).

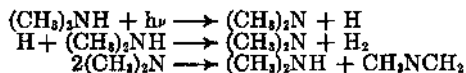
At higher temperatures methane, ethane, and methyl amine are produced, and they suggest the mechanism



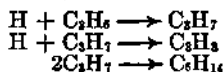
The activation energy of reaction (56) calculated from the collision yield on the assumption that the steric factor is 0.1 is 8 kcal.



The products of the photolysis of dimethyl amine are mainly hydrogen and a polymer, together with a smaller amount of methane. Bamford suggests the mechanism⁷



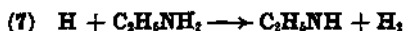
followed by polymerization of the CH_3NCH_2 radical. In the presence of propylene propane and hexane were formed, indicating the occurrence of hydrogen atoms in the photolysis, *i.e.*,



or



There is also evidence⁸ that the thermal decomposition of dimethyl amine involves free radicals, and it is possible that reaction (6) occurs.

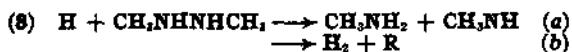


This reaction has been postulated as a step in the photolysis of ethyl amine to explain the formation of hydrogen.⁹

⁷ C. H. Bamford, *J. Chem. Soc.*, **1939**, 17.

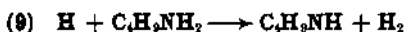
⁸ F. O. Rice and W. R. Johnston, *J. Am. Chem. Soc.*, **56**, 214 (1934); S. Bairstow and C. N. Hinshelwood, *J. Chem. Soc.*, **1933**, 1155; A. G. Carter, P. A. Bosanquet, C. G. Silcocks, M. W. Travers, and A. Wilshire, *J. Chem. Soc.*, **1939**, 495; M. W. Travers and J. A. Hawkes, *J. Chem. Soc.*, **1939**, 1360.

⁹ H. J. Emeleus and L. J. Jolley, *J. Chem. Soc.*, **1935**, 1612.

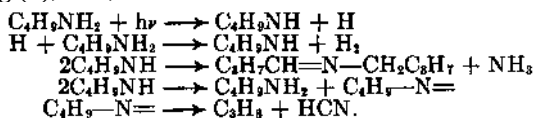


Methyl amine is one of the products of the reaction of hydrogen atoms, produced by the discharge tube method, with azomethane at higher temperatures.³ (See VIII-5.) At low temperatures the sole product is dimethyl hydrazine. The methyl amine produced at higher temperatures probably comes from a reaction of hydrogen atoms with dimethyl hydrazine, such as (8a). If this is the case, its activation energy is about 8 kcal.

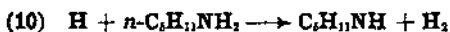
Kay and Taylor¹⁰ have suggested that reaction (8b) is a step in the photolysis of dimethyl hydrazine.



Bamford⁷ investigated the photolysis of n-butyl amine. The products were mainly hydrogen and ammonia in the ratio of about 2 : 1, with traces of methane, propane, and a polymer. Experiments in the presence of added propylene led to the formation of propane and hexane, indicating the production of H-atoms during the reaction. Bamford suggests a mechanism involving (9), viz.,



Reaction (9) has also been suggested as a step in the mechanism of the thermal decomposition of n-butyl amine.¹¹



This reaction has been suggested as a step in the photolysis of n-CaHnNEU to explain the formation of hydrogen (7).



Harteck and Kopsch¹² investigated the reaction of oxygen atoms, produced by the discharge tube method, with hydrogen cyanide. Under the usual experimental conditions about 5 per cent reaction occurred at room temperature, which corresponds to an activation energy of about 7 to 8 kcal.



Geib and Harteck¹ found that addition products were formed when oxygen atoms were mixed with methyl amine at -183° . The activation

¹⁰ W. L. Kay and H. A. Taylor, *J. Chem. Phys.*, 10, 497 (1942).

¹¹ H. C. Beachell and H. A. Taylor, *J. Chem. Phys.*, 10, 106 (1942).

¹² P. Harteck and U. Kopsch, *Z. physik. Chem.*, B12, 327 (1931).

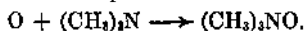
energy of reaction (12) is, therefore, approximately zero, but the reaction is undoubtedly a surface reaction under these conditions.



Harteck and Kopsch¹² found about 4 per cent reaction when oxygen atoms produced by the discharge tube method were mixed with cyanogen at room temperature. This corresponds to an activation energy of 7 to 8 kcal. for reaction (13). Cyanogen bands were emitted during the reaction, and the products were CO₂, H₂O, and oxides of nitrogen.



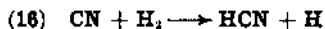
Addition products are formed when oxygen atoms are mixed with trimethyl amine at liquid air temperature.¹



There is considerable information on the equilibrium



but no direct information on the rate of reaction (15). Its activation energy is probably practically zero.¹³



Hartel and Polanyi¹⁴ investigated the reaction of sodium vapor with cyanogen by the dilute flame method. At 260° the collision yield of NaCN was about 1J17000 with nitrogen as a carrier gas, but only about 1J8800 with hydrogen. This is presumably due to the removal of cyanogen radicals by reaction (16), *i.e.*,



They conclude that these results are compatible with a value of 7 kcal. for E₁₆.

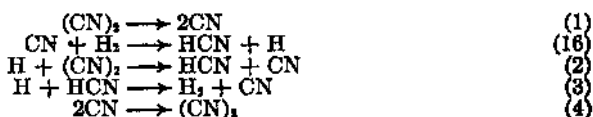
Robertson and Pease² have investigated the thermal reaction between hydrogen and cyanogen at temperatures in the neighbourhood of 625°. The reaction was of the 3J2 order with respect to hydrogen, and of a low order with respect to the total pressure. It is inhibited by the products. The data are reasonably well fitted by an expression of the type given by Bodenstein and Lind for the hydrogen-bromine reaction, *viz.*,

$$\frac{d}{dt} \frac{[\text{HCN}]}{2} = \frac{k[\text{H}_2][(\text{CN})_2]^{\frac{1}{2}}}{1 + \frac{m[\text{HCN}]/2}{[(\text{CN})_2]}}$$

¹³ See, for example, N. C. Robertson and R. N. Pease, *J. Am. Chem. Soc.*, 64, 1880 (1942).

¹⁴ H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, B11, 97 (1930).

This corresponds to the mechanism



when

$$k = 2k_{16}\sqrt{k_1/k_4},$$

and

$$m = k_3/k_2.$$

The mechanism leads to the expression

$$E_{\text{overall}} = E_{16} + \frac{1}{2}E_1 - \frac{1}{2}E_4.$$

If we accept Hartel and Polanyi's estimate of $E_m = 7$ kcal., put $E_4 = 0$, assume the heat of dissociation of cyanogen to be 127 kcal., and put $E_{16} = 127$ kcal., we have

$$E_{\text{overall}} = 7 + \frac{1}{2}127 = 70.5 \text{ kcal.},$$

in agreement with the observed value of 72 kcal. However, this merely means that the mechanism is not inconsistent with the data since estimates of the heat of dissociation of cyanogen vary widely. Thus Kistiakowsky and Gershinowitz¹⁵ gave 77 kcal., while White¹⁶ gave 137 kcal. as a minimum value, with 146 as the most probable value. On the basis of certain photopolymerization experiments Robertson and Pease consider 127 kcal. to be more plausible. However, in a recent note Herzberg¹⁷ has criticized White's determination, and feels that the earlier low value is more reliable. Robertson and Pease¹⁸ are not in agreement with this.



Pearson, Purcell, and Saigh¹⁹ investigated the thermal and photochemical decomposition of diazomethane and of ketene by the mirror method. The decomposition of both substances produces methylene radicals. When the radicals were prepared from ketene the half-life was very long, greater than 0.05 sec, and hence methylene is relatively stable alone or in the presence of ketene. When the radicals were prepared from diazomethane, however, the half-life was short, viz., about 0.0073 sec. This must be due to a reaction between methylene and diazomethane. Reaction (17) must, therefore, have a very small activation energy.

¹⁵ G. B. Kistiakowsky and H. Gershinowitz. *J. Chem. Phys.*, 1, 432 (1933).

¹⁶ J. U. White, *J. Chem. Phys.*, 8, 79, 459 (1940).

¹⁷ G. Herzberg, *J. Chem. Phys.*, 10, 306 (1942).

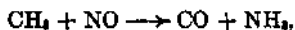
¹⁸ N. C. Robertson and R. N. Pease, *J. Chem. Phys.*, 10, 490 (1942).

¹⁹ T. G. Pearson, R. H. Purcell, and G. S. Saigh, *J. Chem. Soc.*, 1938, 409.

(18) $\text{CH}_3 + \text{NO} \longrightarrow \text{CH}_3\text{NO}$

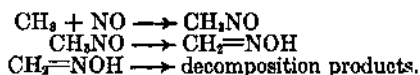
The inhibition of free radical chain reactions by nitric oxide makes it certain that a rapid reaction occurs between alkyl radicals and nitric oxide. The exact reaction occurring is, however, somewhat uncertain.

Thompson and Meissner²⁰ photographed the absorption spectrum of mixtures of nitric oxide and decomposing organic compounds. They concluded that the overall reaction occurring is



and that probable intermediates are formaldoxime and an unstable nitroso compound.

Further light on the reaction occurring comes from the work of Taylor and Bender²¹ who investigated the pyrolysis of formaldoxime. The reaction was of the first order, and the products were HCN and water, together with smaller amounts of CO, NH₃, N₂, H₂, C₂H₆, and traces of unsaturates. They suggest that all the facts of nitric oxide inhibition can be accounted for by assuming that we have the reactions



Forsyth²² investigated the inhibitory effect of nitric oxide by the Paneth technique. Ethylene oxide was decomposed as a source of methyl radicals and the products were passed over tellurium mirrors, with or without the previous addition of NO. The disappearance of the mirrors was followed by a photocell-opacity method. The rate of removal of the radicals was found to be of the first order both in the presence and in the absence of nitric oxide. The rate of decay of the radicals was proportional to the partial pressure of nitric oxide, and was given by

$$\frac{-d\ln[\text{CH}_3]}{dt} = 98.8 + 168.4[\text{NO}] \text{ sec.}^{-1},$$

where [NO] is expressed in mm. Forsyth concludes that one collision in 73,000 of a methyl radical with NO causes its disappearance. On the assumption that the steric factor is unity, this corresponds to an activation energy of 6.5 kcal. for the reaction of a methyl radical with NO, probably by reaction (18).

Anderson and Rollefson²³ investigated the photolysis of acetone in the presence of nitric oxide. A four-fold excess of nitric oxide was found to

²⁰ H. W. Thompson and M. Meissner, *Nature*, **139**, 1018 (1937).

²¹ H. A. Taylor and H. Bender, *J. Chem. Phys.*, **9**, 761 (1941). See also T. W. Davis, F. P. Jahn, and M. Burton, *J. Am. Chem. Soc.*, **60**, 10 (1938).

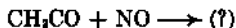
²² J. S. A. Forsyth, *Trans. Faraday Soc.*, **37**, 312 (1941).

²³ H. W. Anderson and G. K. Rollefson, *J. Am. Chem. Soc.*, **63**, 816 (1941).

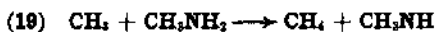
inhibit completely the formation of ethane but not that of carbon monoxide. It may, therefore, be concluded that the activation energy of the reaction



is considerably less than that of



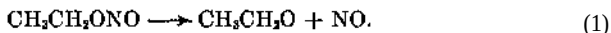
The decomposition of dimethyl ether is inhibited by nitric oxide.²⁴ The chain length calculated in the usual way is about 17 at 813°K. It appears from the results that about 1 collision in 1500 of nitric oxide with radicals is effective in breaking the chains, corresponding to an activation energy of 10 to 12 kcal. for reaction (18) or some analogous process.



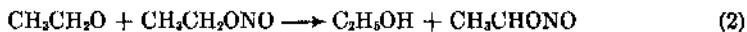
Emeleus and Jolley⁴ suggest that the thermal decomposition of methyl amine occurs by a chain mechanism, which includes reaction (19) as one of the steps.



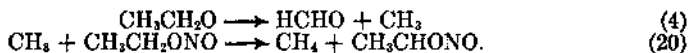
The thermal decomposition of ethyl nitrite was investigated by Steacie and Shaw,²⁵ who concluded that the primary step was the reaction



Rice and Rodowskas²⁶ investigated the same reaction by the Paneth technique. They suggest that the primary reaction should be followed by



At low pressures we might also expect

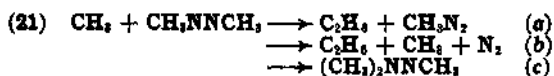


They used the Paneth technique at 425° and found no mirror removal. This is, however, not surprising if it is assumed that reactions (1) and (4) occur in the furnace, and are followed by (20) and (3) which remove the radicals before they can reach the mirror. To verify this they diluted the ethyl nitrite with various gases to cut down the rate of (20). Under these conditions one per cent of ethyl nitrite with the carrier readily removed mirrors at temperatures as low as 400°. They conclude that the failure to obtain mirror removal with pure ethyl nitrite means that E_{20} is less than 10 kcal.

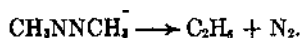
²⁴ L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A159**, 192 (1937), **A154**, 335 (1936); P. F. Gay and M. W. Travers, *Nature*, **138**, 546 (1936).

²⁵ E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.*, **2**, 345 (1934).

²⁶ F. O. Rice and E. L. Rodowskas, *J. Am. Chem. Soc.*, **67**, 350 (1935).



Early work on the thermal decomposition of azomethane²⁷ suggested that ethane was the principal hydrocarbon product, i.e., that the overall reaction was



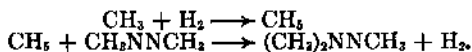
Later investigations²⁸ showed that the azomethane decomposition led to the production of free radicals which could cause the sensitized decomposition of other substances. This suggested that the primary step involved a split into free radicals, and that at least part of the ethane production might be due to (21a). However, the fact that the azomethane decomposition is not itself a chain reaction argues against this.

Further investigations with more emphasis on the analytical side of the problem²⁹ showed that methane was, in reality, the main hydrocarbon product, and that considerable condensable products were formed. Taylor and Jahn suggested, therefore, that the main reaction of methyl radicals with azomethane is (21c).

Heidt and Forbes²⁹ also showed that methane is an important product of the photolysis. Burton, Taylor, and Davis³⁰ made a more thorough analytical investigation of the reaction. Condensable products were found, as in the thermal reaction, and they suggest that reaction (21c) is an important step. They also suggest the possible occurrence of (21&) to some extent, although the fact that the photolysis is not a chain reaction militates against this.

Davis, Jahn, and Burton,³¹ who investigated the effect of nitric oxide on the photolysis, also suggest that reaction (21c) is a major step, and similar conclusions were reached by Cannon and Rice.³²

Taylor and Flowers³³ investigated the photolysis of azomethane in the presence of hydrogen. They discuss the mechanism and conclude that (21c) is important. They suggest, however, that it occurs in stages:



²⁷ H. C. Ramsperger, *J. Am. Chem. Soc.*, 49, 912 (1927).

²⁸ O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, 4, 242 (1936); D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, 4, 239, 608 (1936).

²⁹ E. W. Riblett and L. C. Rubin, *J. Am. Chem. Soc.*, 59, 1537 (1937); L. J. Heidt and G. S. Forbes, *J. Am. Chem. Soc.*, 57, 2331 (1935); H. A. Taylor and F. P. Jahn, *J. Chem. Phys.*, 7, 470 (1939).

³⁰ M. Burton, T. W. Davis, and H. A. Taylor, *J. Am. Chem. Soc.*, 59, 1038, 1989 (1937).

³¹ T. W. Davis, F. P. Jahn, and M. Burton, *J. Am. Chem. Soc.*, 60, 10 (1938).

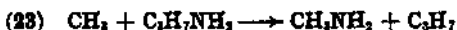
³² C. V. Cannon and O. K. Rice, *J. Am. Chem. Soc.*, 63, 2900 (1941).

³³ H. A. Taylor and R. G. Flowers, *J. Chem. Phys.*, 10, 110 (1942).

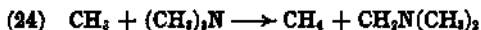
In other words they are suggesting that hydrogen will act as an efficient third body for the association reaction.



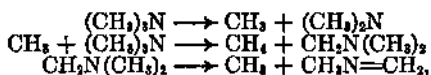
This has been suggested¹⁰ as an important step in the photolysis of dimethyl hydrazine to account for the formation of methane.



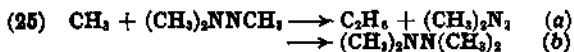
In an attempt to detect the occurrence of this reaction, Rice, Walters, and Ruoff⁸⁴ decomposed propylamine in a flow system. Since the decomposition probably involves a free radical chain it may be assumed that methyl radicals are present, and hence reaction (23) is possible. Under the experimental conditions employed, 650° and 10 mm. pressure, no indications of the formation of methyl amine were obtained, however, and reaction (23) apparently does not occur, to an appreciable extent.



The thermal decomposition of trimethyl amine is catalysed by iodine.³⁵ Rice and Johnston³⁶ detected radicals in the reaction. The decomposition was investigated by Travers and his collaborators,⁸ who found that the main products were methane, methyl methylene imine, and small amounts of hydrogen and ethane. The reaction was somewhat retarded by nitric oxide and by increased surface, and was accelerated by helium, pointing to chain characteristics. They suggest that the mechanism is



followed by polymerization of methyl methylene imine.



The occurrence of both these reactions has been suggested^{30,33} in the mechanism of the photolysis of azomethane.



Reaction (25A) has been suggested⁵⁰ as a step in the mechanism of the photolysis of methyl amine. (See VIII-3.)

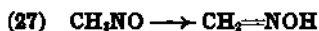
³⁴ F. O. Rice, W. D. Walters, and P. M. Ruoff, *J. Chem. Phys.*, 8, 259 (1940).

³⁵ S. Bairstow and C. N. Hinshelwood, *J. Chem. Soc.*, 1933, 1155.

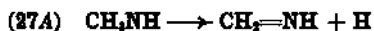
³⁶ F. O. Rice and W. R. Johnston, *J. Am. Chem. Soc.*, 56, 214 (1934).



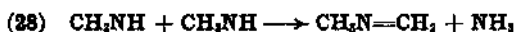
In thermal and photochemical reactions of azomethane the occurrence of the radical CH_3NN has been frequently assumed.³⁷ It seems certain that it disappears rapidly by decomposition, and that reaction (26) thus has a very small activation energy.



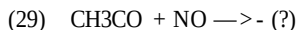
Taylor and Bender²¹ found that the products of the pyrolysis of formaldoxime are similar to the products of nitric oxide inhibited reactions. They suggest that after a methyl radical has combined with nitric oxide to form CH_3NO , the CH_3NO isomerizes rapidly to formaldoxime.



This reaction, with a relatively high activation energy has been suggested as a step in the photolysis of methyl amine.^{5a} (See VIII-3.)



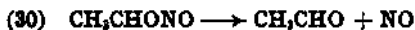
Reaction (28) has been suggested as a step in the mechanism of the photolysis of methyl amine.⁹ The postulated mechanism is, however, highly speculative.



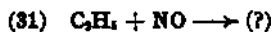
Anderson and Rollefson²³ investigated the photolysis of mixtures of acetone and nitric oxide. Nitric oxide was found to inhibit the formation of CO, but not as strongly as it inhibited the formation of ethane. The activation energy of reaction (29) thus appears to be somewhat greater than that of the reaction



The activation energy of the latter reaction is about 6.5 kcal. (see VIII-18), and hence E_{29} must be greater than 6.5 kcal.



This reaction has been suggested as a step in the mechanism of the thermal decomposition of ethyl nitrite by Rice and Radowskas.²⁶ (See VIII-20.)



In view of the efficiency of nitric oxide as a chain-breaker in free radical reactions, there is no doubt that reaction (31) has a low activation energy.

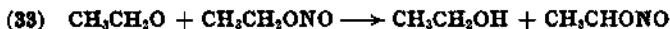
"See, for example, H. Henkin and H. A. Taylor, *J. Chem. Phys.*, 8, 1 (1940); L. Kiichler, *Nach. Ges. Wiss. Göttingen*, III, 1, 215 (1937).

Nothing much is known about the products of the reaction. Thompson and Meissner²⁰ photographed the absorption spectrum of mixtures of nitric oxide and decomposing diethyl ether. They suggest the formation of an unstable complex which decomposes into methyl amine and carbon monoxide.



Leermakers³⁸ decomposed tetraethyl lead in the presence of azomethane at 260° to 275°. No decomposition of azomethane was detectable, and reaction (32), therefore, appears to have a relatively high activation energy.

Leermakers' conclusions have been questioned, however, by Burton, Davis, and Taylor³⁰ on the following grounds. Leermakers detected some falling off in the rate of decomposition of tetraethyl lead in the presence of azomethane. He was looking for chains in the azomethane decomposition, *i.e.* for an increased rate, and hence attached no significance to a small decrease. They suggest that actually some reaction did occur, but that it led not to ethane and a free radical, but rather to an association reaction, followed by polymerization to give condensable products. In view of the fact that later investigations have proved that condensable products are formed in the azomethane decomposition, and to the indications that methyl radicals react fairly readily with azomethane, Burton, Davis, and Taylor's argument appears reasonable.

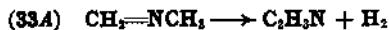


This reaction has been postulated as a step in the mechanism of the thermal decomposition of ethyl nitrite.²⁶ (See VIII-20.)

There is a competition for CH_3CH_2O radicals between reaction (33) and their decomposition by



The latter reaction, however, does not appear to become important until low pressures are reached, and Rice and Rodowskas conclude that $E_i - E_{ss} = 16$ kcal. They suggest that a plausible value for EM is 12 to 18 kcal.



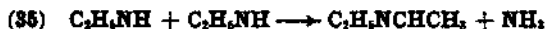
This has been suggested^{5a} as a step in the photolysis of methyl amine. (See VIII-3.)



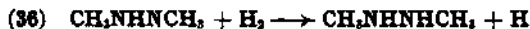
This reaction has been suggested as a step in the mechanism of the photolysis of dimethyl amine⁷ and of dimethyl nitroso amine.³⁹

³⁸ J. A. Leermakers, *J. Am. Chem. Soc.*, 66, 4508 (1933).

³⁹ C. H. Bamford, *J. Chem. Soc.*, 1939, 12.



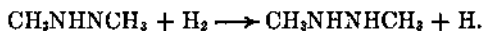
Reaction (35) has been suggested⁹ to explain the formation of ammonia in the photolysis of ethyl amine.



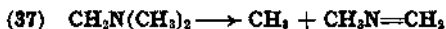
Henkin and Taylor³ investigated the reaction of hydrogen atoms with azomethane (see VIII-5), and found that at room temperature the sole product was dimethyl hydrazine. The reaction was rapid, the overall rate corresponding to an activation energy of 3-4 kcal. They conclude that the primary reaction is



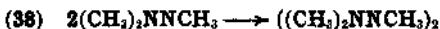
Since two hydrogen atoms are required to hydrogenate one molecule of azomethane, and since the H-atom concentration was much less than that of azomethane, they conclude that molecular hydrogen must be involved in the reaction, *i.e.*,



They suggest that the primary step occurs with practically no activation energy, and that the experimental value of 3-4 kcal. applies to reaction (36).



This has been suggested as a step in the mechanism of the thermal decomposition of trimethyl amine.⁴⁰



This has been suggested as a possible step in the mechanism of the photolysis of azomethane.³⁰ (See V-12.)



This has been suggested as a possible step in the mechanism of the photolysis of n-butyl amine (7).



These reactions have been suggested as steps in the thermal¹¹ and photochemical⁷ decomposition of n-butyl amine.

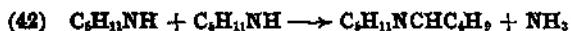
⁴⁰ A. G. Carter, P. A. Bosanquet, C. G. Silcocks, M. W. Travers, and A. Wilshire, *J. Chem. Soc.*, 1939, 495.



In the photolysis of $(\text{C}_2\text{H}_5)_2\text{N} \cdot \text{NO}$, NO , $(\text{C}_2\text{H}_5)_2\text{NH}$, and higher boiling substances are formed.³⁰ Bamford suggested that the primary step was



and that this was followed by reaction (41) and by polymerization of $\text{C}_2\text{H}_5\text{NC}_2\text{H}_5$.



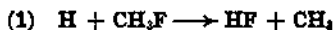
Reaction (42) has been suggested as the source of ammonia in the photolysis of $n\text{-C}_6\text{H}_{11}\text{NH}^\cdot$.⁷

Chapter IX

Systems Containing Chlorine (and Fluorine)

The Occurrence of Cl_3 , Br_3 , and I_3

The radicals Cl_3 and Br_3 have been postulated by a number of workers^{1,2,3} as intermediates in the mechanism of certain photochemical halogenations. Rollefson and Eyring⁴ have calculated by the semi-empirical method that the lifetime of these complexes should be long enough to permit of their occurrence in many reactions. On the other hand, Sherman and Sun⁶ have calculated, also by the semi-empirical method, that the activation energies for the reactions of Cl_3 , Br_3 , and I_3 in systems in which their existence has been postulated are greater than those of the corresponding stable diatomic molecules. It is difficult to decide how much credence should be given to calculations of this kind, but there has been a tendency of late to avoid the assumption of triatomic halogen molecules.^{6*7} For this reason, and because the mechanisms involving the postulation of triatomic halogens have already been discussed (see V-15), the reactions of Cl_3 , Br_3 , and I_3 have not been listed in this and the succeeding chapters with the exception of a reference to the calculated values of activation energies of Sherman and Sun.



Chadwell and Titani,⁸ using the discharge tube method at room temperature, found no reaction of hydrogen atoms with methyl fluoride. The activation energy of reaction (1) is, therefore, greater than 9 kcal.



Smyser and Smallwood⁹ investigated the reaction of atomic hydrogen with carbon tetrachloride by the discharge tube method. The main prod-

¹J. C. Ghosh, S. K. Bhattacharyya, and S. C. Bhattacharyya, *Z. physik. Chem.*, **B32**, 145 (1936).

²G. K. Rollefson, *J. Am. Chem. Soc.*, **66**, 579 (1934).

³G. K. Rollefson, *The Photochemistry of the Halogens*, Paris, 1938.

⁴G. K. Rollefson and H. Eyring, *J. Am. Chem. Soc.*, **54**, 170 (1932).

⁵A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, **56**, 1096 (1934).

⁶H. J. Schumacher, *Z. angew. Chem.*, **49**, 613 (1936).

⁷W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases*, New York, 1941.

⁸H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, **56**, 1363 (1933).

⁹H. F. Smyser and H. M. Smallwood, *J. Am. Chem. Soc.*, **66**, 3499 (1933).

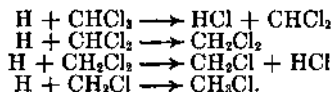
ucts were hydrogen chloride and a solid. They assumed that the primary process was reaction (2), and that this was followed by polymerization and dechlorination of CCl₃ to give the solid product. An explosive product was also found which was probably a chlorinated acetylene derivative.

The reaction was also investigated by the same method by Cremer, Curry, and Polanyi,¹⁰ who found that HCl was the only gaseous product with the exception of traces of methane. They concluded that the activation energy of reaction (2) was less than 3.3 kcal.

A very thorough investigation of the reaction was made by Vance and Baumann¹¹ over the temperature range 20° to 200°. They found an activation energy for reaction (2) of 3.5 kcal., with a steric factor of 0.007.

(3) $\text{H} + \text{CHCl}_2 \longrightarrow \text{CH}_2\text{Cl}_2$

Fromherz and Schneller¹² found that methyl chloride was an important product of the reaction of hydrogen atoms with chloroform. This presumably arises by the sequence



Reaction (3) thus appears to have little activation energy.

**(4) $\text{H} + \text{CHCl}_3 \longrightarrow \text{HCl} + \text{CHCl}_2$ (a)
 $\longrightarrow \text{H}_2 + \text{CCl}_3$ (b)**

Fromherz and Schneller¹² found a fairly rapid reaction of hydrogen atoms with chloroform, leading to HCl, methyl chloride, and a solid product. They suggest reaction (4a) as the primary step, followed by polymerization of CHCl₂. The origin of the methyl chloride has already been discussed under reaction IX-3.

Cremer, Curry, and Polanyi¹⁰ also investigated the reaction and conclude that the activation energy of reaction (4a) is less than 4.3 kcal. Since the amount of atomic hydrogen disappearing was greater than that of HCl formed, they suggest that reaction (4b) also occurs to some extent.

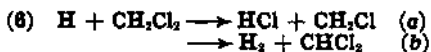
(5) $\text{H} + \text{CH}_2\text{Cl} \longrightarrow \text{CH}_3\text{Cl}$

This reaction has been suggested as a step in the mechanism of the reaction of atomic hydrogen with chloroform. (See IX-3.)

¹⁰ E. Cremer, J. Curry, and M. Polanyi, *Z. physik. Chem.*, B23, 445 (1933).

¹¹ J. E. Vance and W. C. Baumann, *J. Chem. Phys.*, 6, 811 (1938).

¹² H. Fromherz and H. Schneller, *Z. physik. Chem.*, B20, 158 (1933).



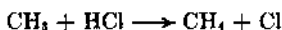
Cremer, Curry, and Polanyi¹⁰ investigated this reaction by a modification of the discharge tube method and found an activation energy of about 5.8 kcal. Since the atomic hydrogen disappearing was about twice the HCl formed, they conclude that both reactions (6a) and (6b) occur.

Further evidence for the occurrence of (6a) comes from the work of Fromherz and Schneller,¹² since methyl chloride was found as a product of the reaction of hydrogen atoms with chloroform, and this presumably arose through the intermediate formation of methylene chloride. (See IX-4.)

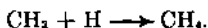


Boehm and Bonhoeffer¹³ found by the discharge-tube method that a rapid reaction occurred between hydrogen atoms and methyl chloride.

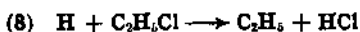
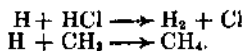
Chadwell and Titani⁸ by the same method found that the products were methane, HCl, and possibly a small amount of ethane. With the conventional type of apparatus they obtained about 9 per cent reaction at a temperature around 105°, corresponding to an activation energy of about 8-9 kcal. They assumed that the primary reaction to which this activation energy applied was (7a), and that methane arose by the reactions



and

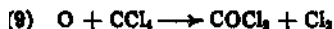


Cremer, Curry, and Polanyi¹⁰ found an activation energy of 7.2 kcal. for the reaction of hydrogen atoms with methyl chloride. The amount of HCl formed was lower than the number of hydrogen atoms disappearing, and they suggest that this is due to the occurrence of (7b) as well as (7a). It is possible, however, that the loss of H-atoms may be due rather to the occurrence of reactions such as



Chadwell and Titani⁸ obtained results with ethyl chloride very similar to those with methyl chloride, the products of the reaction being mainly methane, ethane, and HCl. About 35-40 per cent reaction occurred at temperatures in the neighbourhood of 125°, corresponding to an activation energy of about 8 kcal. for reaction (8).

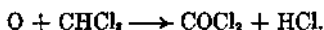
¹³ E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, 119, 385 (1926).



The reaction of oxygen atoms, produced by the discharge-tube method, with carbon tetrachloride was investigated by Harteck and Kopsch¹⁴ at room temperature. The products were equal amounts of phosgene and chlorine. -Under the usual experimental conditions 25 per cent reaction was reported, but in a later and more detailed paper¹⁵ only 2-5 per cent reaction was reported under the same conditions. This corresponds to an activation energy of 7-8 kcal. for reaction (9).



This reaction was also investigated by Harteck and Kopsch,^{14,16} who found the products to be mainly phosgene and HCl, with a small amount of chlorine. The reaction was accompanied by a bright luminescence, and was complete under the usual experimental conditions. This indicates an activation energy < 4 kcal. for the primary reaction, which is possibly



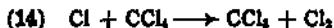
Harteck and Kopsch^{14,15} found the reaction of oxygen atoms with CH_2Cl_2 to be similar to that with CHCl_3 . Luminescence occurred, and the products were phosgene, hydrogen and some chlorine. The reaction went to completion, indicating an activation energy 4 kcal.



Harteck and Kopsch^{14,15} by the discharge-tube method found from 10-25 per cent reaction of oxygen atoms with methyl chloride under the usual experimental conditions. The activation energy is, therefore, about 5-6 kcal. The products were HCl, Cl_2 , H_2O , CO_2 , and CO, but it is uncertain what the primary process is.



The ready occurrence of this reaction has been postulated.¹⁶⁻²²



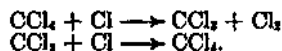
This reaction was investigated by the discharge-tube method by Schwab.¹⁷ It was found that the addition of carbon tetrachloride to the system caused no diminution in the chlorine atom concentration, although it might have been expected that atoms would be destroyed by the sequence

¹⁴ P. Harteck and U. Kopsch, *Z. Elektrochem.*, 36, 714 (1930).

¹⁵ P. Harteck and U. Kopsch, *Z. physik. Chem.*, B12, 327 (1931).

¹⁶ G. M. Schwab and H. Friess *Naturwiss.*, 21, 222 (1933).

¹⁷ G. M. Schwab, *Z. physik. Chem.*, A178, 123 (1936).



The absence of such an effect means that the activation energy of reaction (14) must be greater than about 12 kcal. This is in agreement with estimates that it is about 12 kcal. endothermic.¹⁸

, Taylor and Hanson¹⁹ have estimated E_{14} to be about 20 kcal. from assumed bond strengths and the activation energy of the reverse reaction.

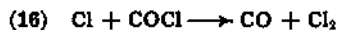


This reaction, with little or no activation energy, has been assumed as a step in the photochemical synthesis of phosgene. (See V-15.) Bodenstein and his collaborators²⁰ have estimated that the equilibrium in the reaction

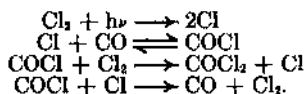


is given by

$$\log K_{\text{COCl}} = \frac{-5676}{4.571T} + 1.770.$$

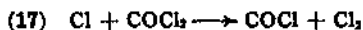


It seems to be well established (see V-15) that this reaction is a step in the mechanism of the photochemical synthesis of phosgene,²¹ i.e.,

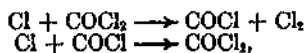


Bodenstein²⁰ has reviewed the mechanism of the phosgene synthesis in detail, and concludes that the activation energy of reaction (16) is 1.94 kcal., and that its rate is given by

$$\log k = \frac{-1940}{4.571T} + \frac{1}{2} \log T + 10.106 - 0.976.$$



Schwab¹⁷ investigated the reaction of chlorine atoms, produced by the discharge-tube method, with phosgene. The addition of phosgene was found to have very little effect on the chlorine atom concentration. Since consumption of atoms would be expected by the sequence



the activation energy of reaction (17) must be relatively high.

¹⁸ G. M. Schwab and U. Heyde, *Z. physik. Chem.*, B8, 157 (1930); H. J. Schumacher and K. Wolff, *Z. physik. Chem.*, B26, 161 (1934).

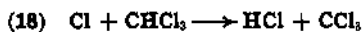
¹⁹ H. A. Taylor and W. E. Hanson, *J. Chem. Phys.*, 7, 418 (1939).

²⁰ M. Bodenstein, W. Brenschede, and H. J. Schumacher, *Z. physik. Chem.*, B40, 121 (1938).

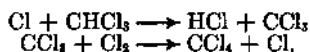
²¹ M. Bodenstein, S. Lenher, and C. Wagner, *Z. physik. Chem.*, B3, 459 (1929).

Reaction (17) is a step in the generally accepted mechanism²¹ of the phosgene synthesis. (See V-15.) Bodenstein, Brenschede, and Schumacher²⁰ have reviewed the work on this reaction in detail and conclude that $E_n = 23.0$, and that the rate constant is given by

$$\log k = \frac{-23036}{4.571T} + \frac{1}{2} \log T + 10.110 - 0.171.$$

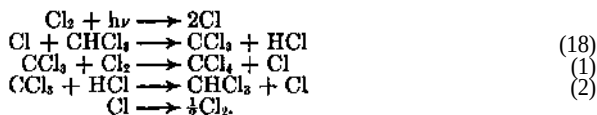


Schwab and Friess^{16,22} investigated this reaction by the discharge-tube method. The products were HCl, CCl₄, and possibly C₂Cl₆. Reaction occurred readily, but there was a relatively small drop in the chlorine atom concentration. This suggests a chain mechanism such as



and a very small activation energy for reaction (18).

Schwab and Heyde²³ have investigated the photochlorination of chloroform in carbon tetrachloride solution. The reaction is a chain process like other photochlorinations, and they suggest the standard type of mechanism, viz.,



A more detailed investigation was made by Schumacher and Wolff,²⁴ who found that the rate was given by

$$\frac{d}{dt} [\text{CCl}_4] = k[\text{Cl}_2]^{\frac{1}{2}} I_{\text{abs.}}^{\frac{1}{2}}.$$

They propose a mechanism similar to the above, except that for the chain ending step they substitute for the last two reactions



A comparison of the mechanism with the experimental rate expression and temperature coefficient leads to the values

$$\begin{aligned} E_{18} &< 4.3 \text{ kcal.}, \\ E_1 &\sim 8 \text{ kcal.}, \\ E_2 &\sim 0. \end{aligned}$$

An investigation of the thermal chlorination of chloroform¹⁹ yields results which are not incompatible with a value of $E_{18} < 4.3$ kcal.

²² G. M. Schwab and H. Friess, *Z. Elektrochem.*, 39, 586 (1933).

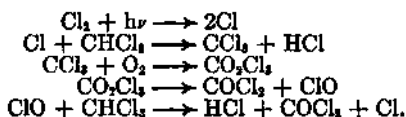
²³ G. M. Schwab and U. Heyde, *Z. physik. Chem.*, B8, 147 (1930); see also D. G. Hill, *J. Am. Chem. Soc.*, 54, 32 (1932).

²⁴ H. J. Schumacher and K. Wolff, *Z. physik. Chem.*, B26, 161 (1934).

Schumacher and Wolff²⁶ have investigated the chlorine sensitized photo-oxidation of chloroform. The reaction leads practically quantitatively to phosgene, and the quantum yield is over 100. The rate follows the expression

$$\frac{d}{dt} [\text{COCl}_2] = k[\text{CHCl}_3]^{\frac{1}{2}} I_{\text{abs.}}$$

The mechanism appears to be similar to that of other sensitized oxidations, and may be explained on the basis of a chain with Cl and CCl_3 as carriers, namely,

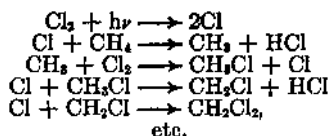


This is, of course, speculative, but is strengthened by the observation of Spinks^{25a} that phosgene is formed when chloroform reacts with ClO produced by the photodecomposition of ClO_2 .

Schumacher and Sundhoff²⁶ found that the photooxidation is completely inhibited by the addition of methyl alcohol, ethyl alcohol, or ammonia. The inhibitors are chlorinated in the process, and once they are completely chlorinated inhibition ceases. The fact that inhibition is so complete suggests that reaction (18), which is competing with the inhibition, is slower than was estimated by Schumacher and Wolff, and from their work Schumacher²⁷ estimates $E_{18} = 8 \pm 1$ kcal.



Coehn and Cordes²⁸ investigated the photochlorination of methane. Various chlorinated methanes were obtained as products, and there seems to be no doubt that the reaction proceeds by a mechanism of the Nernst chain type, viz.,



Schumacher²⁷ estimates from Coehn and Cordes' results that E_{19} is less than 8 kcal.

Reaction (19) is also probably involved in the chlorine photosensitized oxidation of methylene chloride.²⁹

²⁵ H. J. Schumacher and K. Wolff, *Z. physik. Chem.*, **B26**, 453 (1934); see also A. T. Chapman, *J. Am. Chem. Soc.*, 56, 818 (1934), 67, 416 (1935).

^{25a} J. W. T. Spinks, *Chem. Reviews*, **26**, 129 (1940).

²⁶ H. J. Schumacher and D. Sundhoff, *Z. physik. Chem.*, **B34**, 300 (1936).

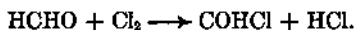
²⁷ H. J. Schumacher, *Angew. Chem.*, **63**, 501 (1940).

²⁸ A. Coehn and H. Cordes, *Z. physik. Chem.*, **B9**, 1 (1930).

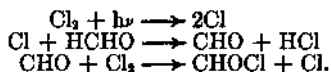
²⁹ W. Brenscede and H. J. Schumacher, *Z. physik. Chem.*, **A177**, 245 (1936).

(20) $\text{Cl} + \text{HCHO} \longrightarrow \text{CHO} + \text{HCl}$

The photochemical reaction between chlorine and formaldehyde has been investigated by Kfaukopf and Rollefson.³⁰ The first stage of the reaction is a long-chain process which involves no pressure change. The quantum yield is approximately 10^4 . Formyl chloride has been identified as a product, so that the overall reaction is presumably



The reaction is caused by light which is absorbed by, chlorine, so that the mechanism is probably the usual type of atom chain, viz.,

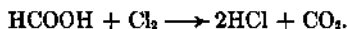


The reaction is complicated by subsequent steps involving a heterogeneous and a chlorine-sensitized decomposition of formyl chloride.

The thermal chlorination of formaldehyde may, perhaps, proceed by a similar mechanism.³¹

(21) $\text{Cl} + \text{HCOOH} \longrightarrow \text{COOH} + \text{HCl}$

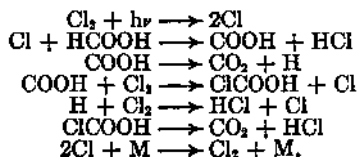
West and Rollefson³² investigated the photochlorination of formic acid vapor, and found that the overall reaction was



The quantum yield was of the order of 2000 at X3650 and 27° . The rate was given by

$$-\frac{d}{dt} [\text{Cl}_2] = k I_{\text{abs}}^{\frac{1}{2}} [\text{HCOOH}].$$

At low chlorine pressures and low light intensities the rate became proportional to I_{abs} , rather than to $I_{\text{abs}}^{1/2}$. The reaction was somewhat inhibited by the intermediate formation of chloroformic acid. The mechanism suggested involves reaction (21), viz.,



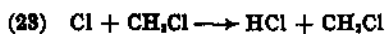
³⁰ K. B. Krauskopf and G. K. Rollefson, *J. Am. Chem. Soc.*, 66, 2542 (1934).

³¹ K. B. Krauskopf and G. K. Rollefson, *J. Am. Chem. Soc.*, 57, 590 (1935); R. Spence and W. Wild, *J. Am. Chem. Soc.*, 57, 1145 (1935); G. K. Rollefson, *J. Am. Chem. Soc.*, 57, 1146 (1935).

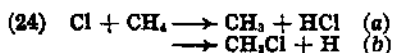
³² W. West and G. K. Rollefson, *J. Am. Chem. Soc.*, 58, 2140 (1936).



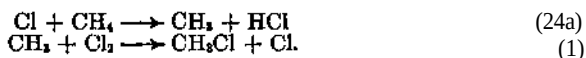
Kimball³³ has discussed reaction (22) and other association reactions theoretically from a classical point of view. He concludes that the complex formed has a life of 4.4×10^{-12} sec, and hence that third body restrictions should be important for this reaction. His calculations, however, have been questioned.³⁴



Coehn and Cordes²⁸ found that methyl chloride, methylene chloride, etc., were products of the photochlorination of methane. (See IX-24.) From their results Schumacher²⁷ estimates that *En* is less than 8 kcal. There is evidence that reaction (23) also occurs as a step in the chlorine sensitized photooxidation of methyl chloride.²⁹



Schwab and Friess²² investigated the reaction of atomic chlorine with methane by the discharge-tube method, and found a rapid decrease in chlorine atom concentration on the addition of methane to the system. It would be expected that the reaction would proceed by a Nernst chain type of mechanism,



If this is the case, then the drop in chlorine atom concentration must be due to the relatively efficient occurrence of recombination reactions such as

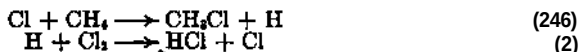


(If reaction (1) were much slower than (24a) so that it was rate-controlling, then the chain carrier would spend most of its time as CH_3 rather than Cl , and a low Cl -atom concentration would result. This, however, is certainly not the explanation since there appears to be no doubt that $E_i < E_W$ (See IX-58.)

The thermal chlorination of methane was investigated by Pease and Walz.³⁵ The reaction was formally bimolecular, but in view of the fact that it is very strongly retarded by oxygen there appears to be no doubt that it has a chain mechanism. They suggested that the primary step was the thermal dissociation of chlorine,



followed by

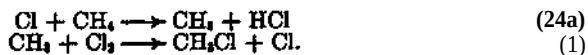


³³ G. E. Kimball, *J. Chern. Phys.*, 5, 310 (1937).

³⁴ L. S. Kassel, *J. Chem. Phys.*, 5, 922 (1937).

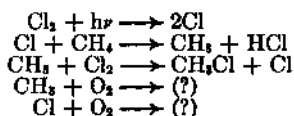
³⁵ R. N. Pease and G. F. Walz, *J. Am. Chem. Soc.*, 53, 3728 (1931).

or by

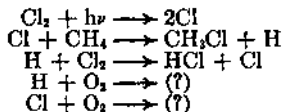


In view of recent estimates of bond strengths, there is no doubt that reaction (246) is strongly endothermic, and if a chain mechanism holds it must involve reactions (24a) and (1) rather than (246) and (2). From estimates of the thermal dissociation of chlorine they calculated a chain length of 10^{14} . However, on the basis of a more reliable value of the equilibrium constant³⁶ the calculated chain length has the more reasonable value of 10^7 . The atomic mechanism thus appears plausible.

The photochlorination of methane was investigated by Jones and Bates³⁷ and by Coehn and Cordes.²⁸ Jones and Bates paid special attention to the effect of oxygen as an inhibitor, and found that their results were well expressed by an equation analogous to that obtained by Thon for the hydrogen-chlorine reaction in the presence of oxygen. (See reference 28.) This is strong evidence for the occurrence of a modified Nernst chain, *i.e.*, either



or



As pointed out above, however, the latter mechanism must be ruled out since reaction (246) is too endothermic.

Coehn and Cordes²⁸ found that the products of the reaction were various chlorinated methanes. Quantum yields up to 10^4 were obtained at X4358 and X2537, together with other characteristics of a chain process, such as an induction period. Schumacher²⁷ estimates from their results that E_{24a} is less than 8 kcal.

Tamura³⁸ has investigated the photochlorination over a range of temperature, and he concludes that $E_{24a} \leq 6.2$ kcal.

Brenschede and Schumacher²⁹ have investigated the chlorine sensitized photooxidation of methane. It appears certain that reaction (24a) is a step in the mechanism.

Further evidence that the foregoing mechanism is correct comes from the work of Bogdandy and Polanyi³⁹ who investigated the reaction of sodium

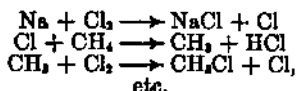
³⁶W. F. Giauque and R. Overstreet, *J. Am. Chem. Soc.*, 64, 1731 (1932).

³⁷L. T. Jones and J. R. Bates, *J. Am. Chem. Soc.*, 56, 2282 (1934).

³⁸M. Tamura, *Rev. Phys. Chem.*, Japan, 15, 86 (1941). (Seen in abstract only.)

³⁹S. v. Bogdandy and M. Polanyi, *Z. Elektrochem.*, 33, 554 (1927).

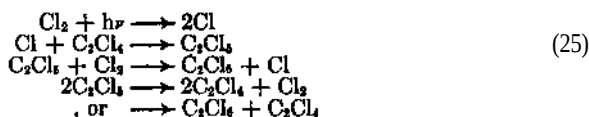
vapor with methane-chlorine mixtures at 150° to 250°. **HC1** and methyl chloride were formed, and there is no doubt that the mechanism is



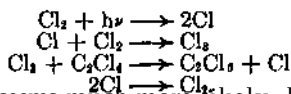
In carbon tetrachloride solution it is found that the photochlorination of tetrachlor ethylene is a chain reaction with a large quantum yield, the rate of which is proportional to $I_{abs}^{1/2}$.⁴⁰ In the presence of oxygen Dickinson and Leermakers⁴¹ found that a chlorine sensitized photooxidation to trichloro acetyl chloride occurred. The rate of this was proportional to I_{abs} , and the quantum yield was relatively small.

The gas phase reactions have been investigated by Dickinson and Carrico.⁴² In the absence of oxygen the products were almost entirely hexachlor ethane, and in the presence of oxygen trichloro acetyl chloride. Quantum yields up to 450 were found for the chlorination and for the sensitized oxidation.

The chlorination results can be explained on the basis of either



or



The former mechanism seems much more likely, but it should be noted that if the CU mechanism holds the occurrence of reaction (25) is no longer postulated. If it is assumed that the former mechanism holds, no direct evaluation of E_{25} is possible, but reaction (25) must be fast. Schumacher²⁷ suggests that the activation energies of all reactions of this type are probably much below 8 kcal.

Schott and Schumacher^{42a} have reinvestigated the gas phase photochlorination of tetrachlor ethylene. Results similar to those of Dickinson and Carrico were obtained, the rate being given by

$$\frac{d}{dt} [\text{C}_2\text{Cl}_5] = k I_{abs}^{1/2} [\text{Cl}_2].$$

⁴⁰ J. A. Leermakers and R. G. Dickinson, J. *Am. Chem. Soc.*, **64**, 4648 (1932).

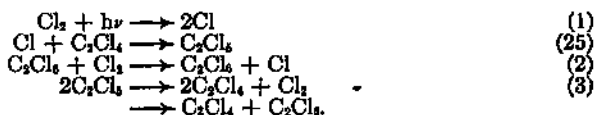
⁴¹ R. G. Dickinson and J. A. Leermakers, *J. Am. Chem. Soc.*, **54**, 3852 (1932).

⁴² R. G. Dickinson and J. L. Carrico, *J. Am. Chem. Soc.*, **66**, 1473 (1934).

^{42a} C. Schott and H. J. Schumacher, *Z. physik. Chem.*, **B49**, 107 (1941). (Seen in abstract only.)

The reaction is strongly inhibited by oxygen, but is not affected by SO_2 . The quantum yield under their experimental conditions was of the order of 350. The temperature coefficient corresponded to an activation energy of 7.4 kcal.

By analogy with the photochlorination of trichlor ethylene (see IX-71), the mechanism is probably



This yields the rate expression

$$\frac{d}{dt} [\text{C}_2\text{Cl}_6] = \frac{k_2}{k_3^{\frac{1}{2}}} I_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2]^{\frac{1}{2}}$$

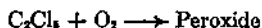
in agreement with experiment. From the observed temperature coefficient

$$E_2 - \frac{1}{2}E_3 = 7.4 \text{ kcal.}$$

If it is assumed that E_3 is small, then $E_2 \sim 8 \text{ kcal.}$

No explicit value for E_{25} is obtained, but it must be small.

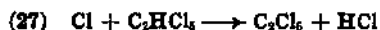
Schott and Schumacher also investigated the chlorine sensitized photooxidation of tetrachlor ethylene. Of the tetrachlor ethylene 80 per cent was found to be converted to trichlor acetyl chloride and 20 per cent to phosgene. The mechanism is similar to that of pentachlor ethane (see IX-64 for details), and apparently involves reactions (1) and (25), together with



followed by reactions of the peroxide formed in (4).



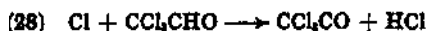
Mtiller and Schumacher⁴³ have investigated the photochlorination of trichlor ethylene. There is no doubt that one step in the mechanism is reaction (26) with a low activation energy. The mechanism of the photochlorination is discussed in some detail in section IX-71.



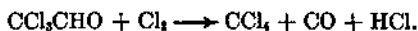
This reaction is undoubtedly a step in the photochlorination and chlorine sensitized photooxidation of pentachlor ethane.⁴⁴ (See IX-63 and IX-64 for details.) Schumacher and Thiirauf suggest that, by analogy with similar reactions, $E_{27} = 5-8 \text{ kcal.}$

⁴³ K. L. Mtiller and H. J. Schumacher, *Z. physik. Chem.*, **B36**, 455 (1937).

⁴⁴ H. J. Schumacher and W. Thiirauf, *Z. physik. Chem.*, **A189**, 183 (1941).



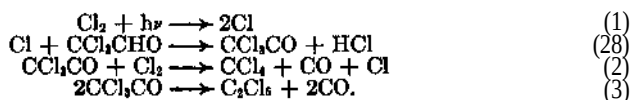
Alexander and Schumacher⁴⁵ have investigated the photochlorination of chloral. The overall reaction is



The quantum yield is in the neighbourhood of 800. The experimental results lead to the rate expression

$$-\frac{d}{dt} [\text{Cl}_2] = k I_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2].$$

They propose the mechanism



Whence

$$-\frac{d}{dt} [\text{Cl}_2] = \frac{k_2}{k_3^{\frac{1}{2}}} I_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2].$$

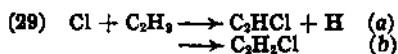
The apparent activation energy of the overall reaction is 5.4 kcal. From the above mechanism

$$E_{\text{overall}} = E_2 - \frac{1}{2}E_3.$$

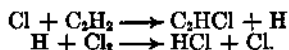
Hence the minimum value of E_2 is 5.4 kcal. E_3 is obviously very small, probably 1-2 kcal., so that $E_2 \sim 6$ kcal. E_{28} must be small, or most chlorine atoms would disappear by recombination, i.e.,

$$E_{28} < 6 \text{ kcal.}$$

Reaction (28) has also been suggested⁴⁶ as a step in the mechanism of the chlorine photosensitized oxidation of chloral. (See IX-65.)



Tominaga and Okamoto⁴⁷ made a spectroscopic investigation of the flame which results when chlorine is mixed with acetylene. They suggest a chain mechanism -

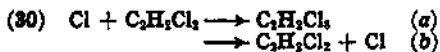


It seems almost certain that this is wrong, and that the primary reaction is (296) rather than (29a).

⁴⁵ W. A. Alexander and H. J. Schumacher, *Z. physik. Chem.*, **B44**, 57 (1939).

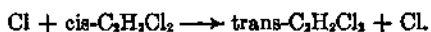
⁴⁶ W. A. Alexander and H. J. Schumacher, *Z. physik. Chem.*, **B44**, 313 (1939).

⁴⁷ H. Tominaga and G. Okamoto, *Bull. Soc. Chem., Japan*, 12, 401 (1937).

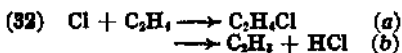


Miiller and Schumacher⁴⁸ investigated the photochlorination of trans-dichlor ethylene. There appears to be no doubt that reaction (30a) is involved and has a small activation energy. For a discussion of the mechanism of the reaction see IX-71. The chlorination of cis-dichlor ethylene is very similar.⁴³

There is some evidence that in the photochemical chlorine sensitized cis-trans isomerization of dichlor ethylene a reaction of the Walden inversion type occurs,⁴⁹ i.e.,

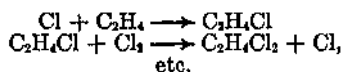


Schmitz and Schumacher⁵⁰ suggest reaction (31) as a step in the photochlorination of vinyl chloride. (See section IX-73.)

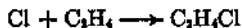


Schwab¹⁷ investigated this reaction, the chlorine atoms being produced by the discharge-tube method. He was unable to obtain reproducible results owing to a series of explosions in the liquid air trap in which the chlorine and products were frozen out. This was presumably due to unstable addition products formed via reaction (32a). E_{32a} must, therefore, be very small.

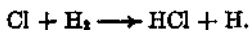
The photochlorination of ethylene was investigated by Stewart and his collaborators.⁶¹ The reaction is a chain process, and the mechanism is presumably similar to that of other chlorinations, viz.,



In mixtures of hydrogen, chlorine, and ethylene, Stewart and Weidenbaum found that ethylene reacted 81 times as fast as hydrogen. This is apparently owing to the reaction



being faster than



If the activation energy of the latter reaction is assumed to be 6.0 kcal., then E_{32a} is not greater than 1.4 kcal.

⁴⁸ K. L. Muller and H. J. Schumacher, *Z. physik. Chem.*, **B36**, 285 (1937); *Z. Elektrochem.*, **43**, 807 (1937).

⁴⁹ A. fe. Olson, *J. Chem. Phys.*, **1**, 418 (1933); H. E. Mahncke and W. A. Noyes, *J. Am. Chem. Soc.*, **68**, 932 (1936).

⁵⁰ H. Schmitz and H. J. Schumacher, *Z. physik. Chem.*, **B52**, 72 (1942).

⁵¹ T. D. Stewart and B. Weidenbaum, *J. Am. Chem. Soc.*, **67**, 2036 (1935); see also T. D. Stewart and M. H. Hanson, *J. Am. Chem. Soc.*, **63**, 1121 (1931).

Schmitz, Schumacher, and Jager⁶² have also investigated the photo chlorination of ethylene. (See IX-81 for details.) They suggest, mainly by analogy with other cases, that $E32a \sim 0$.

The high-temperature chlorination of ethylene has been investigated by Rust and Vaughan⁵³ using a flow system with nitrogen or carbon dioxide as a carrier. The reaction is negligible below ca. 235°. Above this temperature an addition reaction starts. At higher temperatures substitution comes into play, and above about 400° is the only important reaction. At intermediate temperatures as the concentration of the reactants increases more substitution occurs. The products were mainly vinyl chloride, di- and tri-chlor ethane, with smaller amounts of dichlor ethylene and tetrachlor ethane.

The rate was roughly proportional to

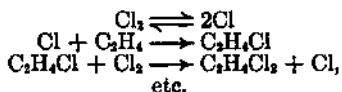
$$[\text{Cl}_2][\text{C}_2\text{H}_4]^{\frac{1}{2}}.$$

The results were, however, only poorly reproducible, and the surface had a pronounced effect on the rate.⁵⁴ At lower temperatures (up to about 285°) the reaction was completely inhibited by oxygen. All these facts point to a chain mechanism, presumably involving free radicals. Further evidence for this is the fact that the reaction is catalysed by tetraethyl lead at temperatures below those at which it normally occurs.

At higher temperatures, oxygen instead of inhibiting the reaction, catalyses it.⁵⁶ Ethane was found to inhibit the oxygen-catalysed reaction, being itself chlorinated in the process.

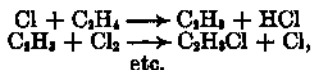
They suggest, for the oxygen-free reaction, standard chain mechanisms

(a) *Addition*



This does not lead to the observed rate equation, but in view of the complexities of the reaction this is not surprising, and probably indicates the simultaneous occurrence of molecular processes.

(6) *Substitution*



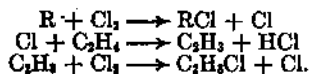
⁵² H. Schmitz, H. J. Schumacher, and A. Jager, *Z. physik. Chem.*, **B51**, 281 (1942).

⁵³ F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, **5**, 472 (1940). See also H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, **31**, 1530 (1939).

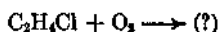
⁵⁴ See R. G. W. Norrish and G. G. Jones, *J. Chem. Soc.*, **1926**, 55.

⁵⁶ H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939).

For the oxygen-promoted reaction they suggest an initial reaction of oxygen with ethylene which leads to the production of free radicals, R, followed by



This suggests that the vinyl radical can persist in the presence of oxygen, possibly owing to stabilization by resonance. As a result the reaction



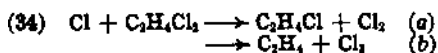
is much faster than



and oxygen-promoted substitution occurs but no oxygen-promoted addition.



This reaction has also been postulated⁶² as a step in the mechanism of the photochlorination of ethylene. (See IX-81.) Schmitz, Schumacher, and Jager suggest $E_{33} = 1$ to 2 kcal.



Sherman and Sun⁶ have calculated the activation energies of these reactions by the semi-empirical method, assuming a C—Cl bond strength of 78.6 kcal. They obtain the values

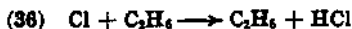
$$\begin{aligned} E_{34a} &= 24.6 \text{ kcal.} \\ E_{34b} &= 95.9 \text{ kcal.} \end{aligned}$$



Kimball³³ has discussed the association reaction



from a classical theoretical standpoint. He concludes that the complex has a life of ca. 6.3 sec, and hence that there should be no third-body restrictions on the occurrence of the reaction. Kassel,³⁴ however, has criticized Kimball's treatment and concludes that it has little meaning.

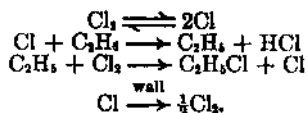


The thermal chlorination of ethane at high temperatures has been investigated by Vaughan and Rust.⁵⁶ The results are expressed by the equation

$$\frac{d[HCl]}{dt} = k[Cl_2][C_2H_6].$$

⁵⁸ W. E. Vaughan and F. F. Rust, *J. Org. Chem.* 6, 449 (1940).

They suggest the usual type of mechanism

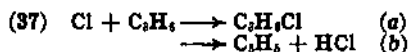


The reaction is strongly inhibited by oxygen, and there seems to be no doubt that it proceeds by a chain mechanism of the type given above.

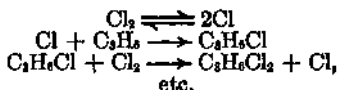
The thermal chlorination of ethane at lower temperatures (130°) could be induced by the addition of tetraethyl lead.

At higher temperatures the ethane chlorination was inhibited by ethylene, propylene, or butylene.⁵³

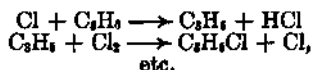
Rust and Vaughan⁵³ also made a few measurements on the photochlorination of ethane, and found it to be inhibited by olefins, ethyl chloride, and vinyl chloride.



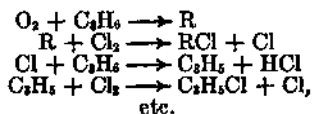
Rust and Vaughan⁵³ have investigated the high-temperature thermal chlorination of propylene. The results were very similar in all respects to those for ethylene (see IX-32) and the reaction is undoubtedly a free-radical chain process. The reaction is sensitive to surface, is inhibited by oxygen, and catalysed by tetraethyl lead. Both substitution and addition occur possibly by the mechanisms



and



At higher temperatures an oxygen catalysed substitution reaction occurs.⁵⁵ They suggest the mechanism



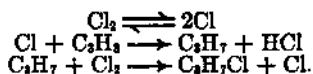
For this mechanism to hold, the allyl radical must be relatively inert as far as the reaction



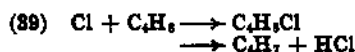
is concerned.



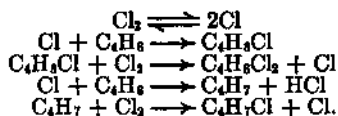
The thermal chlorination of propane has been investigated by Yuster and Reyerson.⁶⁷ The products were HCl and chlorinated propanes. The reaction shows all the characteristics of a chain reaction; and they suggest the usual type of mechanism, involving reaction (38), viz.,



This leads to a calculated chain length of ca. 10^7 . Similar results were obtained by Vaughan and Rust,⁶⁶ who also showed that the reaction could be induced at lower temperatures by the addition of tetraethyl lead.



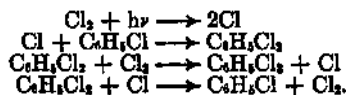
Rust and Vaughan⁶³ postulate this reaction as a step in the mechanism of the thermal chlorination of butene at high temperatures. The results are very similar to those for ethylene and propylene. (See IX-32 and IX-37.) The mechanism is presumably



This reaction is probably involved in the thermal chlorination of pentene in carbon tetrachloride solution.⁵⁸



The photochlorination of chlorobenzene is mainly an addition reaction⁵⁹ as is the case with benzene. The final product is mainly C_6Cl_{12} . The main experimental facts are (a) the rate of reaction is proportional to a power of the light intensity between 0.5 and 1.0, (b) the rate is approximately proportional to $[\text{C}_6\text{H}_5\text{Cl}]$, and is also dependent on the chlorine pressure to some extent, (c) the effect of temperature is small, (d) the quantum yield is considerable but is smaller than that for benzene. Hart and Noyes consider that the main facts can be explained on the basis of the mechanism:

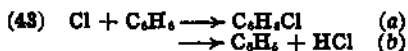


⁵⁷ S. Yuster and L. H. Reyerson, *J. Phys. Chem.*, 39, 859, 1111 (1935).

⁵⁸ T. D. Stewart and B. Weidenbaum, *J. Am. Chem. Soc.*, 58, 98 (1936).



This reaction has been postulated as a step in the photochlorination of chlorobenzene.⁵⁹ For details see IX-41.



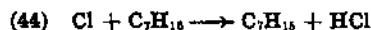
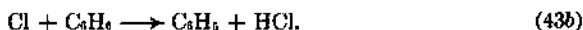
The photochlorination of benzene vapor was found by Lane and Noyes⁶⁰ to lead to phenyl chloride and higher chlorides. In a more thorough investigation Noyes and Hart⁶¹ used $\lambda 3660$ and $\lambda 3130$ and found quantum yields of 20 or more. The rate was proportional to

$$I_{\text{abs.}}^{1/2} [\text{Cl}_2] [\text{C}_6\text{H}_6].$$

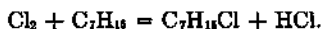
The main reaction is addition, and it appears probable that the major secondary step is the reaction



together with a small amount of



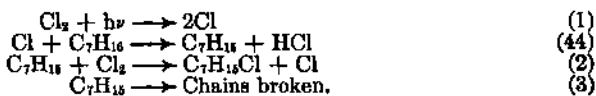
Stauff and Schumacher⁶² investigated the photochlorination of heptane in carbon tetrachloride solution at 25° and 35°. The overall reaction is



The quantum yield under their experimental conditions was 7.3×10^4 at 25°. The results can be expressed by the equation

$$-\frac{d}{dt} [\text{Cl}_2] = k I_{\text{abs.}} [\text{Cl}_2].$$

They propose a mechanism of the usual type, viz.,



The mechanism leads to the expression

$$-\frac{d}{dt} [\text{Cl}_2] = 2 \frac{k_2}{k_3} I_{\text{abs.}} [\text{Cl}_2].$$

Whence

$$E_{\text{overall}} = 6 \pm 2 \text{ kcal.}, = E_2 - E_3.$$

E_3 is undoubtedly very small, and so $E_2 \sim 5 \text{ kcal.}$, in agreement with values for other reactions of this type.

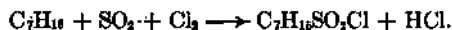
⁵⁹ E. J. Hart and W. A. Noyes, *J. Am. Chem. Soc.*, 56, 1305 (1934).

⁶⁰ C. E. Lane and W. A. Noyes, *J. Am. Chem. Soc.*, 54, 161 (1932).

⁶¹ H. P. Smith, W. A. Noyes, and E. J. Hart, *J. Am. Chem. Soc.*, 65, 4444 (1933).

⁶² J. Stauff and H. J. Schumacher, *Z. Elektrochem.*, 48, 271 (1942).

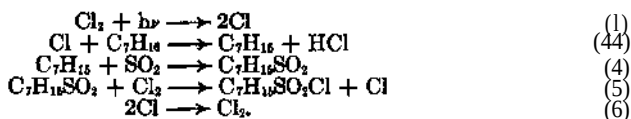
Stauff⁶³ has also investigated the photoreaction between chlorine, sulphur dioxide, and heptane,



The results can be expressed by the rate equation

$$\frac{-d}{dt} [\text{Cl}_2] = k\text{I}_{\text{abs.}}^{\frac{1}{2}} [\text{C}_7\text{H}_{16}].$$

He suggests the mechanism :



This leads to the expression

$$\frac{-d}{dt} [\text{Cl}_2] = k_{44} \sqrt{\frac{2\text{I}_{\text{abs.}}}{k_6}} [\text{C}_7\text{H}_{16}]$$

so that

$$k = k_{44} \left(\frac{2}{k_6} \right)^{\frac{1}{2}}.$$

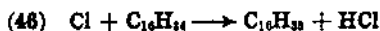
E_6 is certainly approximately zero, and the experimental activation energy thus corresponds to that of reaction (44), i.e., $E_{44} = 6$ kcal.

Since reaction (4) is in competition with (2), E_4 must be small compared with E_2 . Since $E_2 \sim 5$ kcal., $E_4 \ll 5$ kcal.

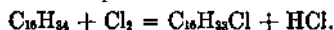
Since oxygen inhibits the reaction strongly, E_5 must be appreciable.



Stauff⁶⁴ suggests this reaction as a step in the mechanism of the photochlorination of hexadecane, and assumes $E_{45} \sim 0$. (For details see IX-46.)



The photochlorination of hexadecane in CCl_4 soln. has been investigated by Stauff.⁶⁴ The quantum yield at room temperature with X4360, was of the order of 7×10^4 under his experimental conditions. The overall reaction is



At high chlorine concentrations the rate law is

$$\frac{-d}{dt} [\text{Cl}_2] = k'\text{I}_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2]^{\frac{1}{2}} [\text{C}_{16}\text{H}_{34}]^{\frac{1}{2}}.$$

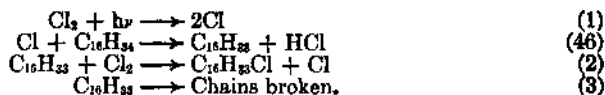
At low chlorine concentrations the rate law became

$$\frac{-d}{dt} [\text{Cl}_2] = k''\text{I}_{\text{abs.}} [\text{Cl}_2]$$

⁶³ J. Stauff, *Z. physik. Chem.*, in press.

⁶⁴ J. Stauff, *Z. Elektrochem.*, 48, 550 (1942).

similar to the rate law for heptane. The latter rate law can be explained by the mechanism



This is analogous to the case of heptane, and leads to

$$-\frac{d}{dt} [\text{Cl}_2] = 2 \frac{k_2}{k_3} I_{\text{abs}} [\text{Cl}_2].$$

Hence

$$k' = 2 \frac{k_2}{k_3}.$$

To explain the results at higher chlorine concentrations it must be assumed that the chains end in a different way, and Stauff suggests



Whence he obtains, with certain approximations

$$-\frac{d}{dt} [\text{Cl}_2] = \sqrt{\frac{k_4 k_2}{k_4}} I_{\text{abs.}} [\text{C}_{15}\text{H}_{34}] [\text{Cl}_2]$$

in agreement with the experimental rate law if

$$k' = \sqrt{\frac{k_4 k_2}{k_4}}.$$

The apparent activation energy at high chlorine concentrations is 7.5 ± 1 kcal. Hence

$$7.5 \pm 1 = \frac{1}{2} (E_{46} + E_2 - E_4).$$

The apparent activation energy is 9 ± 2 kcal. at low chlorine concentrations, *i.e.*

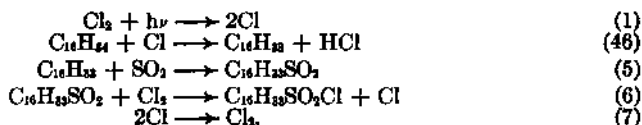
$$9 \pm 2 = E_2 - E_3.$$

He suggests that E_w has the same value as that for



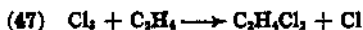
and hence puts $E_{46} = 6$ kcal. E_4 is certainly practically nil. Hence $E_2 = 9$ kcal., and since $E_2 - E_3 = 9 \pm 2$ kcal., E_3 is very small. Reaction (3) is probably a wall reaction.

Stauff⁶⁴ has also investigated the reaction between $\text{C}_{15}\text{H}_{34}$, SO_2 , and Cl_2 in CCl_4 soln. The results obtained are identical with those for $\text{C}_7\text{H}_{16} + \text{SO}_2 + \text{Cl}_2$ (see IX-44), and lead to the corresponding mechanism

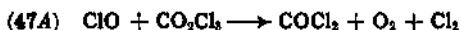


Whence, analogous to the results with heptane,

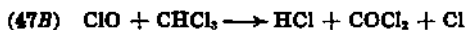
$$\begin{aligned} E_{44} &= 6 \text{ kcal.} \\ E_1 &\ll 5 \text{ kcal.} \\ E_1 &\text{ is appreciable.} \end{aligned}$$



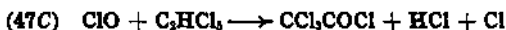
Sherman and Sun⁵ by the semi-empirical method have estimated E_{47} to be 48.2 kcal.



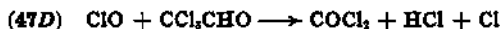
This reaction has been suggested as a step in the mechanism of the chlorine photosensitized oxidation of trichlor brom methane.⁶⁶



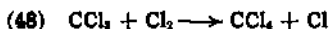
This reaction probably occurs in the chlorine sensitized photooxidation of chloroform. (See IX-18.)



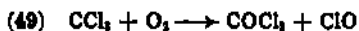
This has been suggested as a step in the chlorine sensitized photooxidation of pentachlor ethane. (See IX-65.)



This is a postulated step in the mechanism of the chlorine sensitized photooxidation of chloral. (See IX-69.)



The rapid occurrence of this reaction has frequently been postulated in the mechanism of halogenations. Examples are the reaction of atomic chlorine with chloroform,²² the thermal chlorination of chloroform,¹⁹ and the photochlorination of trichlor brom methane.^{65,66} More quantitative information comes from investigations of the photochlorination of chloroform.^{23,24} This work has been discussed in section IX-18, and leads to a value of $E\&$ of approximately 8 kcal. Schumacher²⁷ suggests that this value is good to about ± 1.5 kcal.

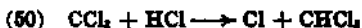


This reaction has been postulated by Franke and Schumacher⁶⁶ as a step in the chlorine and bromine sensitized oxidation of trichlor brom methane. The reactions are very complex and no unique mechanism can be arrived

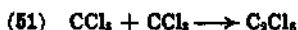
⁶⁵ H. J. Schumacher, *Z. physik. Chem.*, B42, 324 (1939).

⁶⁶ W. K. Franke and H. J. Schumacher, *Z. physik. Chem.*, B42, 297 (1939).

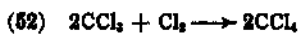
at. However, the bromine sensitized reaction is consistent with a Schumacher type of mechanism in which, among other things, it is assumed that $E_{49} = 1.2$ kcal., and that the steric factor of the reaction is less than 0.001.



This reaction was assumed by Schwab and Heyde²⁵ to be a step in the photochlorination of chloroform. (See IX-18.) It has also been assumed by Taylor and Hanson¹⁹ in the thermal chlorination. The latter authors estimate from thermochemical data and from bond strengths that reaction (50) is 13 kcal. endothermic. The reverse reaction has an activation energy of about 4.2 kcal., and they, therefore, assign a value of 17 kcal. to E_{50} . It may be noted that Schumacher and Sundhof have revised the estimate of E for the reverse reaction to 8 kcal. This would make $E_{50} \sim 21$ kcal., if Taylor and Hanson's estimate of the heat of reaction is correct.



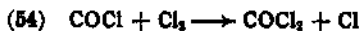
It has been suggested²² that this reaction occurs to some extent in the reaction of atomic chlorine with methane.



Reaction (52) has been suggested as a chain-ending step in the photochemical chlorination of chloroform. (See IX-18.) As discussed previously, Schumacher and Wolff's results¹⁸ lead to the conclusion that $E_{52} \sim 0$.



This is one of the steps in the mechanism of the photochemical synthesis of phosgene. (See V-15.) Bodenstein, Brenschede, and Schumacher²⁰ estimate its activation energy to be 5.6 kcal.

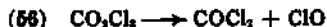


This is one of the chain-carrying steps in the mechanism of the photochemical synthesis of phosgene. (See V-15.) Bodenstein, Brenschede, and Schumacher²⁰ estimate $E_{54} = 2.6$ kcal., and that its rate is given by

$$\log k = \frac{-2612}{4.571 T} + \frac{1}{2} \log T + 10.101 - 3.871.$$



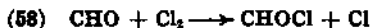
This reaction has been postulated as a step in the mechanism of the bromine sensitized oxidation of trichlorobromomethane.⁶⁶ The mechanism suggested is by no means well established. It is, however, consistent with the data provided that E_{55} is small.



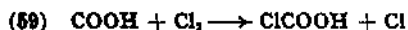
This has been suggested as a step in the mechanism of the chlorine photosensitized oxidation of trichlor brom methane,⁶⁶ and assigned an activation energy of approximately 15 kcal. The mechanism, however, rests on uncertain ground.



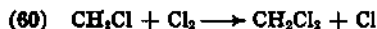
Brenschede and Schumacher²⁹ investigated the chlorine sensitized oxidation of methane and of chlorine substituted methanes. A typical chain mechanism involving reaction (57) was postulated. From their data Schumacher²⁷ has estimated that E_{57} is less than 5 kcal.



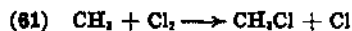
This reaction has been suggested³⁰ as a step in the photochlorination of formaldehyde. (See IX-20.)



This reaction has been postulated³² as a step in the mechanism of the photochlorination of formic acid vapor. (See IX-21.)

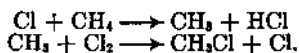


This reaction has been suggested as a step in the mechanism of the chlorine photosensitized oxidation of methyl chloride by Brenschede and Schumacher.²⁹ Schumacher²⁷ has estimated from their data that $E_{60} < 5$ kcal.



Horn, Polanyi, and Style⁶⁷ found that methyl radicals produced by the reaction of sodium and methyl halides could be detected by their reaction with chlorine at temperatures around 250°. Further proof of the occurrence of reaction (61) was obtained with mixtures of chlorine and hydrogen, in which the chlorine atoms formed by (61) initiated the typical hydrogen-chlorine chains. Reaction (61) must, therefore, have a low activation energy.

Reaction (61) has been generally assumed^{23,28,35,37,39} as part of a Nernst chain type of mechanism for the chlorination of methane, viz.,



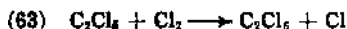
⁶⁷ E. Horn, M. Polanyi, and D. W. G. Style, *Trans. Faraday Soc.*, 30, 189 (1934); M. Polanyi and D. W. G. Style, *Naturwiss.*, 20, 401 (1932).

From Brenschede and Schumacher's²⁹ results on the chlorine photo-sensitized oxidation of methane and chlorine substituted methanes, Schumacher²⁷ estimates $E_{62} < 5$ kcal.

Further evidence for the occurrence of this reaction with a low activation energy is furnished by the fact that thermal chlorination reactions can be induced by the addition to the system of methyl radicals from the decomposition of azomethane.⁵⁶



This has been suggested on the basis of virtually no evidence as a step in the mechanism of the reaction of hydrogen atoms with CH_3Cl .⁸ (See IX-7.)

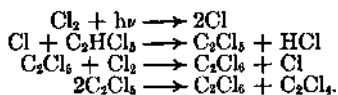


This reaction has been suggested as a step in the photochlorination of tetrachlor ethylene.^{6,42} Schumacher²⁷ suggests, by analogy with other reactions, that E_m is probably considerably below 8 kcal. The work of Schott and Schumacher, however, leads to a value of about 8 kcal. for E_m . (See IX-25.)

More recently, Schumacher and Thiirau⁶⁸ investigated the photochlorination of pentachlor ethane to hexachlor ethane. The quantum yield was about 400 at 90° and 35 mm. of C_2HCl_5 and 190 mm. of Cl_2 . Their results are fitted by the expression

$$\frac{d}{dt} [\text{C}_2\text{Cl}_6] = k I_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2].$$

They suggest a mechanism analogous to that of other halogenations:



This leads to

$$\frac{d}{dt} [\text{C}_2\text{Cl}_6] = \frac{k_{45}}{k_3^{\frac{1}{2}}} I_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2].$$

The temperature coefficient is negligible, so that

$$E_{63} - \frac{1}{2}E_3 \sim 0.$$

E_3 is not large, and hence EM must be small.

Schott and Schumacher's work, however (see IX-25), leads to a value of about 8 kcal. for E_{63} .

⁶⁸ H. J. Schumacher and W. Thurauf, *Z. physik. Chem.*, **A189**, 183 (1941).

(64) $C_2Cl_6 + O_2 \rightarrow (?)$

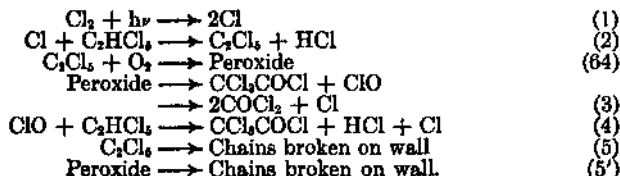
The chlorine sensitized photooxidation of pentachlor ethane has been investigated by Schumacher and Thürauf.⁶⁸ The products corresponded to



The quantum yield at 90°, 200 mm. of Cl_2 and 40 mm. of C_2HCl_5 was about 250.

In contrast to other chlorine sensitized photooxidations, the oxidation does not completely swamp out the photohalogenation, and with 200 mm. of Cl_2 to 20 mm. of O_2 , the chlorination and oxidation proceed at roughly equal rates.

Schumacher and Thürauf suggest the mechanism:



The experimental results are expressed by the equation

$$\frac{dp}{dt} = \frac{I_{abs.}[O_2]}{k' + k''[O_2]}$$

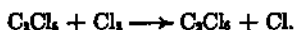
This scheme, neglecting the relatively small phosgene producing step in (3), leads to

$$\frac{d[CCl_3COCl]}{dt} = I_{abs.} \frac{[O_2]}{\frac{k_5}{2k_{44}} + \frac{k_5k_5'}{2k_{44}k_3} + \frac{k_5'[O_2]}{2k_3}}$$

This agrees with experiment when we put

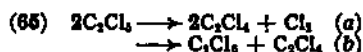
$$\begin{aligned} \frac{k_5k_3 + k_5k_5'}{2k_{44}k_3} &= k' \\ \frac{k_5'}{2k_3} &= k'' \end{aligned}$$

The effect of temperature is small and not much can be concluded about the activation energies. Since the oxidation is about 10 times faster than the chlorination, however, reaction (64) must be about 10 times faster than the reaction

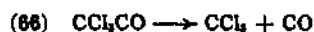


Hence E_{64} must be < 5 kcal.

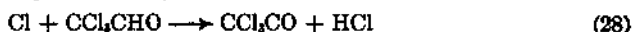
Reaction (64) is probably also involved in the chlorine sensitized photooxidation of trichlor ethylene. The mechanism of the reaction is similar to that of pentachlor ethane. (See IX-25.)



It has been suggested that reaction (65) occurs in the photochlorination of tetrachlor ethylene,⁴² of pentachlor ethane⁴³ (see IX-63), and of trichlor ethylene^{42a}. (See IX-25.) E_{65} appears to be approximately zero.



Alexander and Schumacher's investigation⁴⁵ of the photochlorination of chloral has already been discussed in section IX-28. According to this mechanism CCl_3CO is produced by the reaction



and disappears by

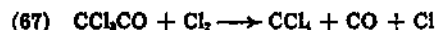


and

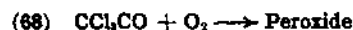


The activation energies arrived at for these reactions are $E_{28} < 6$ kcal., $E_2 \sim 6$ kcal., $E_3 \sim 1-2$ kcal.

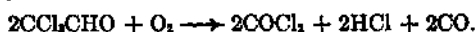
Since the mechanism is in agreement with experiment without the inclusion of reaction (66) they conclude that this must be slow, and that E_{66} must be greater than 22 kcal.



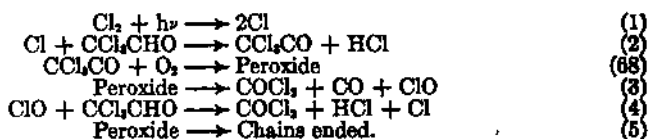
As discussed in section IX-28, Alexander and Schumacher's investigation⁴⁵ of the photochlorination of chloral leads to a value of approximately 6 kcal. for E_{67} .



This reaction with a low activation energy has been postulated as a step in the chlorine sensitized photooxidation of chloral by Alexander and Schumacher.⁴⁶ They found that the overall reaction was



The rate is proportional to $I_{abs.}$, and is independent of pressure and of the relative concentrations of the reactants. The quantum yield is about 3000. They suggest the mechanism

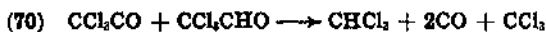


The reaction has also been postulated as a step in the bromine photo-sensitized oxidation of chloral.^{42a}

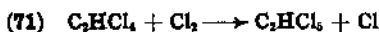
^{45a} J. Stauff and H. J. Schumacher, *Z. physik. Chem.*, **B48**, 154 (1940).



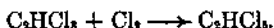
In connection with the investigation of the photochlorination of chloral (see IX-28), Alexander and Schumacher suggest that $E_{69} \sim 1-2$ kcal. The reaction has also been postulated as a step in the photobromination of chloral.^{68b} (See X-13.)



This reaction has been postulated by Klug and Schumacher^{68b} as a step in the photobromination of chloral. (See X-13 for details.) Their mechanism leads to the value $E_{70} = 12 \pm 2$ kcal.



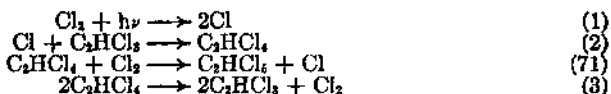
Müller and Schumacher⁴⁸ have investigated the photochlorination of trichlor ethylene. The overall reaction is



The rate is given by

$$\frac{d}{dt} [\text{C}_2\text{HCl}_3] = k I_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2]$$

The mechanism appears to be exactly analogous to that for dichlor ethylene (see IX-74), viz.,



or



This leads to

$$-\frac{d}{dt} [\text{Cl}_2] = \frac{k_1}{k_3^{\frac{1}{2}}} I_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2]$$

The overall activation energy was 5.3 kcal. Hence

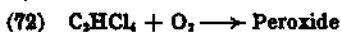
$$E_1 - \frac{1}{2}E_3 = 5.3 \text{ kcal.}$$

E_3 is probably approximately zero, and therefore

$$E_1 \sim 5.3 \text{ kcal.}$$

Reaction (71) has also been suggested as a step in the mechanism of the chlorine photosensitized oxidation of trichlor ethylene.⁶⁹

Schumacher²⁷ in a review of photohalogenations gives $E_{71} = 5.5$ kcal.

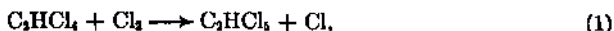


Miiller and Schumacher⁶⁹ have investigated the chlorine sensitized oxidation of trichlor ethylene to dichlor acetyl chloride. This resembles other

^{68b} H. Klug and H. J. Schumacher, *Z. physik. Chem.*, **B47**, 67 (1940).

⁶⁹ K. L. Mailer and H. J. Schumacher, *Z. physik. Chem.*, **B37**, 365 (1937).

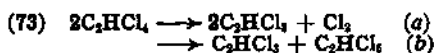
chlorine sensitized photooxidations, and has a quantum yield of about 40 at 95°. The mechanism is that of the photochlorination of trichlor ethylene (IX-71), together with some reaction of the chain carrier with oxygen instead of with chlorine. Thus instead of



the sequence



probably occurs. Since $E_1 = 5.5$ kcal., and reaction (72) must be much faster than (1), E_7 cannot be far from zero.

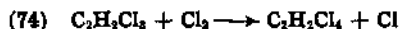


As discussed in section IX-71 this reaction is probably a step in the mechanism of the photochlorination of trichlor ethylene. Comparison of the proposed mechanism with experiment leads to the conclusion that

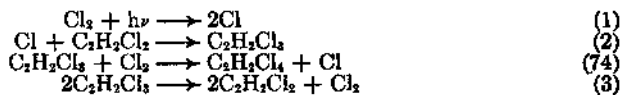
$$E_7 \sim \frac{1}{2}E_8 = 5.3 \text{ kcal.}$$

Müller and Schumacher⁴³ assume $E_7 \sim 0$.

There is no information as to whether (73a) or (73b) is the reaction concerned.



Müller and Schumacher⁴³ have investigated the photochlorination of trans-dichlor ethylene to tetrachlor ethane. The results are in complete agreement with the usual type of mechanism, viz.,



or



Whence

$$-\frac{d}{dt}[\text{Cl}_2] = \frac{k_{74}}{k_3^{\frac{1}{2}}} I_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2].$$

The temperature coefficient of the reaction corresponds to an activation energy of 3.1 kcal. Hence

$$E_{74} - \frac{1}{2}E_3 = 3.1 \text{ kcal.},$$

and assuming $E_3 = 0$,

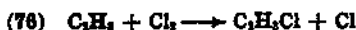
$$E_{74} = 3.1 \text{ kcal.}$$

The same authors⁴³ investigated the photochlorination of cis-dichlor ethylene and found results almost identical with those for the trans compound.

Schumacher²⁷ in a review of photohalogenations puts $E_{74} = 3.5$ kcal.



As discussed in section (IX-74) this reaction is a step in the mechanism of the photochlorination of *cis*- and *trans*-dichlor ethylene, and Müller and Schumacher^{42, 46} assume $E_{75} = 0$.



This is probably involved⁴⁸ in the thermal chlorination of ethylene. (See IX-32.)

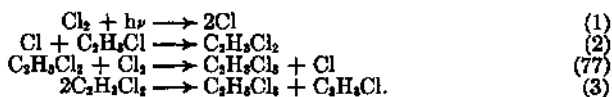


Schmitz and Schumacher⁷⁰ have investigated the photochlorination of vinyl chloride. At pressures above 70 to 100 mm., the rate is given by

$$\frac{d[\text{C}_2\text{H}_3\text{Cl}_2]}{dt} = k\text{I}_{\text{abs.}}^{\frac{1}{2}}[\text{Cl}_2].$$

The quantum yield at 60°, a chlorine pressure of 100 mm., and a vinyl chloride pressure > 70 mm. is about 6×10^6 . The temperature coefficient is only very slightly greater than unity. Oxygen has a very strong inhibiting effect, but no sensitized oxidation occurs.

The rate expression is similar to that for dichlor ethylene, trichlor ethylene, and tetrachlor ethylene, so they propose a similar mechanism:



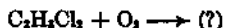
This leads to

$$\frac{d}{dt} [\text{C}_2\text{H}_3\text{Cl}_2] = \frac{k_{77}}{k_3^{\frac{1}{2}}} \text{I}_{\text{abs.}}^{\frac{1}{2}} [\text{Cl}_2].$$

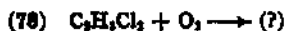
Since the temperature coefficient is approximately unity,

$$E_{77} - \frac{1}{2}E_3 \sim 0.$$

The strong oxygen inhibition shows that the rate of the reaction



is much greater than k_{77} , and hence E_{77} must be appreciable, and they put $E_{77} \geq 6$ kcal., $E_3 \geq 10$ kcal.

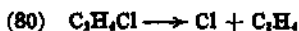


Schmitz and Schumacher⁷⁰ suggest that the inhibition of the photochlorination of vinyl chloride by oxygen is due to this reaction. Its activation energy must, therefore, be very small.

⁷⁰ H. Schmitz and H. J. Schumacher, *Z. physik. Chem.*, B52, 72 (1942).



Schmitz and Schumacher⁷⁰ postulate this reaction as a step in the mechanism of the photochlorination of vinyl chloride, and conclude that $E_{79} \geq 10$ kcal. (For details see IX-77.)

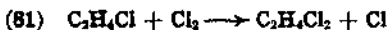


Schmitz, Schumacher, and Jäger⁷¹ investigated the photochlorination of ethylene. (See IX-81.) The proposed mechanism involves the equilibrium



They suggest by analogy with other cases that

$$E_{80} = 8 \pm 5 \text{ kcal.}$$



This reaction has been assumed as a step in the photochlorination of ethylene by Stewart and Weidenbaum.⁵¹ By the semi-empirical method Sherman and Sun⁵ have estimated $E_{81} = 3.0$ kcal.

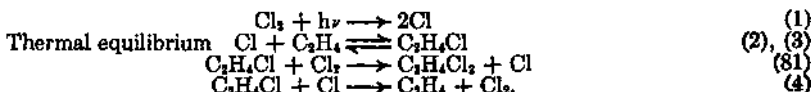
A more detailed investigation of the photochlorination of ethylene was made by Schmitz, Schumacher, and Jäger.⁷¹ The product is dichlorethane, and the quantum yield is very large, being about 3×10^4 at 40° with 100 mm. of chlorine and of ethylene.

At pressures above 100 mm. the rate is given by

$$\frac{d}{dt} [\text{C}_2\text{H}_4\text{Cl}_2] = k_{1,ab.} \frac{1}{2} [\text{Cl}_2] [\text{C}_2\text{H}_4] \frac{1}{2}$$

The temperature coefficient is small, about 1.1 for a 10° rise. The reaction is extraordinarily sensitive to the presence of impurities. It is very strongly inhibited by oxygen, but no sensitized oxidation occurs.

The rate expression is analogous to that of the phosgene synthesis, and they propose a similar mechanism:



This yields the expression

$$\frac{d}{dt} [\text{C}_2\text{H}_4\text{Cl}_2] = \frac{k_{81}}{k_4 \frac{1}{2} K_{2 \rightleftharpoons 3} \frac{1}{2}} I_{ab.} \frac{1}{2} [\text{Cl}_2] [\text{C}_2\text{H}_4] \frac{1}{2}$$

in agreement with experiment if we put

$$k = \frac{k_{81}}{k_4 \frac{1}{2} K_{2 \rightleftharpoons 3} \frac{1}{2}}$$

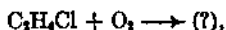
⁷¹ H. Schmitz, H. J. Schumacher, and A. Jäger, *Z. physik. Chem.*, **B51**, 281 (1942).

Since the temperature coefficient is small, it follows that

$$E_{81} - (\frac{1}{2}E_4 + \frac{1}{2}\Delta H_{3\rightleftharpoons 2})$$

is small and positive. In order that the equilibrium may be maintained, it is necessary that reaction (81) be slow compared to (3). Reaction (4) must have a small activation energy, and they suggest a value of 1-2 kcal.

Since oxygen inhibits the reaction very strongly, presumably by



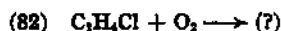
reaction (81) which competes with this must be slower by a factor of roughly 10^6 , hence

$$E_{81} \sim 8 \text{ kcal.}$$

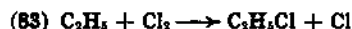
They suggest by analogy with other cases that

$$\begin{aligned} E_2 &\sim 0 \\ E_4 &= 8 \pm 5 \text{ kcal.} \\ E_{81} &= 7 \pm 3 \text{ kcal.} \end{aligned}$$

Reaction (81) is probably also involved in the thermal chlorination of ethylene at high temperatures.⁵³

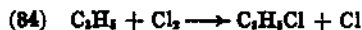


Schmitz, Schumacher, and Jäger⁷¹ suggest that this reaction is the cause, with a very low activation energy, of the strong inhibition by O_2 of the photochlorination of ethylene. (See IX-81.)

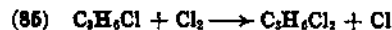


This reaction is probably involved in the thermal chlorination of ethane.⁵⁴ (See IX-36.)

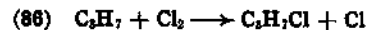
Vaughan and Rust also showed that the chlorination of a number of paraffins could be induced at low temperatures by ethyl radicals from the decomposition of tetraethyl lead. The sensitization undoubtedly occurs via reaction (83).



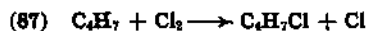
This is probably involved⁵⁵ in the thermal chlorination of propylene. (See IX-37.)



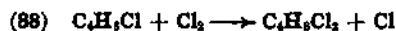
This is probably involved⁵⁵ in the thermal chlorination of propylene. (See IX-37.)



This reaction has been assumed⁵⁷ as a step in the mechanism of the thermal chlorination of propane. (See IX-38.)



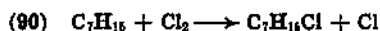
This has been postulated ⁵³ as a step in the thermal chlorination of butene. (See IX-39.)



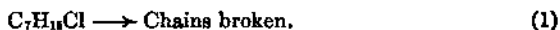
This has been postulated ⁵³ as a step in the thermal chlorination of butene. (See IX-39.)



This reaction has been assumed ⁵⁹ in the mechanism of the photochlorination of chlorobenzene. (See IX-41.)

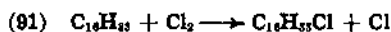


Stauff and Schumacher ⁶² investigated the photochlorination of heptane. (See IX-44.) Their mechanism leads to a value of 6 ± 2 kcal. for $E_{90} - E_1$, where reaction (1) is



Assuming E_1 to be very small,

$$E_{90} \sim 5 \text{ kcal.}$$



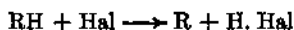
Stauff ⁶⁴ suggests this reaction as a step in the mechanism of the chlorination of hexadecane, and derives the value $E_{91} = 9$ kcal. (See IX-46 for details.)

Chapter X

Systems Containing Bromine

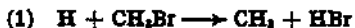
Comparison of Reactions of Chlorine, Bromine, and Iodine

In a review Schumacher¹ compares the reactions of chlorine, bromine, and iodine. He points out that the reaction



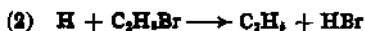
is an important step in the mechanism of the photohalogenations. In the case of chlorine this reaction is exothermic, while with bromine it is slightly endothermic, and with iodine strongly endothermic. The activation energies of such reactions, therefore, differ greatly with different halogens, in general the value being about 5 to 10 kcal. higher with bromine than with chlorine, and that for iodine about 20 kcal. higher still.

The situation is, of course, just the opposite for the reverse reaction, which is, therefore, of much greater importance with iodine and bromine than with chlorine.



Chadwell and Titani² investigated the reaction by the discharge-tube method. It was faster than that of methyl chloride (see IX-7) and about 50 per cent reaction occurred at 135°. The products were methane, ethane, and HBr. There appears to be no doubt that the primary step is reaction (1), and from the rate of reaction its activation energy appears to be about 6-7 kcal.

Cremer, Curry, and Polanyi³ also investigated the reaction by a similar method and found hydrogen, methane, and HBr as products. They estimate the activation energy to be 3.2 kcal.



Chadwell and Titani² found results similar to those with ethyl chloride. The reaction was, however, somewhat faster and the activation energy must, therefore, be less than 8 kcal. and is probably ca. 6 kcal.

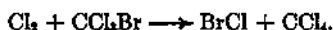
¹ H. J. Schumacher, *Angew. Chem.*, 53, 501 (1940).

² H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, 66, 1363 (1933).

³ E. Cremer, J. Curry, and M. Polanyi, *Z. physik. Chem.*, B23, 445 (1933).

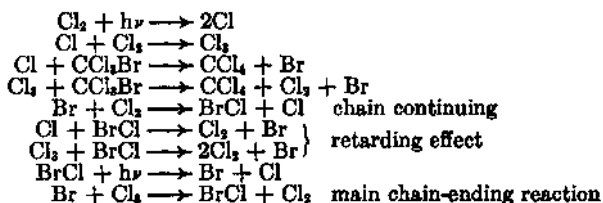
(3) $\text{Cl} + \text{CCl}_3\text{Br} \longrightarrow \text{CCl}_3 + \text{BrCl}$

This reaction has been postulated as a step in the reaction of chlorine with trichlor brom methane. The reaction in solution was investigated by Noddack⁴ and by Griiss.⁵ The gas phase reaction was investigated by Vesper and Rollefson⁶ who found the overall process in the presence of excess chlorine to be almost completely



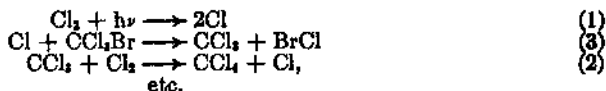
The quantum yield is of the order of 30 initially, but falls off with time on account of inhibition by BrCl. The rate is independent of the pressure and is proportional to $I_{\text{abs.}}^{1/2}$. They ruled out the possibility of the reaction proceeding via CCl_3 on the grounds that some C_2Cl_6 would be formed if this were the case. (Actually if CCl_3Br is photodecomposed alone, C_2Cl_6 is a product.) The temperature coefficient is high, corresponding to an activation energy of ca. 5 kcal. at a chlorine pressure of 54 cm., and to 8 kcal. at 24 cm.

Since they have ruled out CCl_3 as an intermediate the only plausible mechanism appears to be one involving Cl_3 , viz.,



They rule out chain-ending by radical recombination since the rate is proportional to $I_{\text{abs.}}^*$, and hence the chain ending-step is bimolecular. In view of present ideas about association reactions this does not appear to be necessary.

The reaction has been discussed by Schumacher⁷ in connection with the investigation by Franke and Schumacher⁸ of the bromine and chlorine photosensitized oxidation of CCl_3Br . (See X-4.) He points out that the absence of any radicals in Rollefson's mechanism makes it almost impossible to account for a photosensitized oxidation, and he, therefore, suggests a mechanism in line with his general views in other cases,



⁴ W. Noddack, *Z. Elektrochem.*, **27**, 359 (1921).

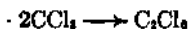
⁵ H. Griiss, *Z. Elektrochem.*, **29**, 144 (1923).

⁶ H. G. Vesper and G. K. Rollefson, *J. Am. Chem. Soc.*, **56**, 1455 (1934).

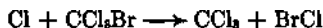
⁷ H. J. Schumacher, *Z. physik. Chem.*, **B42**, 324 (1939).

⁸ W. K. Franke and H. J. Schumacher, *Z. physik. Chem.*, **B42**, 297 (1939).

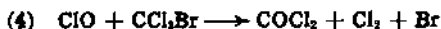
Provided that reaction (2) is fast, as one would expect (see section IX-45), then CCl_3 will be removed so rapidly from the system that the reaction



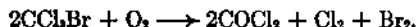
will not occur to an appreciable extent, and Vesper and Rollefson's difficulty will be taken care of. From the foregoing results Schumacher¹ estimates that the activation energy of the reaction



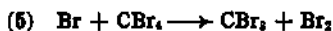
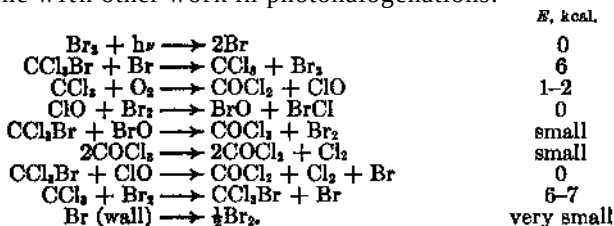
is less than 8 kcal.



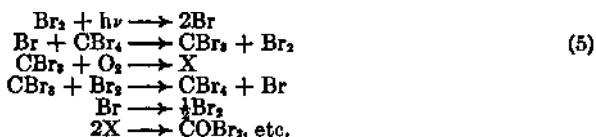
The chlorine and bromine photosensitized oxidation of trichlorobromomethane have been investigated by Franke and Schumacher.⁸ The overall reaction in both cases is



On account of the intervention of BrCl the reactions proceed according to a complex mechanism and a correspondingly complex rate law. The chlorine sensitized reaction is too complicated to permit detailed conclusions as to mechanism, but reaction (4) is a suggested step. The bromine sensitized reaction is somewhat simpler, but is too complex to permit of the formulation of a unique mechanism. Franke and Schumacher suggest, however, that the following mechanism expresses the results satisfactorily and is in line with other work in photohalogenations:



Koblitz, Meissner, and Schumacher⁹ investigated the bromine photosensitized oxidation of carbon tetrabromide in carbon tetrachloride solution. The quantum yield is less than 1, and the products of the reaction are bromophosgene and bromine. The mechanism suggested is of the usual type:



⁹ W. Koblitz, H. Meissner, and H. J. Schumacher, *Ber.*, 70, 1080 (1937).

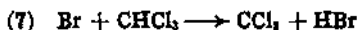
If this mechanism is correct in principle, then reaction (5) must have an activation energy not greater than 5 kcal. For this to be the case the strength of the C—Br bond in carbon tetrabromide must be not greater than 50 kcal., which is considerably lower than the usual estimates.



As discussed in section X-4, the results of Franke and Schumacher⁸ on the bromine photosensitized oxidation of trichlor brom methane are consistent with the assignment of the value

$$E_6 = 6 \text{ kcal.}$$

This value is also consistent with the mechanism of the photobromination of chloroform (see section X-7), and of chloral (see X-13).



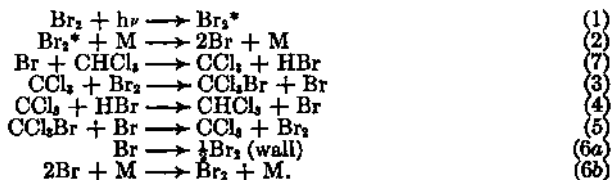
Willard and Daniels¹⁰ made a qualitative investigation of the photobromination of liquid chloroform. The vapor phase reaction was investigated in more detail by Brainwarth and Schumacher¹¹ using X5460. Temperatures of 110° and 130° were used, and pressures from 40 to 400 mm. The quantum yield was about 19. Above 200 mm. the rate was given by

$$\frac{-d}{dt} [\text{Br}_2] = \frac{k I_{\text{abs.}} \frac{1}{2} [\text{CHCl}_3]}{P^{\frac{1}{2}} \left(1 + \frac{k' [\text{HBr}]}{[\text{Br}_2]} \right)},$$

and below 90 mm. by

$$\frac{-d}{dt} [\text{Br}_2] = \frac{k I_{\text{abs.}} [\text{CHCl}_3] P}{1 + \frac{k' [\text{HBr}]}{[\text{Br}_2]}},$$

where P is the total pressure. In going from 110° to 130°, k is approximately doubled, but k' remains constant. The following mechanism, of the usual type, explains the results accurately.



Reaction (4) is necessary to explain the inhibition of the reaction by HBr, either added or formed on the reaction, and (5) is necessary since the reaction is inhibited by CCl₃Br. The mechanism leads to the expression

¹⁰ J. Willard and F. Daniels, *J. Am. Chem. Soc.*, 67, 2240 (1935).

¹¹ V. Braunwarth and H. J. Schumacher, *Kolloid-Z.*, 89, 184 (1939).

$$\frac{-d}{dt} [\text{CHCl}_3] = \frac{\frac{k_7}{k_8} I_{\text{abs.}}^{\frac{1}{2}} [\text{CHCl}_3] - \frac{k_4 k_5}{k_2 k_8} I_{\text{abs.}}^{\frac{1}{2}} \frac{[\text{HBr}]}{[\text{Br}_2]} [\text{CCl}_3\text{Br}]}{P^{\frac{1}{2}} \left(1 + \frac{k_4}{k_8} \frac{[\text{HBr}]}{[\text{Br}_2]} \right)}$$

In the initial stages, when $[\text{CCl}_3\text{Br}] = 0$, this reduces to

$$\frac{-d}{dt} [\text{CHCl}_3] = \frac{\frac{k_7}{k_8} I_{\text{abs.}}^{\frac{1}{2}} [\text{CHCl}_3]}{P^{\frac{1}{2}} \left(1 + \frac{k_4}{k_8} \frac{[\text{HBr}]}{[\text{Br}_2]} \right)}$$

This is equivalent to the first of the experimental equations. Since the temperature coefficient of k' is practically nil,

$$E_8 - E_4 \sim 0.$$

Franke and Schumacher⁸ estimated (see section X-3) that $E_8 = 6-7$ kcal., hence $E_4 = 6-7$ kcal. Franke and Schumacher also estimated $E_5 = 6$ kcal. From the temperature coefficient of the overall reaction

$$E_7 - \frac{1}{2}E_8 = 10 \pm 1 \text{ kcal.}$$

E_8 is probably approximately zero, and hence

$$E_7 = 10 \pm 1 \text{ kcal.}$$

It should be noted that Franke and Schumacher's estimates are based on a mechanism for the bromine sensitized oxidation of trichlorobromomethane which is by no means well established. The uncertainty affects the reliability of the estimate of E_4 , but does not affect that of E_7 .

The reaction has also been postulated as a step in the photobromination of chloral. (See X-13.)

(8) $\text{Br} + \text{CH}_3 \longrightarrow \text{CH}_3\text{Br}$

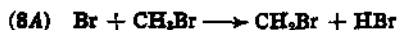
In connection with the mechanism of the photolysis of methyl bromide, Gordon and Taylor¹² assume $E_8 = 0$, since the quantum yield is low, only 4×10^{-8} , and the obvious cause of this is a very efficient back reaction. (See section X-36.)

Kimball¹³ has discussed the reaction from a theoretical standpoint and concludes that the complex formed in the association reaction should have a life of only about 4.3×10^{-12} sec., and hence third-body restrictions should be important. Kassel,¹⁴ however, has criticized Kimball's treatment and concludes that it has little meaning.

¹² A. Gordon and H. A. Taylor, *J. Am. Chem. Soc.*, 63, 3435 (1941).

¹³ G. E. Kimball, *J. Chem. Phys.*, 5, 310 (1937).

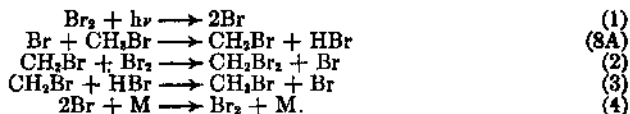
¹⁴ L. S. Kassel, *J. Chem. Phys.*, 6, 922 (1937).



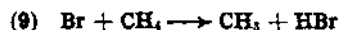
Kistiakowsky and Van Artsdalen^{14a} have investigated the photobromination of methyl bromide at 150° to 230°. The reaction is similar to the photobromination of methane. (See X-9.) The results are expressed by

$$-\frac{d}{dt}[\text{Br}_2] = k[\text{CH}_3\text{Br}][\text{Br}_2]^{\frac{1}{2}}(1/P)^{\frac{1}{2}},$$

where P is the total pressure. The reaction is not inhibited by the HBr formed. They suggest the mechanism



This agrees with experiment if we put $k = kSA$, and assume reaction (3) to be negligible, *i.e.*, E_3 to be appreciable. The temperature coefficient of the reaction corresponds to an activation energy of 15.6 kcal., which is to be ascribed to reaction (8A). The agreement of the mechanism with experiment requires that E_2 be small.



Kistiakowsky and Van Artsdalen¹⁵ have investigated the photobromination of methane from 150° to 230°. The products were HBr, methyl bromide, and some methylene bromide produced by the secondary bromination of methyl bromide. The reaction is inhibited by the HBr formed. The results were expressed by the rate equation

$$-\frac{d}{dt}[\text{Br}_2] = \frac{k[\text{CH}_4][\text{Br}_2]^{\frac{1}{2}}(1/P)^{\frac{1}{2}}}{1 + \frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]}}, \quad (A)$$

where P is the total pressure, and k is a constant which includes the absorption coefficient. The temperature coefficient of k corresponded to an activation energy of 17.8 kcal. This is not affected by the change of absorption with temperature, since the change is negligible.

The thermal bromination of methane, at 300°, was also investigated. This followed the rate law

$$-\frac{d}{dt}[\text{Br}_2] = k'[\text{CH}_4][\text{Br}_2]^{\frac{1}{2}}. \quad (B)$$

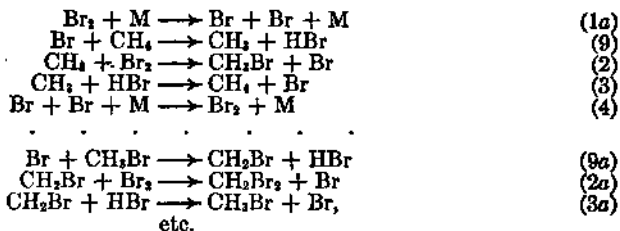
They suggest the mechanism:



^{14a} G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, 12, 469 (1944).

¹⁶ G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, 12, 469 (1944); H. G. Andersen, G. B. Kistiakowsky, and E. R. Van Artsdalen, *J. Chem. Phys.*, 10, 305 (1942).

or



As a first approximation, neglecting the secondary bromination of methyl bromide, this leads to

$$\frac{d}{dt} [\text{CH}_3\text{Br}] = \frac{k_2[\text{CH}_4](n/k_3[M])^{\frac{1}{2}}}{1 + \frac{k_3[\text{HBr}]}{k_2[\text{Br}_2]}}, \quad (C)$$

where n is the number of quanta absorbed, and $[M]$ is the total concentration. Obviously

$$n \propto I[\text{Br}_2],$$

and hence (C) is identical with (A). This is only a first approximation, but if corrections are applied to account for the bromination of methyl bromide, it is found to agree with the experimental data.

For the thermal reaction, as a first approximation, they obtain in a similar way

$$\frac{d}{dt} [\text{CH}_3\text{Br}] = \frac{k[\text{CH}_4][\text{Br}_2]^{\frac{1}{2}}}{1 + \frac{k_3[\text{HBr}]}{k_2[\text{Br}_2]}}, \quad (D)$$

in which $k = k_2K^{1/2}$, where K is the equilibrium constant for the dissociation of bromine. This reduces to equation (B) at zero time when $[\text{HBr}] = 0$.

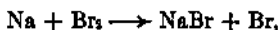
The rate determining step is obviously reaction (9), and hence $E_9 = 17.8$ kcal. This agrees with energetic considerations since (9) is certainly endothermic.

The temperature dependence of inhibition by HBr corresponds to an apparent activation energy of 2 kcal. Hence

$$E_3 - E_2 = 2 \text{ kcal.}$$

E_i is almost certainly approximately zero, and hence $E_z = 2$ kcal. in good agreement with the value of 1.5 kcal. obtained from experiments on the photolysis of methyl iodide-hydrogen iodide mixtures. (See X-35.)

Bogdandy and Polanyi¹⁶ investigated the reaction of sodium vapor with bromine, which gives bromine atoms by the reaction

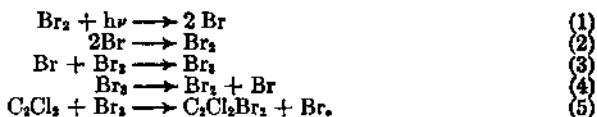


in the presence of methane. No reaction with methane occurred and this is consistent with a high value of E_9 , such as 17.8 kcal.

¹⁶ S. v. Bogdandy and M. Polanyi, *Z. Elektrochem.*, 33, 554 (1927).



The bromination of dichlor acetylene has been investigated in the gas phase and in solution by Ghosh and his co-workers.¹⁷ The mechanism suggested is analogous to others proposed by Ghosh, viz.,

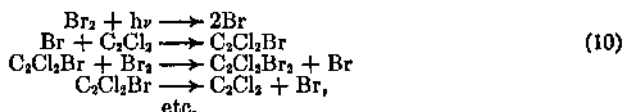


For reasonably high concentrations of acetylene dichloride this leads to the expression

$$-\frac{d}{dt}[\text{Br}_2] = k_3[\text{Br}_2]k_2^{\frac{1}{2}}I_{\text{abs}}^{\frac{1}{2}}$$

in agreement with experiment. At low concentrations of C_2Cl_2 , however, the rate becomes dependent on its concentration. The temperature coefficient of the reaction is in the neighbourhood of 1.4, and the quantum yield has values in the range 2-10 in solution and of 100-250 in the gas phase.

The same general argument between the radical and the Br_3 schools exists here, and the results could undoubtedly be explained on the assumption of a mechanism involving reaction (10),

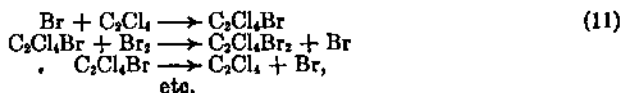


The bromination of tetrachlor ethylene was investigated by Willard and Daniels.¹⁰ In the liquid phase the reaction was inhibited by the product, and accelerated by oxygen. The temperature coefficient is small, and the rate is almost independent of $[\text{C}_2\text{Cl}_4]$.

In the gas phase there appears to be a bromine sensitized decomposition of the $\text{C}_2\text{Cl}_4\text{Br}_2$ formed, and little overall reaction. This is in general agreement with the results of Carrico and Dickinson¹⁸ who found that an equilibrium exists

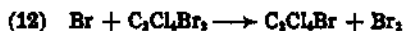


Willard and Daniels suggest the usual type of mechanism



¹⁷ J. C. Ghosh, S. K. Bhattacharyya, and S. C. Bhattacharyya, *Z. physik. Chem.*, **B32**, 145 (1936); J. C. Ghosh, S. K. Bhattacharyya, and M. L. N. Murthi, *J. Indian Chem. Soc.*, **14**, 425 (1937).

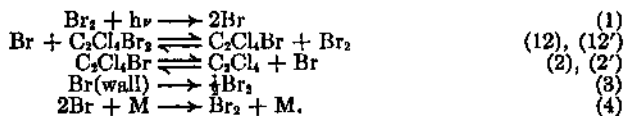
¹⁸ J. L. Carrico and R. G. Dickinson, *J. Am. Chem. Soc.*, **57**, 1343 (1935).



Carrico and Dickinson¹⁸ found that an equilibrium exists in the photobromination of tetrachlor dibrom ethane,



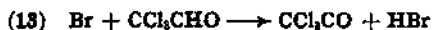
At high temperatures the equilibrium is on the right-hand side, and the decomposition is photosensitized by bromine. A mechanism analogous to that of Schumacher and Wiig for the decomposition of ethylene iodide (see XI-11) is suggested, viz.,



For low pressures and intensities this leads to the expression

$$\frac{d}{dt} [\text{Br}_2] = \frac{2k_{12}I_{\text{abs}}}{k_2} \cdot \frac{k_2[\text{C}_2\text{Cl}_4\text{Br}_2]}{k_2 + k_{13}'[\text{Br}_2]}$$

in agreement with experiment.



Klug and Schumacher¹⁹ have investigated the photobromination of chloral in the range 70° to 90°. The overall reaction is in the main



together with the occurrence to some extent of



and

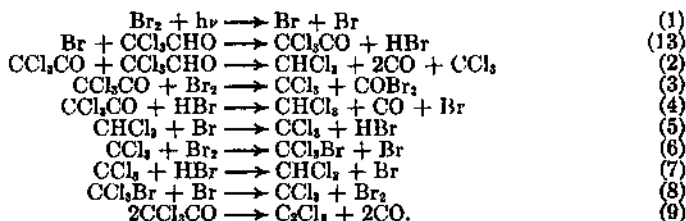


The reaction involves chains, the quantum yield under their experimental conditions being about 120. The main facts are:

- The rate is proportional to $I_{\text{abs.}}^{1/2}$.
- The rate of CO formation is approximately proportional to $[\text{CCl}_3\text{CHO}]$.
- The total pressure has no effect.
- The rate is a maximum for a 1 : 1 mixture of bromine and chloral.
- The products inhibit the reaction, but HBr and CCl_3Br have no effect. Trichlor acetyl bromide has a very strong inhibiting action.
- The reaction is very sensitive to the condition of the surface.

In view of the complexity of the reaction, it can hardly be said that the mechanism is established. The following mechanism, however, agrees in general with the results:

¹⁹ H. Klug and H. J. Schumacher, *Z. physik. Chern.*, **B47**, 67 (1940).



At the start of the reaction when $[\text{CHCl}_3] = [\text{CCl}_3\text{Br}] = [\text{HBr}] = 0$, this leads approximately to

$$\frac{d[\text{CO}]}{dt} = \frac{2k}{2} \sqrt{\frac{I_{\text{abs}}}{k_7}} [\text{CCl}_3\text{CHO}]$$

in agreement with experiment.

The temperature coefficient of the reaction corresponds to an apparent activation energy of 11 kcal., hence $E_2 - \frac{1}{2}E_9 = 11$ kcal. E_9 must be small, and hence they put $E_2 = 12 \pm 2$ kcal.

Schumacher¹ concludes from their results that $E_2 < 8$ kcal.

Stauff and Schumacher^{19a} also postulate reaction (13) as a step in the mechanism of the bromine sensitized photooxidation of chloral. By analogy with other substances they suggest

$$E_{13} = 8 \pm 3 \text{ kcal.}$$



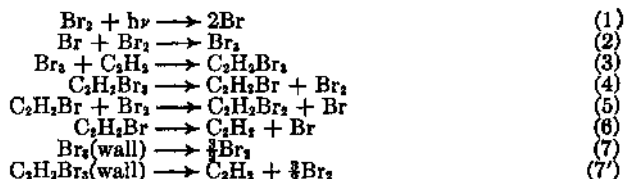
The photobromination of acetylene was investigated by Booher and Rollefson.²⁰ The ultimate product is $\text{C}_2\text{H}_2\text{Br}_2$ and the reaction is a chain reaction with a quantum yield of about 500 at 15° and of 3000 at 20°. The quantum yield is independent of wave length at XX4358, 5461, and 5791. The results are expressed by

$$-\frac{d}{dt} [\text{Br}_2] = 2I_{\text{abs.}} \frac{k_4}{k_7} \cdot \frac{k_5[\text{Br}_2]}{k_5[\text{Br}_2] + k_4}$$

at high concentrations of acetylene, and by

$$-\frac{d}{dt} [\text{Br}_2] = 2I_{\text{abs.}} \frac{k_2}{k_7} [\text{C}_2\text{H}_2] \cdot \frac{k_5[\text{Br}_2]}{k_5[\text{Br}_2] + k_4}$$

at low acetylene concentrations. They suggest the mechanism



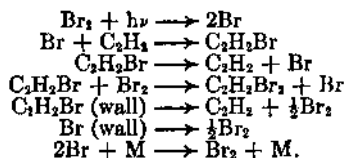
or



¹⁹ J. Stauff and H. J. Schumacher, *Z. physik. Chem.*, **B48**, 154 (1940).

²⁰ J. E. Booher and G. K. Rollefson, *J. Am. Chem. Soc.*, **66**, 2288 (1934).

Franke and Schumacher²¹ reinvestigated the reaction. They suggested that Booher and Rollefson's results are vitiated by effects due to stopcock grease, etc., and that their mechanism should not be taken too seriously. As a result of a brief investigation they proposed the mechanism

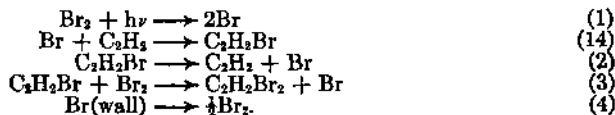


Rollefson²² has replied to the criticisms of Franke and Schumacher. He points out that Booher and Rollefson's results were much more reproducible than those of Franke and Schumacher, and disputes the claim that impurities vitiated his results. He admits the simplicity of Schumacher's mechanism, but claims that it is not in accordance with the facts.

In a further, more detailed investigation, Müller and Schumacher²³ took great care in purifying the gases used. They found that under all conditions their results were expressed by the equation

$$\frac{d}{dt}[\text{C}_2\text{H}_5\text{Br}_2] = kI_{\text{abs}}[\text{C}_2\text{H}_4] \cdot \frac{[\text{Br}_2]}{k' + [\text{Br}_2]}.$$

The quantum yields were much higher than before, being as high as 40,000, and this suggests the presence of an inhibitor in former work. They propose a mechanism similar to that suggested by Franke and Schumacher, but simpler, viz.,



From this they get

$$\frac{d}{dt}[\text{C}_2\text{H}_5\text{Br}_2] = \frac{2k_{14}}{k_4} I_{\text{abs}}[\text{C}_2\text{H}_4] \frac{[\text{Br}_2]}{[\text{Br}_2] + k_3/k_2}.$$

From the temperature coefficient of k' this gives

$$E_3 - E_4 = 5.8 \pm 0.5 \text{ kcal.}$$

The temperature coefficient of k is small, hence

$$E_{14} - E_4 = 0.$$

E_4 would be expected to be very small, and hence

$$E_{14} \sim 0.$$

If it is assumed that $E_3 \sim 5 \text{ kcal.}$, which seems a reasonable value, then

$$E_2 \sim 11 \text{ kcal.}$$

²¹ W. K. Franke and H. J. Schumacher, *Z. physik. Chem.*, **B34**, 181 (1936).

²² G. K. Rollefson, *Z. physik. Chem.*, **B37**, 472 (1937).

²³ K. L. Müller and H. J. Schumacher, *Z. physik. Chem.*, **B39**, 352 (1938), **B40**, 318 (1938).



The photobromination of dichlor ethylene in the gas phase was first investigated by Ghosh and Bhattacharyya.²⁴ The quantum yield was about 100. For high concentrations of dichlor ethylene the results were expressed by the equation

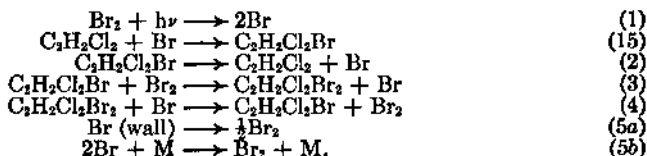
$$-\frac{d}{dt}[\text{Br}_2] = k\text{I}_{\text{abs.}}^{1/2}[\text{Br}_2].$$

Ghosh gives a very complex mechanism of the Br_3 type.

Miiller and Schumacher²⁶ made a more detailed investigation of the photobromination of trans-dichlor ethylene, and of the accompanying bromine sensitized decomposition of dichlor dibrom ethane. The reaction is complicated by the existence of the equilibrium



As a result of the complicated nature of the reaction a unique mechanism can hardly be said to have been established, but they interpret their results on the basis of a mechanism in line with others proposed by Schumacher, viz.,



A comparison with experiment yields the following activation energies:

$$\begin{array}{l} E_2 - E_3 = 6.2 \text{ kcal.} \\ E_4 - E_{15} = 11.1 \text{ kcal.} \\ E_3 \sim 5 \text{ kcal.} \\ E_2 \sim 11 \text{ kcal.} \\ E_{5b} \sim 0. \end{array}$$

Too much reliance should not be placed on these values. No explicit value for E_{15} is obtained, but it is probably small, and E_4 is thus somewhat greater, but not much greater than 11 kcal.



This reaction has been assumed as a step in the photobromination of vinyl chloride.²⁶ (See X-47.)



Reaction (17) has been assumed²⁶ with an activation energy of approximately zero, as a chain-ending step in the photobromination of vinyl

²⁴ J. C. Ghosh and S. K. Bhattacharyya, *Z. physik. Chem.*, **B32**, 140 (1936).

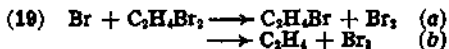
²⁶ K. L. Miiller and H. J. Schumacher, *Z. physik. Chem.*, **B42**, 327 (1939).

²⁶ H. Schmitz and H. J. Schumacher, *Z. physik. Chem.*, **B52**, 72 (1942).

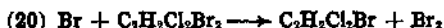
chloride. (See X-47 for details.) To explain the inhibition of the reaction by bromine and by $C_2H_5ClBr_2$, Schmitz and Schumacher suggest that they are specific third bodies for reaction (17).



Reaction (18) has been assumed as a step in the mechanism of the photobromination of ethylene.²⁷ It appears probable that E_{18} is approximately zero. (See X-51 for a detailed discussion.)



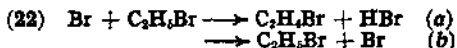
Sherman and Sun²⁸ by the semi-empirical method have estimated E_{19a} to be 22.4 kcal., and E_{19b} to be 55.3 kcal.



As discussed in section X-15, Müller and Schumacher²⁸ conclude that $E_{16} > 11$ kcal. This value is not very certain.

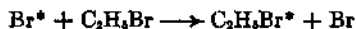


As with other association reactions of this type, the activation energy is probably very small. This reaction is probably involved in the thermal and photochemical reactions of ethyl bromide.²⁹

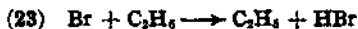


Reaction (22a) has been postulated as a step in the mechanism of the thermal decomposition of ethyl bromide.²⁹

Liberatore and Wiig³⁰ investigated the exchange of radioactive bromine with gaseous ethyl bromide. They found exchange only at temperatures of 200° or higher, and conclude that the Walden inversion type of reaction



has a relatively high activation energy. A calculation by the semi-empirical method leads to a value of about 25 kcal. for E_{22b} .



Andersen, Kistiakowsky, and Van Artsdalen^{30a} have investigated the photobromination of ethane. The results were similar to those for methane.

²⁷ H. Schmitz, H. J. Schumacher, and A. Jager, *Z. physik. Chem.*, B61, 281 (1942).

²⁸ A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, 66, 1096 (1934); A. Sherman, O. T. Quimby, and R. O. Sutherland, *J. Chem. Phys.*, 4, 732 (1936).

²⁹ See F. Daniels, *Chemical Kinetics*, Ithaca, 1938.

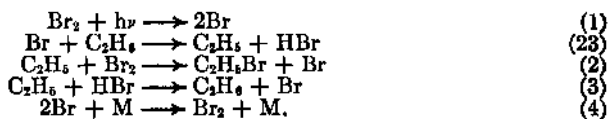
³⁰ L. C. Liberatore and E. O. Wiig, *J. Chem. Phys.*, 8, 349 (1940).

^{30a} H. G. Andersen, G. B. Kistiakowsky, and E. R. Van Artsdalen, *J. Chem. Phys.*, 10, 305 (1942); H. G. Andersen and E. R. Van Artsdalen, *J. Chem. Phys.*, 12, 479 (1944).

(See X-9.) In the early stages of the reaction the products consisted almost completely of ethyl bromide. The results corresponded to the rate equation

$$-\frac{d}{dt}[\text{Br}_2] = \frac{k[\text{C}_2\text{H}_6][\text{Br}_2]^{\frac{1}{2}}}{P^{\frac{1}{2}}},$$

where P is the total pressure. The agreement with experiment is not exact, since k tends to increase with increasing $[\text{C}_2\text{H}_6]$ and decreasing $[\text{Br}_2]$. The temperature coefficient of the rate over the range 35° to 90° corresponded to an activation energy of 13.3 kcal. The reaction is inhibited by the HBr formed. They suggest the mechanism



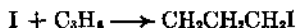
This leads to the experimental rate law at the start of the reaction when $[\text{HBr}] = 0$. The overall activation energy becomes that of reaction (23), *i.e.* $E_2 = 13.3$ kcal. E_2 must be small. The inhibition of the reaction by HBr is temperature independent. Since HBr inhibition will introduce a term in the denominator of the rate equation of the form

$$1 + \frac{k_3[\text{HBr}]}{k_2[\text{Br}_2]},$$

this means that $E_2 \sim E_3$. Hence E_3 is also small.



Ogg and Priest³¹ investigated the thermal and photochemical reaction between iodine and cyclopropane (see section XI-14), and concluded that the activation energy of the reaction

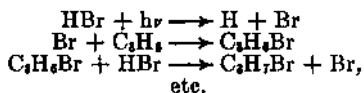


was 17.3 kcal. A few qualitative experiments were also made on the corresponding reaction with bromine, and they conclude that reaction (24) has a much smaller activation energy than the analogous reaction with iodine, *i.e.*, $E_{24} < 17.3$ kcal.

The reaction

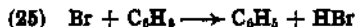


is probably involved³² in the photoaddition of HBr to propylene, *i.e.*,



³¹ R. A. Ogg and W. J. Priest, *J. Am. Chem. Soc.*, 60, 217 (1938); *J. Chem. Phys.*, 7, 736 (1939).

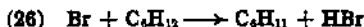
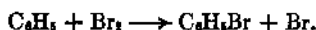
³² F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, 7, 491 (1942); W. E. Vaughan, F. F. Rust, and T. W. Evans, *J. Org. Chem.*, 7, 477 (1942).



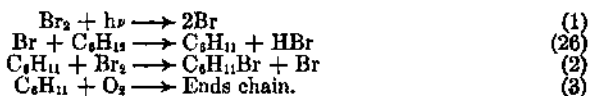
The photobromination of benzene leads to products of both substitution and addition.³³ The mechanism appears to be similar to those of other photobrominations. The reaction has a high temperature coefficient, suggesting an appreciable activation energy for one or both of the reactions



and



The photobromination of cyclohexane has been investigated by a number of workers.³⁴ The investigation of Jost is the most detailed. The rate is somewhat dependent on the cyclohexane concentration (very roughly proportional to $[\text{C}_6\text{H}_{12}]^{1/2}$). The reaction is strongly inhibited by oxygen, and the temperature coefficient is appreciable. Jost suggests the mechanism



This leads to the expression

$$-\frac{d}{dt}[\text{Br}_2] = \frac{kI_{\text{abs.}}[\text{Br}_2]}{[\text{O}_2]}.$$

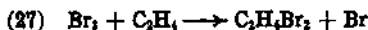
However, the rate is not as strongly dependent on the bromine concentration as this would indicate, and is dependent to some extent on the cyclohexane concentration. If we assume a mechanism consisting of (1), (2), (26), and a new fourth step



we get

$$-\frac{d}{dt}[\text{Br}_2] = kI_{\text{abs.}}[\text{C}_6\text{H}_{12}].$$

A combination of the two mechanisms of chain-breaking will give agreement with experiment, and is probably what occurs. The high temperature coefficient (2 for a 30° rise) means an appreciable activation energy for reactions (2) and (26).



Sherman and Sun²⁸ by the semi-empirical method have estimated a value of 35.6 kcal. for E_{27} .

³³ W. Meidinger, *Z. physik. Chem.*, B5, 29 (1929); E. Rabinowitsch, *Z. physik. Chem.*, B19, 190 (1932).

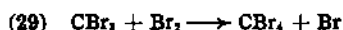
³⁴ L. Pusch, *Z. Elektrochem.*, 24, 336 (1918); W. Noddack, *Z. Elektrochem.*, 27, 359 (1921); B. J. Wood and E. K. Rideal, *J. Chem. Soc.*, 1927, 2466; W. Jost, *Z. physik. Chem. Bodenstein Festband*, 291 (1931).



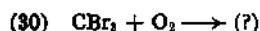
As discussed in section X-4, Franke and Schumacher,⁸ on the basis of a mechanism which is not too definitely established, have estimated that E_{28} is small.



This has been suggested as a step in the bromine sensitized photooxidation of chloral. (See X-13.)



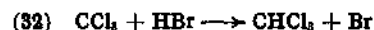
This reaction has been proposed as a step in the bromine photosensitized oxidation of carbon tetrabromide.⁹ (See X-5.)



This reaction has been proposed as a step in the mechanism of the bromine photosensitized oxidation of carbon tetrabromide.⁹ (See section X-5.)



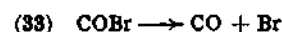
As discussed in section X-4, Franke and Schumacher have estimated E_n to be 6-7 kcal. This is based on a somewhat speculative mechanism for the bromine photosensitized oxidation of trichlorobromomethane. This value is consistent with the mechanism for the photobromination of chloroform proposed by Braunwarth and Schumacher.¹¹ (See section X-7 for details.) The reaction has also been suggested as a step in the photobromination of chloral. (See X-13.)



Braunwarth and Schumacher,¹¹ as discussed in section X-7 have estimated

$$E_{31} - E_{32} \sim 0.$$

If Franke and Schumacher's estimate⁸ of $E_{31} = 6-7$ kcal. is accepted, then $E_{32} = 6-7$ kcal. The reaction has also been suggested as a step in the mechanism of the photobromination of chloral. (See X-13.)



This reaction is probably involved, with a low activation energy, in the photolysis of oxalyl bromide,³⁵ and of brom phosgene.³⁶

³⁵ J. E. Tuttle and G. K. Rollefson, *J. Am. Chem. Soc.*, **63**, 1525 (1941).

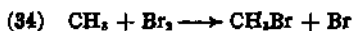
³⁶ H. J. Schumacher and P. Bergmann, *Z. physik. Chem.*, **B13**, 269 (1931).



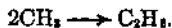
As discussed in section X-8A, experiments on the photobromination of methyl bromide indicate that E_{33A} is small.



As discussed in X-8A, the lack of inhibition of the photobromination of methyl bromide by HBr indicates that E_{33B} must be appreciable.



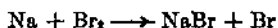
In the photolysis of acetyl bromide, Etzler and Rollefson³⁷ suggest that the absence of ethane as a product is perhaps due to the rapid destruction of methyl radicals by (34) before they have a chance to form ethane by the reaction



(See section X-49.)

Reaction (34) has also been assumed to occur with zero activation energy as a step in the photobromination of methane.¹⁸ (See X-9.)

Bogdandy and Polanyi¹⁶ from experiments in which bromine atoms were produced in the presence of methane by the reaction



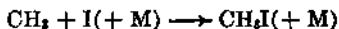
conclude that reaction (34) is about 3 times faster than the corresponding reaction with chlorine.



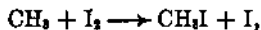
Reaction (35) has been assumed as a step in the reaction of H-atoms with methyl bromide.²

As discussed in section X-9, reaction (35) has also been proposed as a step in the mechanism of the photobromination of methane¹⁵ to account for the inhibition of the reaction by HBr. The temperature coefficient of the inhibition corresponds to a value of approximately 2 kcal. for E_{35} .

Andersen and Kistiakowsky³⁸ also investigated the photolysis of CH_3I —HBr mixtures in order to arrive at an independent estimate of E_{35} . They confirmed the low quantum yield of the methyl iodide photolysis. This is due to the very high efficiency of the reactions:



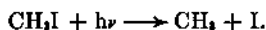
and



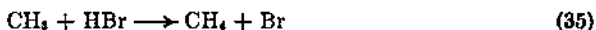
³⁷ D. H. Etzler and G. K. Rollefson, *J. Am. Chem. Soc.*, 61, 800 (1939).

³⁸ H. G. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, 11, 6 (1943).

which have activation energies of approximately zero. In the mixture of CH_3I and HBr , the primary process is



The methyl radicals then disappear either by



or



(See section XI-26 for a justification of the assumption that reaction (1) is the important CH_3I forming reaction rather than



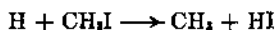
It thus follows that

$$\frac{\text{Rate of formation of CH}_4}{\text{Rate of formation of CH}_3\text{I}} = \frac{A_{35}e^{-E_{35}/RT}}{A_{16}e^{-E_1/RT}}$$

There is one complication. The reaction



also occurs. However, this does not affect the situation since it is followed by



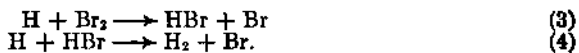
and thus merely increases the production of methyl radicals.

The yield of methyl iodide from the reaction of methyls with iodine is arrived at as follows: when there is no added iodine in the system the rate of production of methane is a maximum since there is no competition from reaction (1). The relative rates of (35) and (1) can then be calculated by comparing the amounts of methane produced with various amounts of iodine in the system with that in the absence of iodine. This leads to the simple relation

$$\frac{\text{Rate of formation of CH}_4 \text{ in presence of iodine}}{\text{Rate of formation of CH}_4 \text{ in absence of iodine}} = \frac{k_{35}[\text{HBr}]}{k_{35}[\text{HBr}] + k_1[\text{I}_2]}$$

They thus obtain the ratio k_{35}/k_1 . To get E_{35}/E_1 it is then necessary to determine the ratio of the steric factors A_{35}/A_1 .

For the analogous reactions



Bodenstein and Jung³⁹ found $k_3/k_4 = 8.6$. For the relative rates of the reactions



Andersen and Kistiakowsky found in one experiment $k_5/k_6 = 6.3$. If it is assumed that (3), (4), (5), and (6) all have zero activation energy, these

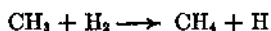
³⁹ M. Bodenstein and G. Jung, *Z. physik. Chem.*, **121**, 127 (1926).

ratios then apply to the steric factors. By analogy they, therefore, assume $A_{35}/A_1 = 7.5$.

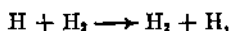
From a number of experiments they thus get the values $E_{35} - E_1 = 0.7, 1.0, 0.5, 1.2, 0.5$, giving an average of $E_{35} - E_1 = 0.8 \pm 0.3$ kcal. It has generally been assumed that $E_1 = 0$. It seems certain that the reaction



has zero activation energy. On the analogy that



probably has an activation energy 1 kcal. or so greater than



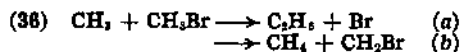
they suggest that at the most E_1 will be 1 kcal., *i.e.*,

$$E_1 = 0.5 \pm 0.5 \text{ kcal.}$$

Hence

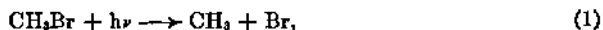
$$E_{35} = 1.5 \pm 1 \text{ kcal.}$$

If this value is combined with the heat of formation of HBr, a value of 102 ± 1 kcal. is obtained for the C—H bond strength in methane, in excellent agreement with other recent estimates.

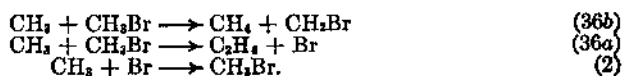


The photolysis of methyl bromide has been investigated by Gordon and Taylor,¹² who found that the principal products were bromine and methane. Carbon monoxide was also formed, presumably by a reaction of CH_2Br or of Br with the silica reaction vessel. With n2537 at room temperature, the quantum yield was 4×10^{-3} based on the bromine produced. The low yield is analogous to that in the photolysis of iodides, and is presumably to be explained by an efficient back reaction. In the presence of nitric oxide the quantum yield based on NOBr produced is approximately 1. The reaction under these conditions is complex, but the obvious function of the nitric oxide is to inhibit the back reaction. In the presence of silver the quantum yield of methane formation is approximately 1 for the same reason.

The primary step is obviously



and they consider the following secondary reactions:



They assume that E_{36b} is approximately 16 kcal. by analogy with the activation energy of the reaction



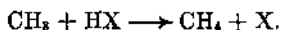
E_{36a} is assumed to be approximately 22 kcal. This value is arrived at as follows. Eyring⁴⁰ by the semi-empirical method calculated a value of 37 kcal. for the activation energy of the reaction



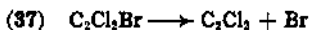
Since the bond broken in reaction (36a) is C—Br instead of C—H, they reduce E in the ratio of the bond strengths and get $E_{36a} = 22$ kcal. The whole calculation seems highly dubious.

Z_2 is assumed to be zero as usual for such reactions. On the basis of this mechanism the predominance of methane and absence of ethane is explained since $E_{36a} > E_{36b}$. The effect of NO and of silver on the yield is obviously due to the suppression of reaction (2).

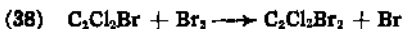
The effect of temperature on the nature of the products is negligible. The temperature coefficient of methane production corresponds to an activation energy of 6.6 kcal. Since E_2 is zero, and reaction (36a) is unimportant, the temperature coefficient of methane production should be that of reaction (36b). In this way $E_{36b} = 6.6$ kcal., in good agreement with estimates for other reactions of the type



They explain the discrepancy between this and their assumed value of 16 kcal. as due to the carrying over of excess energy from the primary step. However, there seems to be little reason why the experimental value of 6.6 kcal. should not be accepted, since their assignment of $E_{36a} = 16$ kcal. is purely on the basis of a highly doubtful analogy.



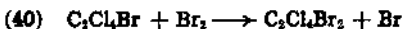
This reaction is probably involved in the photobromination of dichloroacetylene. (See X-10.)



This reaction, with a low activation energy, is probably a step in the mechanism of the photobromination of dichloroacetylene. (See X-10.)



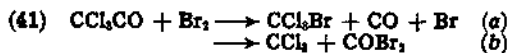
This reaction has been postulated as a step in the mechanism of the photochemical reaction of bromine with tetrachlorodibromethane (see X-12), and in the photobromination of tetrachloroethylene. (See X-11.)



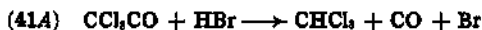
This reaction, with a low activation energy, has been postulated as a step in the mechanism of the photobromination of tetrachloroethylene (see

⁴⁰ E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

X-11), and of the bromine photosensitized decomposition of tetrachlor dibrom ethane. (See X-12.)



Reaction (416) has been postulated as a step in the mechanism of the photobromination of chloral¹⁹ by Klug and Schumacher. (See X-13.) Schumacher¹ suggests that the distinct difference between the photobromination and the photochlorination of chloral are due to the fact that the chlorine analogue of (41a) occurs readily ($E \sim 6$ kcal.), while reaction (41a) does not occur at all with bromine. He, therefore, puts $E_{41a} > 16$ kcal.



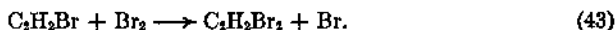
Reaction (41A) has been suggested^{1a} as a step in the photobromination of chloral. (See X-13.)



Reaction (42) has been postulated as a step in the mechanism of the photobromination of acetylene by Müller and Schumacher.²³ The results are discussed in detail in section X-14. Müller and Schumacher's mechanism leads to

$$E_{42} - E_{43} = 5.8 \pm 0.5 \text{ kcal.},$$

where reaction (43) is

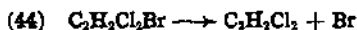


They assume $E_{43} = 5$ kcal., and thus get $E_{42} = 11$ kcal. In a review¹ Schumacher suggests $E_{43} = 5$ to 10 kcal., and thus obtains

$$E_{42} = 14 \pm 3 \text{ kcal.}$$



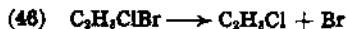
As discussed in the previous section, Schumacher¹ suggests that $E_{43} = 5$ to 10 kcal.



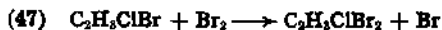
As discussed in section X-15, Müller and Schumacher²⁵ from their results on the photobromination of dichlor ethylene have estimated $E_{44} \sim 11$ kcal. Schumacher¹ in a review of photohalogenations puts the value at 14 ± 3 kcal.



Müller and Schumacher²⁵ from work on the photobromination of dichlorethylene (see X-15) arrive at a value of E_{46} of approximately 5 kcal.



Schmitz and Schumacher²⁶ have assumed this reaction as a step in the photobromination of vinyl chloride. (See X-47.)



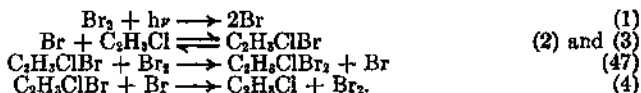
Schmitz and Schumacher²⁶ have investigated the photobromination of vinyl chloride to 1,2-dibrom chlor ethane. Above 60° the rate was given by

$$\frac{d}{dt} [\text{C}_2\text{H}_3\text{ClBr}] = k[\text{Br}_2]I_{\text{abs.}}^{\frac{1}{2}}[\text{C}_2\text{H}_3\text{Cl}]^{\frac{1}{2}}.$$

The values of k were constant in a given experiment, but the reaction was found to be inhibited by bromine and by the reaction product, i.e., $k = k'k''$, where k'' is a function of the sum of the concentrations of bromine and the reaction product. In a given experiment k was constant since the fall in $[\text{Br}_2]$ is offset by the increase in $[\text{C}_2\text{H}_3\text{ClBr}_2]$. There was no inhibition of the reaction by inert foreign gases such as CF_2Cl_2 or CO_2 .

The quantum yield of the reaction was virtually the same for X4360 and X5460, and at 80° with 100 mm. of each reactant was about 2×10^6 . The temperature coefficient corresponded to an apparent activation energy of — 4 kcal. The reaction was strongly inhibited by oxygen, but there was no sensitized oxidation.

The rate expression is of the same type as that for the phosgene synthesis at low temperatures, and they, therefore, suggested a similar mechanism, viz.,



This leads to an expression of the type found experimentally, viz.,

$$-\frac{d}{dt} [\text{Br}_2] = \frac{k_{47}}{k_4^{\frac{1}{2}} K_2 \rightleftharpoons s^{\frac{1}{2}}} [\text{Br}_2] I_{\text{abs.}}^{\frac{1}{2}} [\text{C}_2\text{H}_3\text{Cl}]^{\frac{1}{2}}.$$

It does not, however, explain the inhibition by bromine and the reaction product. They, therefore, replace (4) by



where M = bromine or the reaction product, is assumed to be a specific third body for the chain-ending step.

This leads to

$$-\frac{d}{dt} [\text{Br}_2] = \frac{k_{47}}{k_4^{\frac{1}{2}} K_2 \rightleftharpoons s^{\frac{1}{2}}} \cdot \frac{1}{\sqrt{\frac{k_4}{k_5} + [\text{M}]}} [\text{Br}_2] I_{\text{abs.}}^{\frac{1}{2}} [\text{C}_2\text{H}_3\text{Cl}]^{\frac{1}{2}}.$$

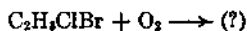
If we put

$$\begin{aligned} k' &= \frac{k_{47}}{k_4^{\frac{1}{2}} K_2 \rightleftharpoons s^{\frac{1}{2}}} \\ k'' &= \sqrt{\frac{k_4}{k_5} + [\text{M}]}, \end{aligned}$$

this gives the experimental equation

$$-\frac{d}{dt}[\text{Br}_2] = \frac{k'}{k''} [\text{Br}_2] I_{\text{abs.}}^{\frac{1}{2}} [\text{C}_2\text{H}_5\text{Cl}]^{\frac{1}{2}}.$$

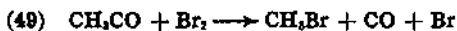
Not much can be said about the activation energies of the part reactions. Since the oxygen inhibition is very strong, (47) must be 10^5 times slower than



Hence, $E_7 \geq 7$ kcal. E_4 and E_5 are probably ~ 0 .

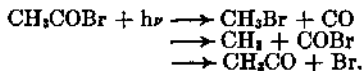


Schmitz and Schumacher²⁶ found the photobromination of vinyl chloride to be strongly inhibited by oxygen, presumably by reaction (48) which must, therefore, have a very small activation energy. (For details see X-47.)

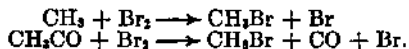


The photolysis of acetyl bromide was investigated by Etzler and Rollefson³⁷ using light of wave lengths 2537A and 2652A. The rate was found to be proportional to $I_{\text{abs.}}$ and independent of pressure, and the products were CO, CH_3Br , CH_4 , Br_2 , and $\text{C}_2\text{H}_4\text{Br}_2$. The quantum yield was approximately 0.5. Nitric oxide was found to have a strong retarding effect on the pressure increase, and at high concentrations resulted in a pressure decrease instead of the normal increase. It thus appears to be forming a compound of some sort with the radicals produced.

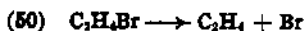
They suggest that three different primary steps are all occurring simultaneously:



Since no ethane or diacetyl are produced, it appears that CH_3 and CH_3CO must be rapidly removed from the system by reactions such as



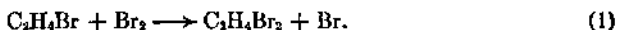
This is, of course, highly speculative, but if correct it means that reaction (49) must have a low activation energy.



This reaction has been postulated as a step in the mechanism of the photobromination of ethylene by Schmitz, Schumacher, and Jäger.²⁷ (See X-51.) Their results lead to

$$E_{50} - E_1 = 6.1 \text{ kcal.},$$

where (1) is the reaction



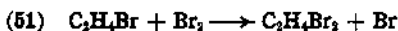
They conclude that $E_1 > 5$ kcal., and hence

$$E_{50} > 11.1 \text{ kcal.}$$

By analogy with other cases they suggest, therefore, that

$$E_{50} = 13 \pm 2 \text{ kcal.}$$

The reaction has also been postulated as a step in the photolysis of ethyl bromide.²⁹



Schmitz, Schumacher, and Jager²⁷ have investigated the photobromination of ethylene to dibromethane. The quantum yield is very high, being 2×10^5 at 60° with 100 mm. of each reactant. The rate is dependent on the total pressure. In this connection bromine, freon, and ethylene bromide are about equally effective, ethylene has about 5 times stronger and helium a weaker influence. The rate is given by

(I) at low pressures

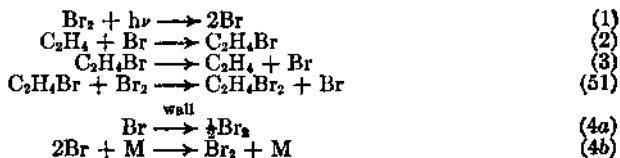
$$\frac{d}{dt} [\text{C}_2\text{H}_4\text{Br}_2] = k_1 I_{\text{abs.}} P [\text{C}_2\text{H}_4] \frac{[\text{Br}_2]}{[\text{Br}_2] + k'}$$

(II) at higher pressures

$$\frac{d}{dt} [\text{C}_2\text{H}_4\text{Br}_2] = k_{II} \sqrt{\frac{I_{\text{abs.}}}{P}} [\text{C}_2\text{H}_4] \frac{[\text{Br}_2]}{[\text{Br}_2] + k'}$$

The temperature coefficient of the reaction is slightly less than unity. The reaction is strongly inhibited by oxygen, but a sensitized oxidation does not occur.

The rate expressions are similar to those of Miiller and Schumacher²⁵ for the photobromination of transdichlorethylene, and they, therefore, propose a similar mechanism:



Whence, with (4a) as the chain ending step

$$\frac{d}{dt} [\text{C}_2\text{H}_4\text{Br}_2] = \frac{2k_2}{k_{4a}} I_{\text{abs.}} [\text{C}_2\text{H}_4] \frac{[\text{Br}_2]}{[\text{Br}_2] + k_3/k_{51}}$$

Now k_{4a} is roughly proportional to $1/P$, and hence, in the low pressure range, this agrees with the experimental equation (J) with

$$\frac{2k_2}{k_{4a}} = k_1 P$$

$$k_3/k_{51} = k'$$

In the higher pressure range, with (4b) as the chain ending step, this gives

$$\frac{d}{dt} [C_2H_4Br_2] = k_2 \sqrt{\frac{I_{0,br.}}{k_{4b}[M]}} [C_2H_4] \frac{[Br_2]}{[Br_2] + k_3/k_{51}}$$

This agrees with II, with

$$k_2 \sqrt{\frac{1}{k_{4b}}} = k_{11}$$

$$k_3/k_{51} = k'$$

$$[M] = P.$$

From the temperature coefficient of k' , i.e., k_3/k_{51} , we have

$$E_1 - E_{51} = 6.1 \text{ kcal.}$$

Since there is strong oxygen inhibition, reaction (51) must be much slower than



Hence

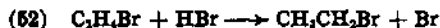
$$E_{51} > 5 \text{ kcal.}$$

E_2 is therefore greater than 11.1 kcal., and by analogy with other cases they put it as $E_2 = 13 \pm 2 \text{ kcal.}$

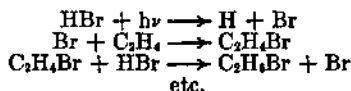
The temperature coefficient of $k_{11} = k_2 \cdot \frac{1}{\sqrt{k_{4b}}}$ is very small. E_{4b} is undoubtedly ~ 0 , and hence $E_2 \sim 0$.

At low temperatures the thermal bromination of ethylene is mainly a surface reaction.⁴¹ At higher temperatures the mechanism is probably similar to that of the photoreaction.⁴²

Sherman and Sun²⁸ by the semi-empirical method have estimated $E_{51} = 2.3 \text{ kcal.}$

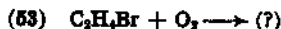


This reaction is probably involved in the photoaddition of HBr to ethylene,³² i.e.,

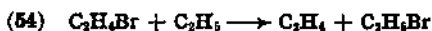


⁴¹ R. G. W. Norrish, *J. Chem. Soc.*, **123**, 3006 (1923); G. Williams, *J. Chem. Soc.*, **1932**, 1747, 1758.

⁴² H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, **31**, 1530 (1939).



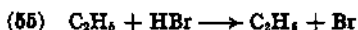
The photobromination of ethylene is very strongly inhibited by oxygen.²⁷ This is presumably due to the occurrence of the above reaction with an activation energy of ~ 0 . (See X-51 for details.)



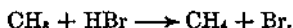
This may be a step in the ethyl bromide decomposition.²⁹



Results on the photobromination of ethane (see X-23), indicate that E_{54A} is small.



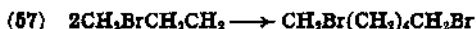
Andersen, Kistiakowsky, and van Artsdalen¹⁵ obtained results for the photobromination of ethane which were very similar to those for methane, and as pointed out in section X-9, they estimated an activation energy of 1.5 ± 1 kcal. for the reaction



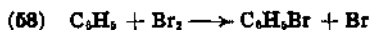
Since the two reactions are very similar they assign a value by analogy of $E_{55} \sim 2$ kcal.



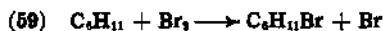
This has been postulated as a step in the photoaddition of HBr to propylene. (See X-24.)



Bawn and Hunter⁴³ investigated the reaction of sodium atoms with 1 : 3 dibromopropane by the diffusion flame technique. With low sodium atom concentrations they found that 1 : 6 dibrom *n*-hexane was a product. This was undoubtedly formed by recombination of radicals by reaction (57).



This reaction is probably involved in the photobromination of benzene (See X-25.) The high temperature coefficient of the reaction suggests a relatively high activation energy for reaction (58).

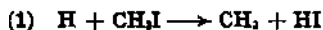


Reaction (59) has been suggested as a step in the mechanism of the photobromination of cyclohexane. (See X-26.) The reaction has a high temperature coefficient, which suggests that reaction (59) has a high activation energy.

⁴³ C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938).

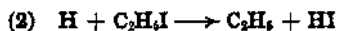
Chapter XI

Systems Containing Iodine



Chadwell and Titani* investigated the reaction of H-atoms, produced by the discharge-tube method, with methyl iodide. The results were similar to those with methyl chloride and methyl bromide, but the reaction was faster, being virtually complete at 125°. The activation energy of reaction (1) is thus less than 5 kcal.

Cremer, Curry, and Polanyi² obtained similar results, and estimated *Ei* to be < 4.5 kcal.



Cremer, Curry, and Polanyi² found results similar to those with methyl iodide, and estimated *Ei* to be less than 4.5 kcal.

It is of interest to compare the reactions of H-atoms with the various alkyl halides, as shown in Table LIV.

TABLE LIV. REACTIONS OF H-ATOMS WITH ALKYL HALIDES

Substance	Chadwell and Titani	<i>E</i> , kcal.	
		Polanyi et al.	Vance and Baumann ³
CH ₃ F	> 9		
CH ₃ Cl	9	7.2	
CH ₃ Br	6.5	3.2	
CH ₃ I	< 5	< 4.5	
C ₂ H ₅ Cl	8		
C ₂ H ₅ Br	6		
C ₂ H ₅ I		< 4.5	
CH ₂ Cl ₂		5.8	
CHCl ₃		< 4.3	
CCl ₄		< 3.3	3.5

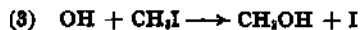
It will be observed that the activation energy falls steadily down the series fluoride, chloride, bromide, iodide. The same sequence is observed in the reactions of sodium atoms with the alkyl halides, and the effect is

¹ H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, 65, 1363 (1933).

² E. Cremer, J. Curry, and M. Polanyi, *Z. physik. Chem.*, B23, 445 (1933).

³ J. E. Vance and W. C. Baumann, *J. Chem. Phys.*, 6, 811 (1938).

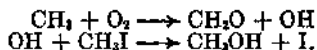
paralleled by the diminishing bond strengths in the order C—F, C—Cl, C—Br, C—I.



Bates and Spence⁴ investigated the photooxidation of methyl iodide and found as products iodine, paraformaldehyde, methylal and water, as approximately represented by

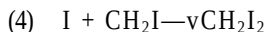


The reaction was about 100 times faster than the decomposition under the same conditions. The rate was proportional to the light intensity, and the quantum yield was very roughly 2. They suggest that the main processes occurring are those which occur in the decomposition (see XI-5) together with



The reaction is complicated, however, and the mechanism is by no means certain.

Blaedel, Ogg, and Leighton^B were unable to detect the hydroxyl radical by absorption spectroscopy in the photooxidation of gaseous methyl iodide. Accepting Bates and Spence's idea that OH should disappear by (3), and assuming for reasons not stated that $E_z = 15\text{--}20$ kcal., they conclude that a high stationary concentration of hydroxyl would be expected. Since this was not found, they rule out Bates and Spence's mechanism. It is thus not certain whether reaction (3) is involved or not.



Reaction (4) has been assumed by West and Schlessinger⁶ to be a step in the mechanism of the photolysis of methyl iodide.



The photolysis of methyl iodide has a very low quantum yield, and virtually all workers have assumed that this is due to the ready occurrence of methyl iodide re-forming reactions,⁶⁻¹² i.e.,

⁴ J. R. Bates and R. Spence, *Trans. Faraday Soc.*, 27, 468 (1931); *J. Am. Chem. Soc.*, 63, 381, 1689 (1931).

⁵ W. J. Blaedel, R. A. Ogg, and P. A. Leighton, *J. Am. Chem. Soc.*, 64, 2499, 2500 (1942).

⁶ W. West and L. Schlessinger, *J. Am. Chem. Soc.*, 60, 961 (1938).

⁷ J. R. Bates and R. Spence, *J. Am. Chem. Soc.*, 63, 1689 (1931); *Trans. Faraday Soc.*, 27, 468 (1931).

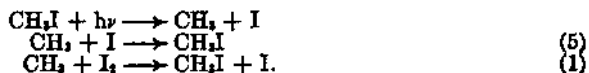
⁸ W. West and B. Paul, *Trans. Faraday Soc.*, 28, 688 (1932).

⁹ R. Spence and W. Wild, *Proc. Leeds Phil. Soc.*, 3, 141 (1936).

¹⁰ T. Iredale and D. Stephan, *Trans. Faraday Soc.*, 33, 800 (1937).

¹¹ T. Iredale, *Trans. Faraday Soc.*, 35, 458 (1939).

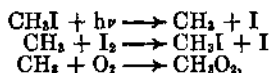
¹² J. C. Jungers and L. M. Yeddanapalli, *Trans. Faraday Soc.*, 36, 483 (1940).



Further support for this conclusion comes from experiments with added nitric oxide,¹¹ or in the presence of silver.⁶ Under these circumstances the radicals formed in the primary step are "fixed" before reactions (1) or (5) can occur, and the quantum yield rises to about one. All this indicates that the activation energy of reaction (5) must be close to zero. (For a discussion of the photolysis of methyl iodide see V-14.)

The only doubtful point about the above argument is the possibility that the low quantum yield in the photolysis of CH_3I might be due solely to the occurrence of reaction (1) rather than reaction (5). A number of workers^{7f, 10-11} have assumed that both reactions are important in the photolysis. West and Paul⁸ studied the photolysis in hexane solution. The temperature coefficient of the reaction was practically unity, and the rate was independent of the concentration of the alkyl halide. The reaction was zero order in the early stages, and they, therefore, conclude that reaction (1) cannot be of much importance and that the low quantum yield (0.05 at X2610 and 0.008 at X3130) must be due to reaction (5).

On the other hand Blaedel, Ogg, and Leighton⁶ reached an opposite conclusion. They investigated the photooxidation of gaseous methyl iodide and concluded that the main reactions involved were



and that reaction (5) was relatively unimportant. Their mechanism is not necessarily unique, however.

Andersen and Kistiakowsky¹³ investigated the photolysis of mixtures of CH_3I , HBr , and iodine, and concluded that reaction (1) was the only important methyl iodide re-forming step. (See V-14.) This conclusion is based, however, only on experiments in the presence of a large amount of added iodine which would strongly favor (1) relative to (5). It does not, therefore, necessarily follow that (5) is not of major importance in the absence of added iodine. In any case it appears probable that both iodide re-forming reactions occur at almost every collision.

Further evidence for a low activation energy for (5) comes from work of Bates and Spence⁷ on the photolysis of methyl iodide in the presence of hydrogen. It was found that hydrogen had no effect on the rate of the photolysis, so that the reaction



¹³ H. G. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, **11**, 6 (1943).

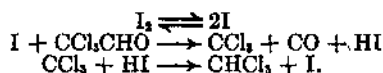
must be much slower than reaction (5), and hence reaction (5) cannot have a high activation energy.

Bawn¹⁴ has concluded on theoretical grounds that virtually every collision between CH_3 and I will be effective. On the other hand Kimball¹⁵ has concluded from a classical theoretical treatment that the complex formed from CH_3 and I has a very short life, 3.6×10^{-12} sec, and hence that third-body restrictions should come into play. Kassel,¹⁶ however, considers that Kimball's calculations are unreliable.

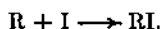
There is also evidence¹⁷ that the unexpectedly slow rate of the thermal decomposition of methyl iodide may be due to the ready occurrence of reaction (5).



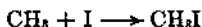
The thermal decomposition of chloral¹⁸ is similar to that of acetaldehyde. (See III-10.) The reaction is catalysed by iodine, possibly by the mechanism



West and Paul⁹ have compared the photolyses of a number of iodides. If, as seems reasonable, the quantum yield is largely determined by the efficiency of the back reaction



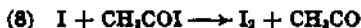
then the relative efficiencies of the recombination of radicals with iodine atoms are, in the order of decreasing efficiency, methyl, allyl, vinyl, ethyl, propyl, isopropyl. Since the activation energies of the reactions



and



are not far from zero, it appears that E_7 is also very small.



As discussed in section V-6, Gorin¹⁹ investigated the photolysis of acetone in the presence of iodine, which served to "fix" the radicals pro-

¹⁴ C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 1536 (1935).

¹⁵ G. E. Kimball, *J. Chem. Phys.*, **5**, 310 (1937).

¹⁶ L. S. Kassel, *J. Chem. Phys.*, **5**, 922 (1937).

¹⁷ R. A. Ogg, *J. Am. Chem. Soc.*, **56**, 526 (1934); E. W. R. Steacie and R. D. McDonald, *J. Am. Chem. Soc.*, **57**, 488 (1935).

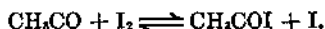
¹⁸ F. H. Verhoek and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A146**, 334 (1934).

¹⁹ E. Gorin, *Acta Physicochimica*, U.R.S.S., **8**, 513 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

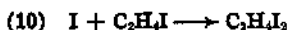
duced as methyl iodide, acetyl iodide, etc. At temperatures from 60° to 80° the quantum yield of methyl iodide production was approximately unity, indicating that the only important primary process is



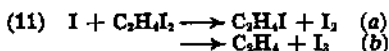
Very little CO was formed in the presence of iodine, which indicates that the acetyl radical is relatively stable. Much less acetyl iodide was formed than methyl iodide, however, and Gorin concludes that this is due to the rapid establishment of the equilibrium



This reaction has been suggested as a step in the photolysis and photochemical synthesis of $\text{C}_2\text{H}_4\text{I}_2$. (See XI-11.) The reaction is undoubtedly also involved in the photoiodination of ethylene.²⁰



This reaction has been suggested as a step in the mechanism of the photolysis of ethyl iodide. (See XI-12 and V-14.)

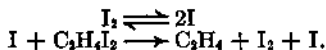


Considerable work has been done on both the thermal and the photochemical decomposition of ethylene iodide (or, more accurately, diiodo ethane).

Polissar²¹ and Mooney and Ludlam²² investigated the thermal reaction in carbon tetrachloride solution. Both authors found that the rate was given by

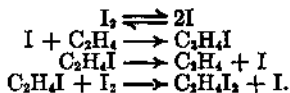
$$-\frac{d}{dt} [\text{C}_2\text{H}_4\text{I}_2] = k[\text{C}_2\text{H}_4\text{I}_2][\text{I}_2]^{\frac{1}{2}}.$$

Polissar interpreted his results on the basis of the rather unconvincing mechanism:



Schumacher²³ has discussed the mechanism on the basis of Polissar's results, and suggested the following:

Synthesis



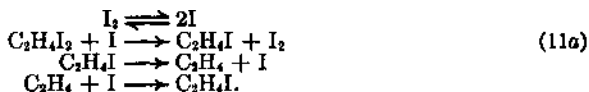
²⁰ G. S. Forbes and A. F. Nelson, *J. Am. Chem. Soc.*, **59**, 693 (1937).

²¹ M. J. Polissar, *J. Am. Chem. Soc.*, **52**, 956 (1930).

²² R. B. Mooney and E. B. Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929).

²³ H. J. Schumacher, *J. Am. Chem. Soc.*, **52**, 3132 (1930).

Decomposition



This leads to the observed rate equation. Comparison with experiment gives

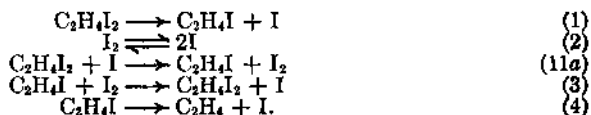
$$E_{11a} = 11.5 \pm 2 \text{ kcal.}$$

Arnold and Kistiakowsky²⁴ investigated the reaction in the gas phase at 205° to 230°. They found the rate equation to be

$$-\frac{d}{dt}[\text{C}_2\text{H}_4\text{I}_2] = k_1[\text{C}_2\text{H}_4\text{I}_2] + k_2[\text{C}_2\text{H}_4\text{I}_2][\text{I}_2]^{\frac{1}{2}}$$

i.e., both a unimolecular decomposition and an iodine catalysed decomposition occur. The activation energies found were 36 ± 3 kcal. for the unimolecular decomposition and 30 ± 3 kcal. for the iodine catalysed reaction. Accepting Schumacher's mechanism for the uncatalysed reaction, this gives $E_{11a} - 11.9 \pm 3$ kcal., in excellent agreement with the value found in solution. The absolute rate also appears to be the same in the gas phase and in solution. Other workers^{25,26} on the gas phase reaction have been unable to obtain consistent results on account of the reaction occurring heterogeneously on glass.

Ogg²⁷ has discussed the mechanism of the reaction, and has shown that Arnold and Kistiakowsky's rate expression can be arrived at also on the basis of a mechanism which does not involve two separate processes:

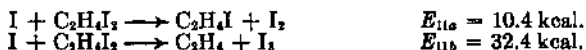


This leads to the expression

$$-\frac{d}{dt}[\text{C}_2\text{H}_4\text{I}_2] = \frac{k_1[\text{C}_2\text{H}_4\text{I}_2] + K_2^{\frac{1}{2}}k_{11a}[\text{I}_2]^{\frac{1}{2}}[\text{C}_2\text{H}_4\text{I}_2]}{1 + \frac{k_3}{k_4[\text{I}_2]}}$$

where K_2 is the equilibrium constant of reaction (2). This yields Arnold and Kistiakowsky's rate expression if $k_3/k_4[\text{I}_2]$ is small compared with unity, which is the case.

Sherman and Sun²⁸ have used the semi-empirical method to calculate the activation energies of reactions (11a) and (11b). The results were



²⁴ L. B. Arnold and G. B. Kistiakowsky, *J. Chem. Phys.*, 1, 166 (1933).

²⁵ T. Iredale and L. W. O. Martin, *J. Phys. Chem.*, 38, 365 (1934).

²⁶ W. H. Janneck and E. O. Wiig, *J. Am. Chem. Soc.*, 62, 1877 (1940).

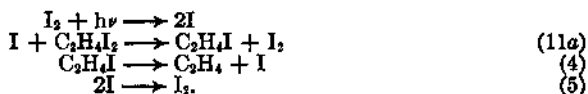
²⁷ R. A. Ogg, *J. Am. Chem. Soc.*, 68, 607 (1936).

²⁸ A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, 66, 1096 (1934).

The photolysis and the photochemical synthesis of ethylene iodide have also been investigated. Schumacher and Wiig²⁹ investigated the iodine photosensitized decomposition in carbon tetrachloride solution. The rate was given by the expression

$$-\frac{d}{dt}[\text{C}_2\text{H}_4\text{I}_2] = k_{\text{I,abs.}}^{\frac{1}{2}}[\text{C}_2\text{H}_4\text{I}_2],$$

i.e., the iodine concentration had no effect on the rate. The quantum yield in the region 4000Å to 4360Å was about 25, and the temperature coefficient corresponded to an activation energy of 11.8 kcal. By analogy with the dark reaction they suggest the mechanism:



This leads to

$$-\frac{d}{dt}[\text{C}_2\text{H}_4\text{I}_2] = k_{\text{I,abs.}} \sqrt{\frac{2\text{I}_{\text{abs.}}}{k_5}} [\text{C}_2\text{H}_4\text{I}_2].$$

Since Eh is certainly zero, the overall activation energy is that of reaction (11a), *i.e.*, $E_{\text{ua}} = 11.8$ kcal., in excellent agreement with the value calculated for the thermal decomposition. Comparison of the experimental value with a collision theory calculation yields a steric factor of 1/32 for reaction (11a).

Schumacher and Stieger³⁰ investigated the effect of wave-length in more detail. They found that Schumacher and Wiig's value of the quantum yield was about twice too high, and that f_{aw} is only about 1/7 that of 0.4360. X5460 is in the banded region of absorption by iodine (the convergence limit is 4995Å). In a careful re-examination of the effect of wave-length on the iodine sensitized decomposition, Dickinson and Nies³¹ found the quantum yields at XX4358, 5461, and 5770-90 to be in the ratio 1 : 0.93 : 0.87. Light in the iodine continuum is thus slightly more effective than light in the banded region.

DeRight and Wiig³² investigated the direct photolysis of ethylene iodide in carbon tetrachloride solution, using X3030 and X3130. The quantum yield was about 0.76, and the results are given by the expression

$$-\frac{d}{dt}[\text{C}_2\text{H}_4\text{I}_2] = \text{I}_{\text{abs.}} \left(1 + \frac{k_2}{k_4} [\text{I}_2] \right),$$

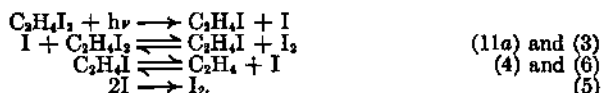
²⁹ H. J. Schumacher and E. O. Wiig, *Z. physik. Chem.*, B11, 45 (1930).

³⁰ H. J. Schumacher and G. Stieger, *Z. physik. Chem.*, B12, 348 (1931).

³¹ R. G. Dickinson and N. P. Nies, *J. Am. Chem. Soc.*, 57, 2382 (1935).

³² R. E. DeRight and E. O. Wiig, *J. Am. Chem. Soc.*, 67, 2411 (1935); see also G. Emschwiller, *Compt. Rend.*, 199, 854 (1934).

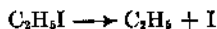
which agrees with the mechanism



Janneck and Wiig³³ have reported briefly on an investigation of the photolysis and iodine photosensitized decomposition in the gas phase. On account of difficulties due to lack of reproducibility of the dark reaction and its, at least partial, heterogeneity, they were unable to obtain much information. It appears, however, that the mechanism in the gas phase is probably the same as that in solution.



In connection with an investigation of the thermal reaction between HI and $\text{C}_2\text{H}_5\text{I}$, Ogg³⁴ has concluded that the reaction



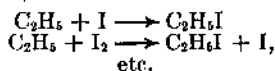
is of the first order, with a rate given by

$$k = 1.82 \times 10^{12} e^{-43000/RT} \text{sec.}^{-1}.$$

More recent work³⁵ indicates, however, that Ogg's value of the activation energy is in error, and that the activation energy of the reaction



is about 52 kcal. (See III-20.) This primary reaction is evidently followed in the case of the thermal decomposition of ethyl iodide alone by processes such as

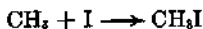


As a result, the overall reaction is mainly due to slow secondary reactions leading to ethylene, polymers, etc.³⁶

The photolysis of ethyl iodide has a low quantum yield, as with methyl iodide, and this is undoubtedly due to the occurrence of reaction (12) with a very low activation energy. (For a more detailed discussion of the photolysis see V-14.)



West and Paul⁸ (see XI-7) found that reaction (13) was slower than



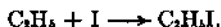
³³ W. H. Janneck and E. O. Wiig, *J. Am. Chem. Soc.*, **62**, 1877 (1940).

³⁴ R. A. Ogg, *J. Am. Chem. Soc.*, **56**, 526 (1934).

³⁵ E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943).

³⁶ E. T. Lessig, *J. Phys. Chem.*, **36**, 2325 (1932).

and faster than



The reaction must, therefore, have an activation energy not far from zero.

(14) $\text{I} + \text{C}_3\text{H}_6$ (cyclopropane) $\longrightarrow \text{C}_3\text{H}_5\text{I}$

Ogg and Priest³⁷ have investigated the reaction between cyclopropane and iodine in the gas phase: the main reaction is the reversible formation of 1,3-diiodo propane. The only important side reaction is a slow iodine-catalysed conversion of cyclopropane to propylene. For the thermal reaction in the range 245° to 280° the rate expression is

$$\frac{d}{dt} [\text{C}_3\text{H}_6\text{I}_2] = k' \left\{ [\text{C}_3\text{H}_6][\text{I}_2]^{\frac{1}{2}} - K_e \frac{[\text{C}_3\text{H}_6\text{I}_2]}{[\text{I}_2]^{\frac{1}{2}}} \right\},$$

where K_e is the equilibrium constant for the reaction



For the photoreaction in the range 180° to 230°, the rate expression is

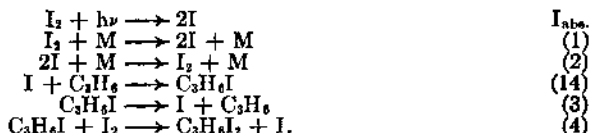
$$\frac{d}{dt} [\text{C}_3\text{H}_6\text{I}_2] = k'' I_{\text{abs.}}^{\frac{1}{2}} [\text{C}_3\text{H}_6].$$

The values found for the constants were

$$k' = 1.17 \times 10^{13} e^{-35230/RT} (\text{mole/cc})^{-\frac{1}{2}} \text{sec.}^{-1}$$

$$k'' = 8.5 \times 10^6 e^{-18800/RT} (\text{Einstein/cc})^{-\frac{1}{2}} \text{sec.}^{-\frac{1}{2}}.$$

The results are fitted by the proposed mechanism



Reaction (14) is assumed to be the rate-controlling step, i.e.,

$$k_4[\text{I}_2] \gg k_3.$$

By the usual steady-state method the mechanism gives

For the thermal reaction

$$\frac{d}{dt} [\text{C}_3\text{H}_6\text{I}_2] = k_{14} K_{\text{I}_2}^{\frac{1}{2}} [\text{C}_3\text{H}_6][\text{I}_2]^{\frac{1}{2}},$$

whence, with the known values of K_{I_2} ,

$$k_{14} = 7.36 \times 10^{12} e^{-17280/RT} (\text{mole/cc})^{-1} \text{sec.}^{-1}.$$

For the photoreaction

$$\frac{d}{dt} [\text{C}_3\text{H}_6\text{I}_2] = k_{14} (k_2[\text{M}])^{-\frac{1}{2}} I_{\text{abs.}}^{\frac{1}{2}} [\text{C}_3\text{H}_6],$$

³⁷ R. A. Ogg and W. J. Priest, *J. Am. Chem. Soc.*, **60**, 217 (1938); *J. Chem. Phys.*, **736** (1939).

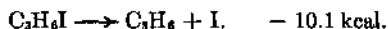
whence, with certain assumptions as to the relative efficiencies of various "third bodies,"

$$k_{14} = 1.45 \times 10^{12} e^{-18800/RT}.$$

The two values of k_{14} are in excellent agreement, but the thermal value is more reliable, so that they take

$$E_{14} = 17.3 \text{ kcal.}$$

Assuming 43 kcal. for the strength of the C—I bond in both $C_3H_5I_2$ and C_3H_5I ,



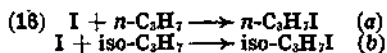
Combining this with the activation energy of the reverse reaction, E_{14} , gives

$$E_2 = 27.4 \text{ kcal.}$$

This value is, of course, open to question in view of the uncertainty about the strengths of the C—I bonds.

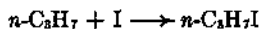


This reaction is probably involved in the photoiodination of propylene.²⁰

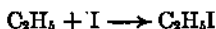


West and Paul⁸ investigated the photolysis of n-propyl iodide in hexane solution. At 2610Å, the quantum yield was 0.68, and at 3130Å, 0.33. These values are slightly above those for ethyl iodide. West and Schlessinger⁶ found the iodine yield for gaseous n-propyl iodide to be about 0.01 at 2026Å and 2610Å. This is about 10 times smaller than that for ethyl iodide. However, this is only the iodine yield, and other products may be formed, so that the quantum efficiency of the overall decomposition may be greater than this value. In any case the small quantum yield suggests a high efficiency for the iodide re-forming reaction.^{16a}

Jungers and Yeddnapalli¹² showed that the ethylene polymerization could be sensitized by radicals from the photodecomposition of n-propyl iodide. The results were similar to those for ethyl iodide, discussed above. They conclude that the reaction



is slower than the corresponding reactions



and



West and Paul⁸ investigated the photolysis of iso-propyl iodide in hexane solution. Values of the quantum yield were 1.15 at 26101, and 0.65 at

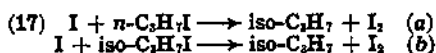
3130A. These are almost double the values for *n*-propyl iodide under similar conditions. This is perhaps due to a less rapid back reaction



in this case.

Jungers and Yeddanapalli also investigated the polymerization of ethylene photosensitized by iso-propyl iodide. The polymerization yield is lower for the iso- than for the normal compound, which they explain on the basis of a somewhat lower steric factor.

While there may be some doubt about the relative rate of reaction (16) as compared with other reactions of a similar type, there is no doubt that *Emu* and *Em* are not far from zero.



Jones and Ogg³⁸ investigated the pyrolysis of *n*-propyl iodide, alone and in the presence of added iodine. The overall reaction is



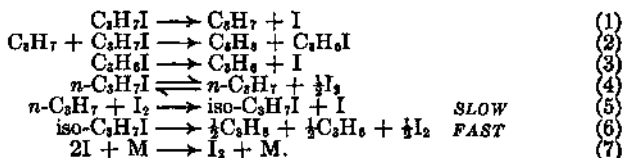
They conclude that their data are well expressed by the equation

$$-\frac{d}{dt} [\text{C}_3\text{H}_7\text{I}] = k[\text{C}_3\text{H}_7\text{I}][\text{I}_2]^{\frac{1}{2}},$$

i.e., the reaction appears to involve iodine atoms. The above expression is equivalent to

$$-\frac{d}{dt} [\text{C}_3\text{H}_7\text{I}] = k'K_{\text{I}_2}^{\frac{1}{2}}[\text{C}_3\text{H}_7\text{I}][\text{I}],$$

where K_{I_2} is the equilibrium constant for the dissociation of iodine. They discuss all possible mechanisms in considerable detail, and accept the following:

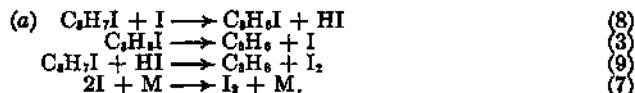


Reactions (1), (2), (3), and (7) constitute the main reactions at the start in the absence of added iodine. Once iodine has built up, or in the presence of added iodine, reactions (4), (5), and (6) become important. Reaction (3) is similar to the intermediate step in the ethylene iodide decomposition, and probably has an activation energy of about 13.4 kcal. Reaction (5) is assumed to be the rate-determining step, and the decomposition of the iso-propyl iodide formed is more rapid than that of *n*-propyl iodide. From spectroscopic and other data they conclude that *E*₅ is 13.2 kcal., and that

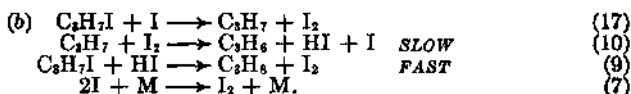
³⁸ J. L. Jones and R. A. Ogg, *J. Am. Chem. Soc.*, 59, 1931 (1937).

there is a steric factor of about 10^{-5} . This mechanism appears to be consistent with their results. Their estimates of E_s and E_t , however, are unreliable.

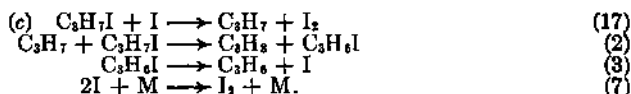
They rule out other mechanisms which appear to be more plausible at first sight on the following grounds:



This must be ruled out since Ogg³⁴ has investigated reaction (9) and found it to be much slower than would be necessary to explain the rate of disappearance of propyl iodide.



The same objection holds here, *i.e.*, reaction (9) is too slow to account for the observed rate.



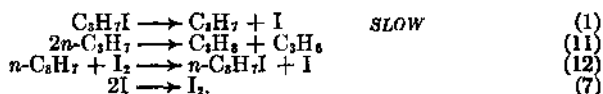
From Ogg's work the reaction of C_3H_7 with I_2 is much faster than reaction (2), and hence this mechanism must be rejected also.

They thus conclude that the first mechanism discussed must be the correct one.

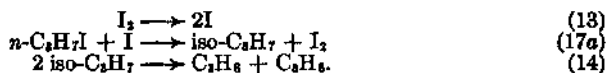
Schumacher³⁹ has criticised this mechanism, however. In the absence of excess iodine he considers that the strongly exothermic reaction



should be considered. The mechanism would thus be



This explains the retardation of the reaction by iodine as it progresses. In the presence of iodine his suggested mechanism is



This mechanism is also in agreement with experiment. It leads to a value of E_{17a} of 20 ± 2 kcal.⁴⁰ The steric factor of reaction (17a) appears to be about 5×10^{-2} . It is not possible to decide between the two mechanisms, but that of Schumacher is perhaps more plausible on general grounds.

³⁹ H. J. Schumacher, *Chemische Gasreaktionen*, Leipzig, 1938, p. 448.

⁴⁰ H. J. Schumacher, *Angew. Chem.*, 63, 501 (1940).

Jones and Ogg⁴¹ also investigated the thermal decomposition of iso-propyl iodide. The products corresponded to the overall reaction



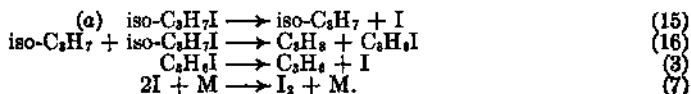
together with a small amount of HI. Their data are expressed by the equation

$$-\frac{d}{dt} [\text{iso-C}_3\text{H}_7\text{I}] = k[\text{C}_3\text{H}_7\text{I}].$$

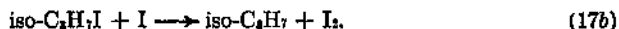
The overall activation energy was 42.9 kcal., i.e.,

$$k = 1.59 \times 10^{14} e^{-42900/RT} \text{ sec.}^{-1}.$$

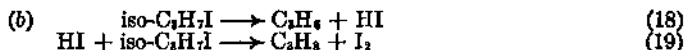
Two possible mechanisms are suggested:



Reaction (15) is assumed to be the slow rate-determining step. The main objection to this mechanism is the necessity of assuming that the possible reaction



is negligibly slow, since it is found that the reaction is not influenced by the presence of iodine.



with (18) as the rate-determining step. The objection to this mechanism is that it is necessary to assume that (19) is about 1000 times slower than the corresponding reaction of n-propyl iodide, the rate of which has been measured.⁴²

Schumacher⁴³ suggests that in (a) it would perhaps be possible to substitute



for reactions (16) and (3). However, in view of the distinct differences between n- and iso-propyl iodides, they probably have different mechanisms, and hence mechanism (6) is the more likely. It is thus not possible to say anything definite about the rate of reaction (176).

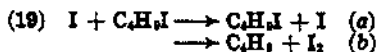
(18) $\text{I} + \text{C}_4\text{H}_8 \longrightarrow \text{C}_4\text{H}_8\text{I}$

Reaction (18) is probably involved in the photoiodination of butene.²⁰

⁴¹ J. L. Jones and R. A. Ogg, *J. Am. Chem. Soc.*, 69, 1939 (1937); see also J. V. S. Glass and C. N. Hinshelwood, *J. Chem. Soc.*, 1929, 1817.

⁴² R. A. Ogg, *J. Am. Chem. Soc.*, 56, 532 (1934).

⁴³ H. J. Schumacher, *Chemische Gasreaktionen*, Leipzig, 1938, p. 215.



Ogg and Polanyi⁴⁴ have investigated the decomposition and racemization of sec-butyl iodide. The racemization of the optically active compound proceeds by reaction (19a), with an activation energy of 13.8 kcal.

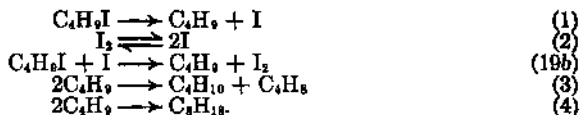
The decomposition of the substance occurs mainly according to the overall equation



The results are given by

$$-\frac{d}{dt}[\text{C}_4\text{H}_9\text{I}] = k[\text{C}_4\text{H}_9\text{I}] + k'[\text{I}_2]^{\frac{1}{2}}[\text{C}_4\text{H}_9\text{I}]$$

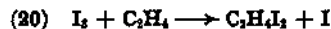
They interpret this on the basis of the following mechanism



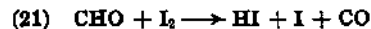
Reaction (4) is unimportant. This yields the above equation if we put $k = fci$, and $k' = k19b$. Iodine has no retarding effect on the reaction, and it thus appears that the reverse of reaction (1) is not of importance here. This distinct difference from the methyl iodide decomposition is perhaps explainable on the basis that reaction (3) is much faster here than is the analogous process with methyl radicals. From a comparison of the mechanism with experiment, $E1 = 39.4$ kcal., $E19b = 16.8$ kcal. Using $E1$ as the strength of the C—I bond, and the above value of E_m , they get for the reverse of (19b), i.e.,



an activation energy of 14.2 kcal. However, a value of about 46 kcal. seems much more likely for the C—I bond strength. (See III-1 and III-20.) If this is assumed, $E_5 \sim 8$ kcal.



By the semi-empirical method Sherman and Sun have estimated²⁸ E_{20} to be 29.7 kcal.

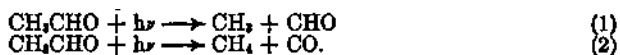


As discussed in section V-3, Gorin⁴⁵ investigated the photolysis of acetaldehyde in the presence of iodine, which by combining with free radicals

⁴⁴ R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 31, 482 (1935).

⁴⁵ E. Gorin, *Acta Physicochimica*, U.R.S.S., 9, 681 (1938); *J. Chem. Phys.*, 7, 250 (1939).

serves to "fix" them and thus to prevent secondary reactions. He assumed that there were two primary processes

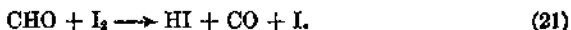


The results showed that the ratio of methane to methyl iodide was constant at any one wave-length, and independent of pressure, intensity or temperature. He therefore assumed that the ratio gave a measure of the relative occurrence of (1) and (2).

$\phi_{\text{CH}_3\text{I}} + \phi_{\text{CH}_3}$ was found to be approximately unity at both 3130Å and 2537Å, no chain processes occur, and the formyl radical appears to be stable with respect to the possible reactions



and

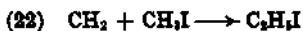


This is substantiated by the fact that ϕ_{HI} is very small at temperatures below 100°. E21, therefore appears to be quite high.

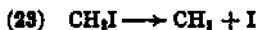
Blacet and his co-workers⁴⁶ have repeated Gorin's work and have obtained results on this phase of it which are completely at variance with his. With X3130, $\phi_{\text{CH}_3} + \phi_{\text{CH}_3\text{I}}$ was considerably less than 1, and considerable HI was produced. They, therefore, conclude, contrary to Gorin that at n3130 the only important primary process is



and that iodine reacts readily with both CH_3 and CHO . They suggest that the reaction occurring in the latter case is (21). At other wave lengths somewhat different results were obtained, but iodine still appeared to react readily with all radicals including formyl. Reaction (21) thus appears to have a low activation energy, contrary to the results of Gorin. In view of their much more detailed nature the results of Blacet *et al.* appear to be the more reliable.



West and Schlessinger⁶ have suggested this as a step in the photolysis of methyl iodide.



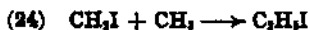
Gregory and Style⁴⁷ investigated the photooxidation of methylene iodide, and found as products I_2 , HCHO , HCOOH , and ethylene glycol. One alternative for the primary process is

⁴⁶ F. E. Blacet and J. D. Heldman, *J. Am. Chem. Soc.*, 64, 889 (1942); F. E. Blacet and D. E. Loeffler, *J. Am. Chem. Soc.*, 64, 893 (1942).

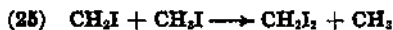
⁴⁷ R. A. Gregory and D. W. G. Style, *Trans. Faraday Soc.*, 32, 724 (1936).



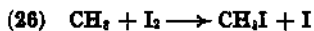
followed by (23).



This has been suggested as a step in the photolysis of methyl iodide by West and Schlessinger.⁶



This has also been suggested as a step in the photolysis of methyl iodide.



As we have seen in sections V-14 and XI-5, the quantum yield of the photolysis of methyl iodide is low, and it has been assumed that this is due to re-formation of methyl iodide by either or both of the reactions

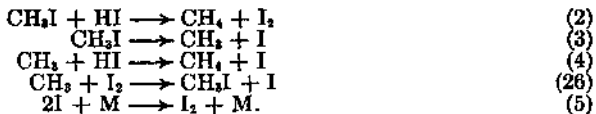


and



There is some difference of opinion as to the relative importance of the two reactions. Bates and Spence,⁷ Iredale and Stephan,¹⁰ and Iredale¹¹ conclude that reaction (26) is important in this connection, while West and Paul⁸ and West and Schlessinger⁶ conclude that reaction (1) is responsible for the low quantum yield, and that reaction (26) is relatively unimportant. Blaedel, Ogg, and Leighton⁵ from experiments on the photooxidation of methyl iodide conclude that reaction (26) predominates over (1) as a methyl iodide re-forming reaction.

Ogg³⁴ has investigated the thermal reaction of methyl iodide with hydrogen iodide. He explains his results by the mechanism:



Reaction (26) is thus tacitly assumed to be faster than (1). Jones⁴⁸ has investigated the thermal decomposition of acetyl iodide. (See XI-29.) He concludes that (26) is a step in the mechanism of the reaction, and from Ogg's results he estimates $E_{26} = 12$ kcal. This seems impossibly high.

Horn, Polanyi, and Style⁴⁹ found that methyl radicals produced by the

⁴⁸ J. L. Jones, *J. Am. Chem. Soc.*, 61, 3284 (1939).

⁴⁹ E. Horn, M. Polanyi, and D. W. G. Style, *Trans. Faraday Soc.*, 30, 189 (1934); M. Polanyi and D. W. G. Style, *Naturwiss.*, 20, 401 (1932).

reaction of sodium and methyl halides could be detected by their reaction with iodine vapor at temperatures in the range 215° to 306°, viz.,



This indicates a low activation energy for reaction (26).

Further evidence for the occurrence of reaction (26) with a low activation energy is furnished by the work of Gorin and others^{46,46} who have shown that methyl radicals can be "fixed" by iodine vapor by reaction (26). In order that the radicals can thus be fixed rather than enter into other possible secondary reactions, reaction (26) must have a relatively low activation energy.

Anderson and Kistiakowsky¹³ have concluded that reaction (26) is the main methyl iodide re-forming reaction in the methyl iodide photolysis. They estimate its activation energy by a rather dubious process of reasoning by analogy as follows: The reaction



almost certainly has zero activation energy, while



probably has an activation energy of ca. 9 kcal. This is about 1 kcal. greater than the activation energy of the reaction



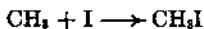
Hence they suggest that E_{26} is probably about 1 kcal. higher than E_8 , i.e.,

$$E_{26} = 0.5 \pm 0.5.$$

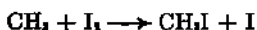
This value seems very reasonable, but the argument is far from convincing.



Iredale and Stephan¹⁰ investigated the photolysis of CH_3I — HI mixtures. With 40 per cent or more of HI in the mixture they obtained a quantum yield of about 2 in place of the usual low quantum yield of the methyl iodide photolysis. This indicates that reaction (27) occurs sufficiently rapidly to render the reactions

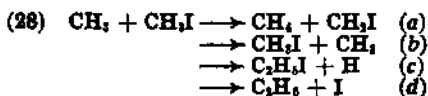


and



relatively unimportant. Since these reactions themselves have low activation energies, E_{27} must be small.

As discussed in section XI-26 Ogg³⁴ has assumed reaction (27) as a step in the reaction of methyl iodide with HI .



Reaction (28a) has been suggested as the source of methane in the photolysis of methyl iodide.^{6,9}

Saffer and Davis⁶⁰ heated molten sodium at 320° with methyl iodide. The result is presumably the formation of NaI and methyl radicals. The gaseous products were approximately: H₂ — 7 per cent, CH₄ — 64.1 per cent, C₂H₄ — 1.9 per cent, and C₂H₆ — 27.0 per cent. They conclude that under their conditions recombination is unimportant, and that the main reactions are (28a), (6), (c), and (d). They suggest, as far as one can see on the basis of no evidence, that $22\text{B}_a \sim 16$ kcal., $E_m \sim 16$ kcal., $E2^*c > 16$ kcal., $E2sd =$ possibly about 16 kcal. In any case it appears certain that the reactions are heterogeneous.⁵⁰⁰

Gordon and Taylor⁶¹ on the basis of a somewhat dubious calculation (q.v.) have estimated the activation energy of the reaction



to be about 22 kcal. On the same basis this would lead to $E_{2sd} \sim 15$ kcal.

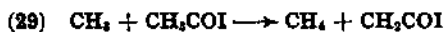
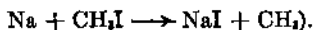
Bawn⁵² has cited unpublished work with W. J. Dunning in which methyl radicals were prepared by



In the presence of CH₃I, this is apparently followed by



The temperature coefficient corresponds to an activation energy of 12 kcal. for reaction (28a). (Note it seems probable that reaction (1) is really a misprint for



The thermal decomposition of acetyl iodide has been investigated by Jones.⁴⁸ The reaction is approximately first order. The main products are CO, CH₄, I₂, and a polymer, which is probably polymerized ketene. The decomposition is retarded by packing the reaction vessel, and the rate is slightly increased by the addition of inert gases, both of which facts point to a chain mechanism for the reaction. The activation energy of the reaction is 43.1 kcal., which Jones suggests is approximately equal to the C—I

⁸⁰ A. Saffer and T. W. Davis, *J. Am. Chem. Soc.*, 64, 2039 (1942).

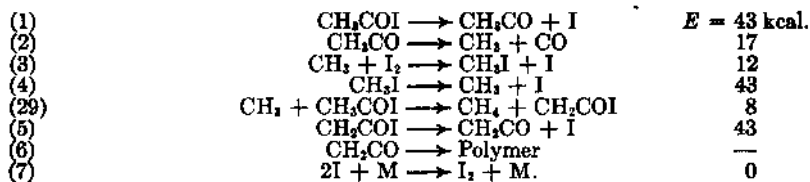
^{50a} A. Saffer and T. W. Davis, *J. Am. Chem. Soc.*, 67, 641 (1945).

⁵¹ A. Gordon and H. A. Taylor, *J. Am. Chem. Soc.*, 63, 3435 (1941).

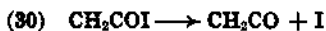
⁶² C. E. H. Bawn, *Trans. Faraday Soc.*, 35, 898 (1939).

bond strength, although later work (111-20), suggests a somewhat higher value.

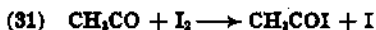
Jones suggests the following free radical mechanism:



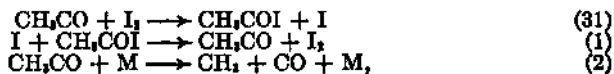
The activation energies for (1), (4), and (5) are based on a C—I bond strength of 43 kcal. which is definitely too low. (See 111-20.) E_2 is assumed from the acetaldehyde and acetone decompositions. E_i is taken to be zero as usual. E_z is taken from Ogg's work on iodides and is unquestionably far too high. E_{29} is assumed by analogy with acetaldehyde and other reactions of the type



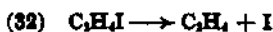
As discussed in section XI-29, Jones has assumed $E_{30} = 43 \text{ kcal.}$



As discussed in section XI-8 Goring work on the photolysis of acetone in the presence of iodine leads to the conclusion that E_{31} is small. Benson and Forbes⁵³ have also investigated the photolysis of acetone-iodine mixtures. (See V-3.) They did not determine acetyl iodide, but inferred its formation from a material balance. A plot of $\log [\text{CH}_3\text{CO}]$ against $1/T$ from such data corresponded to an activation energy of 6 kcal. If it is assumed that acetyl iodide is formed and disappears by



then the observed activation energy of 6 kcal. is equal to $E_2 - E_{31}$. Whence $E_{31} \sim 9 \text{ kcal.}$ This value, however, can hardly be said to be on very reliable ground.

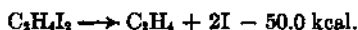


Reaction (32) has been assumed as a step in the mechanism of the photolysis of ethyl iodide. (See V-14.)

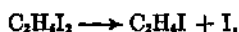
The reaction also is a step in the mechanism of the decomposition of

⁵³ S. W. Benson and G. S. Forbes, *J. Am. Chem. Soc.*, 65, 1399 (1943).

ethylene iodide. (See XI-11.) Ogg²⁷ has estimated the activation energy to be 13.4 kcal. by the following argument. From thermochemical data

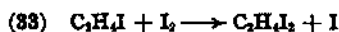


He assumes $E = 36.6$ kcal. for the reaction



and that $E = 0$ for the reverse reaction. Whence

$$E_{22} = 50.0 - 36.6 = 13.4 \text{ kcal.}$$



This reaction is undoubtedly involved in the thermal and photochemical decomposition of ethylene iodide. (See XI-11.) The activation energy is probably small, and Sherman and Sun²⁸ by the semi-empirical method have estimated $E_{33} = 1.8$ kcal.

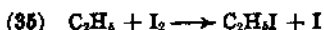
Ogg²⁷ has discussed the mechanism of the ethylene iodide decomposition, and concludes that the reaction



is thermoneutral. The activation energy of the forward reaction is 11.9 kcal., and hence E_{33} is also 11.9 kcal. This conclusion rests on somewhat arbitrary assumptions about bond strengths.



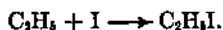
Reaction (34) has been suggested as a step in the photolysis of ethyl iodide by West and Schlessinger.⁶ (See V-14.)



The quantum yield of the ethyl iodide photolysis is small, and this is undoubtedly due to rapid re-formation of ethyl iodide. (See V-14.) It seems certain that this involves both the reactions

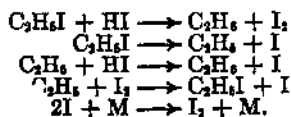


and



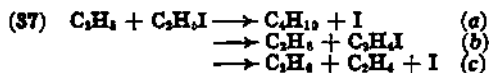
They must, therefore, have activation energies which are not far from zero.

Ogg³⁴ investigated the thermal reaction of ethyl iodide with hydrogen iodide. His results are fitted by the mechanism:

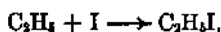




This reaction is also assumed by Ogg³⁴ as a step in the mechanism of the thermal reaction of ethyl iodide with hydrogen iodide. (See XI-35.)

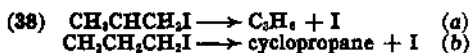


These reactions are possible steps in the mechanism of the photolysis of ethyl iodide. (See V-14.) West and Paul⁸ postulated the occurrence of (37a) in the photolysis in hexane solution. In the gas phase, however, no butane is formed, and hence West and Schlessinger⁶ ruled out (37a) and suggested the occurrence of (376). Joris and Jungers⁵⁴ point out that the small quantum yield of the ethyl iodide photolysis means that reaction (37) must be improbable compared with

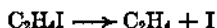


and hence its activation energy must be appreciable. Jungers and Yeddanapalli¹² conclude that (376) is important in the photolysis.

Saffer and Davis⁵⁰ heated molten sodium at 320° with ethyl iodide. The products were complex, and consisted mainly of C₂H₄, C₂H₆, and CsH₈, with lesser amounts of H₂, CH₄, C₃H₆, C₄H₈, and C₄H₁₀. They suggest that reactions (37a) and (376) occur. However, the reaction is undoubtedly heterogeneous.

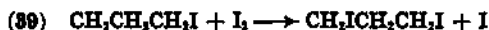


Jones and Ogg³⁸ (see XI-17) assumed reaction (38a) as a step in the thermal decomposition of *n*-propyl iodide. By analogy with the reaction



they assume JEW = 13.4 kcal. They also assume that the reaction occurs in the decomposition of isopropyl iodide.⁴¹

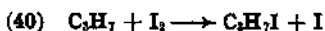
As discussed in section XI-14, Ogg and Priest³⁷ have investigated the thermal and photochemical reaction between cyclopropane and iodine, and suggest the occurrence of (386). Their results, together with certain assumptions as to bond strengths lead to *E*_{38b} = 27.4 kcal. The basis on which this value rests is, however, by no means secure.



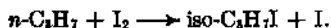
This reaction has also been assumed by Ogg and Priest³⁷ as a step in the mechanism of the thermal and photochemical reaction between cyclo-

⁸⁴ G. G. Joris and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 47, 135 (1938).

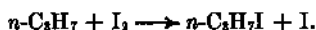
propane and iodine. (See XI-14.) They assume a value of about 12 kcal. for E_0 by analogy with the reaction



As discussed in section XI-17, Jones and Ogg,³⁸ from experiments on the thermal decomposition of *n*-propyl iodide concluded that reaction (40) was the rate-controlling step, the actual reaction being



Their mechanism is consistent with a value of E_{40} of 13.2 kcal., and a rather unlikely steric factor of about 10^{-5} . Schumacher³⁹ has criticized the mechanism. His proposed mechanism does not lead to a value for E_{40} , but he suggests that the reaction occurring is

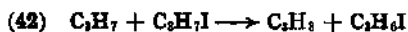
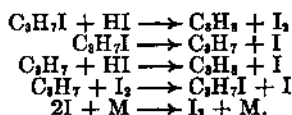


Jones⁵⁵ in summing up the results of a number of investigations on the decomposition of iodides gives $E_{40} = 12.6$ kcal. This is merely Jones' and Ogg's value of 13.2 kcal. corrected to the "true" activation energy by subtracting $\frac{1}{2}RT$.

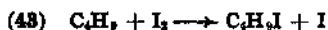
Ogg³⁴ has suggested the occurrence of reaction (40) as a step in the reaction between *n*-propyl iodide and hydrogen iodide. (See XI-41.)



Ogg³⁴ has investigated the thermal reaction of *n*-propyl iodide with hydrogen iodide, and proposes a mechanism similar to that for the corresponding reactions of methyl and ethyl iodides, viz.,



This reaction has been assumed^{38, 41} as a step in the pyrolysis of *n*- and iso-propyl iodides. (See XI-17.)



Ogg and Polanyi⁴⁴ have investigated the decomposition of sec-butyl iodide. As discussed in section XI-19, they conclude from the C—I bond strength and the activation energy of the reverse reaction that $E_{43} = 14.2$ kcal., but more recent estimates of the C—I bond strength would give a value of ca. 8 kcal.

"J. L. Jones, *J. Am. Chem. Soc.*, 60, 1877 (1938).

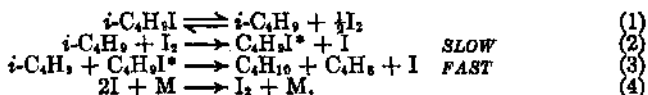
The kinetics of the pyrolysis of iso-butyl iodide have been investigated by Jones.⁵⁶ The overall reaction is similar to that of the other iodides, viz.,



The rate data are expressed by the equation

$$-\frac{d}{dt} [\text{C}_4\text{H}_9\text{I}] = k[\text{C}_4\text{H}_9\text{I}][\text{I}_2]^{\frac{1}{2}},$$

and the overall activation energy is 37.8 kcal. The following mechanism is consistent with the results



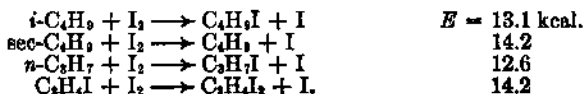
where $\text{C}_4\text{H}_9\text{I}^*$ is an activated molecule of some sort. In view of the history of activated molecule mechanisms in thermal reactions, this seems open to considerable doubt. The mechanism yields the value

$$E_2 \sim 13.1 \text{ kcal.}$$

If we assume that the rate of the reaction



is the same as that of reaction (2), then for reactions of this type we have the following activation energies:



The results thus form a rather consistent picture. The actual values, however, should be taken with reserve, in view of the work of Butler and Polanyi³⁵ (see III-1), which indicates that the C—I bond strength is considerably higher than the values derived by Ogg and by Jones.

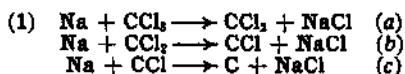


This reaction has been assumed to be a step in the mechanism of the pyrolysis of iso-butyl iodide by Jones. (See section XI-43.)

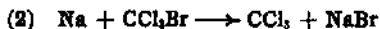
Chapter XII

Systems Containing Sodium

The data on the reactions of sodium atoms with organic compounds have all been obtained by the "diffusion flame" method or by the "life period" modification of it, as described in section II-3. For a review of early work, and a comparison of the results with a variety of compounds see ref. (1), and for a more recent review see ref. (1a). Practically all authors have followed Hartel and Polanyi² in calculating collision yields on the assumption of a collision cross-section of $35 \times 10^{-16} \text{ cm}^2$. This value is undoubtedly too high, but makes no difference in the relative values of the activation energies calculated for different substances. Unless otherwise indicated all activation energies have been calculated from the collision yield, C , at a single temperature, assuming a steric factor of unity.



Bawn and Dunning³ explain the luminescence produced in the reaction of sodium atoms with CCl_4 as due to the occurrence of (1a). From an energetic standpoint it is necessary to assume that the CCl_2 is produced directly in a singlet state and not as a diradical which later isomerizes to CCl_2 . (See section XII-18 for the analogous case of CH_2 .) The main product of the reaction is carbon, which suggests the occurrence of (1b) and (1c)



Haresnape, Stevels, and Warhurst⁴ investigated the reaction at 240° using hydrogen as a carrier gas. By the diffusion flame method a collision yield of 1J1.7 was obtained, corresponding to an activation energy of 0.5 kcal.⁶ By the "life period" method the collision yield was 1J5.3.

¹ M. Polanyi, *Atomic Reactions*, London, 1932.

¹⁰ C. E. H. Bawn, *Ann. Repts. Chem. Soc.*, **1942**, 36.

² H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

³ C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, 36, 185 (1939).

⁴ J. N. Haresnape, J. M. Stevels, and E. Warhurst, *Trans. Faraday Soc.*, 36, 465 (1940).

⁵ D. J. Le Roy and E. W. R. Steacie, *Annual Tables of Physical Constants*, Section 602(c), 1942.

(3) $\text{Na} + \text{CCl}_4 \longrightarrow \text{CCl}_3 + \text{NaCl}$

Hartel and Polanyi,² by the diffusion flame method using hydrogen as a carrier found a collision yield of 1/1.7 for the reaction, corresponding to an activation energy of approximately zero.

By the same method Hartel, Meer, and Polanyi⁶ compared the rates of a large number of organic halogen compounds. Assuming a collision yield of 1/10000 for CH_3Cl at 275°, they found a value of 1/25 for reaction (7).

Heller and Polanyi⁷ quote unpublished work by Heller as leading to a collision yield of 1/2. The temperature is not stated but was probably about 270°. Heller and Polanyi's own results, also by the diffusion flame method led to a velocity constant at 270° of $9.63 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. This corresponds to a collision yield of 1/6.5.

Bawn and Dunning³ found that the reaction was accompanied by intense luminescence. (See also XII-1.)

Haresnape, Stevels, and Warhurst,⁴ using hydrogen as a carrier and a temperature of 240° found a collision yield of 1/5.5 by the diffusion flame method, and of 1/5.3 by the life period method. The value by the diffusion flame method corresponds to an activation energy of 1.7 kcal.⁵

(4) $\text{Na} + \text{CFBr}_3 \longrightarrow \text{CFBr}_2 + \text{NaBr}$

By the "life period" method, Haresnape, Stevels, and Warhurst⁴ at 255° obtained values of the rate constant in two experiments of 91.0 and $89.7 \times 10^{-12} \text{ cc. mol}^{-1} \text{ sec}^{-1}$. This corresponds to a collision yield of 1/5.5, assuming a collision cross-section of $3.5 \times 10^{-15} \text{ cm}^2$. This cross-section is probably somewhat high, but they follow Hartel and Polanyi² in assuming this value for all the substances investigated. Results obtained by the diffusion flame method gave a collision yield of 1/2.3, but the "life period" method results are probably more reliable. The value of 1/5.5 corresponds to an activation energy of 0.9 kcal., assuming a steric factor of unity.⁶

**(5) $\text{Na} + \text{CNBr} \longrightarrow \text{CN} + \text{NaBr}$ (a)
 $\longrightarrow \text{Br} + \text{NaCN}$ (b)**

Curry and Polanyi⁸ investigated the products formed in the reaction. At 320° to 400° the ratio $\frac{\text{NaCN}}{\text{NaBr}}$ was in the region 1/20 to 1/200, the results being very erratic. It follows that (5a) is considerably faster than (5b). The activation energy and collision yield were not determined, but

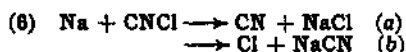
⁶ H. v. Hartel, N. Meer, and M. Polanyi, *Z. physik. Chem.*, **B19**, 139 (1932).

⁷ W. Heller and M. Polanyi, *Trans. Faraday Soc.*, **32**, 633 (1936).

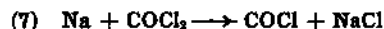
⁸ J. Curry and M. Polanyi, *Z. physik. Chem.*, **B20**, 276 (1933).

on general grounds E_s would be expected to be less than that of the corresponding reaction with CNCl , i.e., $E_s < 2.0$ kcal.

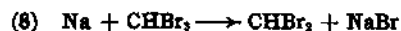
Evans and Walker⁸⁰ have recently reinvestigated the reaction by the diffusion flame method. They obtained a collision yield of 1/4.2 at 273°, corresponding to an activation energy of 1.6 kcal.



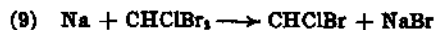
Hartel and Polanyi² investigated the reaction by the diffusion flame method, and found a collision yield of 1/6.3 at 250° corresponding to an activation energy of 2.0 kcal. Curry and Polanyi⁸ paid special attention to the relative importance of reactions (a) and (b). It was found that at temperatures from 320° to 400° the ratio $\frac{\text{NaCN}}{\text{NaCl}}$ was in the range 1/40 to 1/500, the results being very much scattered. This shows definitely, however, that (6a) is considerably faster than (6b). In a more recent investigation Evans and Walker⁸⁰ found a collision yield of 1/4.7 at 285°, equivalent to an activation energy of 1.7 kcal.



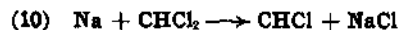
Heller and Polanyi⁷ investigated the reaction by the diffusion flame method. The reaction was accompanied by luminescence. The velocity constant at 270° was $8.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, corresponding to a collision yield of 1/7.4, and to an activation energy of 2.3 kcal.⁶



Haresnape, Stevels, and Warhurst⁴ by the diffusion flame method found $C = 1/1.4$ at 250°, and by the life period method found $C = 1/6.3$ at 255°. Hydrogen was used as a carrier gas in both cases. The diffusion flame result corresponds to an activation energy of 0.3 kcal.



Haresnape, Stevels, and Warhurst⁴ found a collision yield of 1/2.8 by the diffusion flame method at 250° and of 1/9.0 by the life period at 255°. The velocity constant at 250° (diffusion flame method) was $1.80 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. The diffusion flame results correspond to an activation energy of 1.0 kcal.⁵



Bawn and Dunning³ suggest that the luminescence observed in the reaction of sodium atoms with CHCl_3 is due to the occurrence of this reaction.

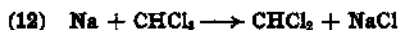
⁸⁰ A. G. Evans and H. Walker, *Trans. Faraday Soc.*, 40, 384 (1944).



Haresnape, Stevels, and Warhurst⁴ using hydrogen as a carrier found values of the collision yield of 1/4.4 by the diffusion flame method at 250°, and of 1/13.5 at 255° by the life period method. The diffusion flame result corresponds to an activation energy of 1.5 kcal.⁵

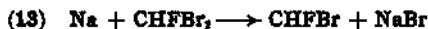
The substitution of bromine for chlorine in halogenated methanes results in an increase in the collision yield, as exemplified by the series:

CHCl ₃	CHCl ₂ Br	CHClBr ₂	CHBr ₃
1/50	1/4.4	1/2.8	1/1.4



Hartel and Polanyi² by the diffusion flame method found a collision yield of 1/6.5 at 270°, corresponding to $E_{12} = 2.0$ kcal. Hartel, Meer, and Polanyi⁶ by the same method found $C = 1/100$ at 275°, relative to an assumed value of $C = 1/10000$ for CH₃Cl. Heller, in unpublished work quoted by Heller and Polanyi⁷ found $C = 1/22$, at a temperature which was not stated but was probably about 250°. Heller and Polanyi⁷ themselves found $C = 1/50$ at 250°. The latter value is probably as reliable as any, and corresponds to $E_{12} = 4.0$ kcal.⁵

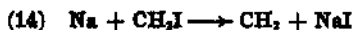
Bawn and Dunning³ have observed that the reaction is accompanied by luminescence.



Haresnape, Stevels, and Warhurst⁴ investigated the reaction by the life period method. In a number of experiments with varying sodium pressure at 255° they obtained the following values of the velocity constant.

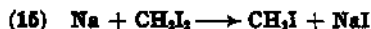
Temperature of sodium	
192°	$4.85 \times 10^{13} \text{ cm.}^3 \text{ mol.}^{-1} \text{ sec.}^{-1}$
	4.17 "
	5.90 "
	5.75 "
220°	4.60 "
	4.50 "
	4.30 "

These correspond to a collision yield of 1/11 at 255° and to an activation energy of 2.5 kcal.



Bawn and Dunning⁸ suggest that the luminescence produced in the reaction of sodium atoms with CH₂I₂ is due to the occurrence of reaction (14). For a discussion of the mechanism, see the analogous case of CH₂Cl₂. (See sections XII-18 and XII-20.)

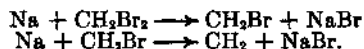
Bawn and Milsted⁹ using nitrogen as a carrier, found ethylene to be the sole product of the reaction.



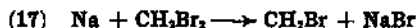
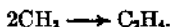
The reaction is accompanied by luminescence, and with nitrogen as a carrier ethylene is the sole product.⁹ (See sections XII-18 and XII-20.)



Bawn and Dunning³ have suggested that the luminescence observed in the reaction of sodium atoms with CH_2Br_2 is due to the occurrence of the steps



(For a discussion see the analogous case of CH_2Cl_2 in sections XII-18 and XII-20.) Bawn and Milsted⁹ found ethylene to be the sole product of the reaction, obviously by

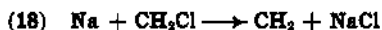


Haresnape, Stevels, and Warhurst⁴ by the life period method using hydrogen as a carrier found values of the velocity constant of the reaction at 255° of 31.0, 31.5, 25.0, and $29.8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, corresponding to $C = 1/17.0$. By the diffusion flame method at 250° they found $C = 1/13.2$, equivalent to $E_{17} = 2.6 \text{ kcal}.$ ⁵

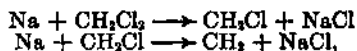
Bawn and his co-workers^{3, 9} found that the reaction was accompanied by luminescence and that with nitrogen as a carrier ethylene was the sole product of the reaction. (See XII-18 and XII-20.)

The successive replacement of hydrogen by F, Cl, and Br in the halogen compound results in a greater reactivity, as shown by the series:

Compound	CH_2Br_2	CH_2FBr	CHClBr	CHBr
Collision yield (by the diffusion flame method)	1/13.2	1/11	1/2.8	1/1.4



Bawn and Dunning³ investigated the luminescence produced in the reaction of sodium atoms with methylene chloride. They conclude that the reaction proceeds in steps:

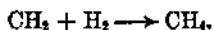


and that the light (the sodium *D* doublet) is produced in the latter reaction. Reaction (18) is only about 25 to 30 kcal. exothermic if the CH_2 produced

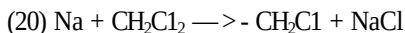
⁹ C. E. H. Bawn and J. Milsted, *Trans. Faraday Soc.*, 36, 889 (1939).

is in the triplet state (*i.e.*, as the biradical $\text{—CH}_2\text{—}$), while the excitation energy of the *D* doublet is 48 kcal. The mechanism is, therefore, only possible if the methylene formed in reaction (18) is produced directly in the singlet state (*i.e.*, as a molecule with divalent carbon), since the transition from the singlet to the triplet state is about 27 kcal. exothermic.

Bawn and Milsted⁹ found ethylene to be the sole product of the reaction when nitrogen was used as the carrier gas. In the presence of hydrogen methane was also formed, presumably by the reaction



Haresnape, Stevels, and Warhurst⁴ using the life period method with hydrogen as a carrier found values of the velocity constant of reaction (19) at 255° of 17.8, 16.6, 16.4, and 18.7 $\times 10^{12} \text{ cm.}^8 \text{ mol.}^{-1} \text{ sec.}^{-1}$. This corresponds to a collision yield of 1/28 at 255°. By the diffusion flame method the same authors found $C = 1/26$ at 250°, leading to a value of 3.3 kcal. for the activation energy.⁵

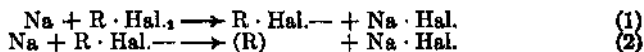


Hartel and Polanyi² by the diffusion flame method found $C = 1/122$ at 240°, corresponding to $E_{20} = 4.9$ kcal. Hartel, Meer, and Polanyi⁶ found $C = 1/900$ at 275°, relative to an assumed collision yield of 1/10000 for CH_3Cl . Heller and Polanyi⁷ quote an unpublished value of $C = 1/310$ obtained by Heller. The temperature was not stated, but was probably about 250°.

Haresnape, Stevels, and Warhurst⁴ investigated the reaction by the diffusion flame method with an improved technique, and by the life period method. In both cases hydrogen was used as a carrier. By the life period method they obtained values of the velocity constant at 255° of 0.60, and 0.59 $\times 10^{12} \text{ cm.}^3 \text{ mol.}^{-1} \text{ sec.}^{-1}$, corresponding to a value of $C = 1/833$. By the diffusion flame method they found $C = 1/760$ at 250°, leading to $E_{20} = 6.8$ kcal.⁵

Bawn and Milsted⁹ found that the reaction was accompanied by luminescence. Nitrogen was used as a carrier, and ethylene was the sole product of the reaction. Bawn and Dunning³ made a more detailed investigation of the luminescence of this and a large number of other reactions involving dihalides. Since their conclusions apply equally to all the reactions, it will be convenient to discuss them in a general way here.

In practically all reactions of sodium vapor with dihalides intense luminescence is produced, and this is mainly the sodium *D* doublet, the excitation energy of which is 48.6 kcal. In all cases the light is produced homogeneously, and it seems certain that the reaction proceeds in steps:

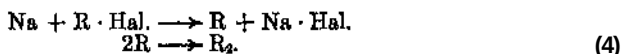


The light is produced in the second step, and (R) is either a biradical, an olefin, or a cyclic compound. Normally accepted bond strength values lead to the conclusion that reaction (1) is exothermic to the extent of 25 to 30 kcal. irrespective of the compound under investigation, and of the nature of the halogen atoms. Reaction (1) cannot, therefore, be the source of the light. If (R) is a biradical, it seems very unlikely that reaction (2) can be the source of the luminescence, since it is most unlikely that the second halogen atom should be 20-30 kcal. more weakly bound than the first. It follows, therefore, that (R) must be produced directly as a molecule of some sort in which the rearrangement from the biradical to the molecule is exothermic to the extent of 25 kcal. or so.

In the case of the methylene halides, the sole product of the reaction with sodium vapor is ethylene, and the only possible mechanism for its formation appears to be



A termolecular mechanism is far too slow to account for the fast reaction, and they, therefore, conclude that reaction (3) is heterogeneous. The light producing reaction is homogeneous and is therefore not (3). Further evidence for this conclusion lies in the fact that light is not produced with monohalogen compounds. These undoubtedly proceed by the mechanism



Since (4) is highly exothermic but never leads to luminescence, it is unlikely that (3) should be the source of luminescence with dihalides.

They conclude further that luminescence cannot arise from reactions involving sodium molecules since (a) such reactions are not sufficiently exothermic, and (6) the luminescence is independent of temperature, while the equilibrium



is of course strongly temperature dependent.

It appears, therefore, that in the reaction



CH₂ is formed as a molecule with divalent carbon rather than as a biradical CH₂·. This transition is about 27 kcal. exothermic, and thus supplies the energy deficiency.



Hartel and Polanyi² by the diffusion flame method with both hydrogen and nitrogen as a carrier found a collision yield of 1/1.6 at 240°, correspond-

ing to an activation energy of 0.30 kcal. Hartel, Meer, and Polanyi⁶ found $C = 1$ at 275° relative to an assumed value of $C = 1/10000$ for methyl chloride. Heller and Polanyi⁹ quote unpublished work by Heller as leading to values of $C = 1$, $E_{21} = 0$: the temperature was not stated.

Evans and Warhurst¹⁰ have discussed the reaction theoretically. They assumed a C—I bond strength of 44 kcal., which makes reaction (21) 26.8 kcal. exothermic. By the transition state method with various approximations they obtained values of E_{21} of 2.0, 6.1, 12.7, 0, 2.8, and 6.0 kcal.

Haresnape, Stevels, and Warhurst⁴ found values of the collision yield of 1/10.6 by the life period method at 255°, and of 1/11.4 by the diffusion flame method at 250°. The latter corresponds to an activation energy of 2.5 kcal.⁵

(22) $\text{Na} + \text{CH}_3\text{Br} \longrightarrow \text{CH}_3 + \text{NaBr}$

Hartel and Polanyi² by the diffusion flame method at 240° with both hydrogen and nitrogen as a carrier found a collision yield of 1/25, and calculated from it an activation energy of 3.2 kcal. Hartel, Meer, and Polanyi⁶ by the same method found $C = 1/50$ at 275° relative to an assumed value of 1/10000 for CH_3Cl . Frommer and Polanyiⁿ by the life period method obtained a value of approximately $1.7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ for the velocity constant at 200°. This is about 5 times higher than previous values under the same conditions. Heller and Polanyi⁷ quote unpublished work by Heller as leading to $C = 1/75$. The temperature was not stated. From this result Evans and Warhurst¹⁰ estimate an activation energy of 4.7 kcal.

Evans and Warhurst¹⁰ have discussed the reaction by the transition state method. They assume a $\text{CH}_3\text{—Br}$ bond strength of 59 kcal., which leads to the conclusion that reaction (22) is 28.8 kcal. exothermic. The calculations by the transition state method with various alternative approximations lead to values of E_{22} of 4.6, 8.7, 14.3, 4.2, 7.1, and 10.0 kcal. These are of the right general order of magnitude, but otherwise the uncertainty is too great to make the results of any value.

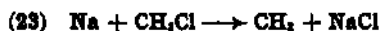
Haresnape, Stevels, and Warhurst⁴ by improved technique with the diffusion flame method with hydrogen as a carrier found $C = 1/135$ at 250°. This corresponds to an activation energy of 5.0 kcal.⁵

Allen and Bawn¹² investigated the reaction by the Paneth technique. The products of the reaction removed both antimony and tellurium mirrors. With antimony they were unable to identify the substance formed. With tellurium the product was definitely identified as dimethyl ditelluride. Methyl radicals have thus been definitely shown to be present.

¹⁰ M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, 35, 593 (1939).

¹¹ L. Frommer and M. Polanyi, *Trans. Faraday Soc.*, 30, 519 (1934).

¹² A. O. Allen and C. E. H. Bawn, *Trans. Faraday Soc.*, 34, 463 (1938).

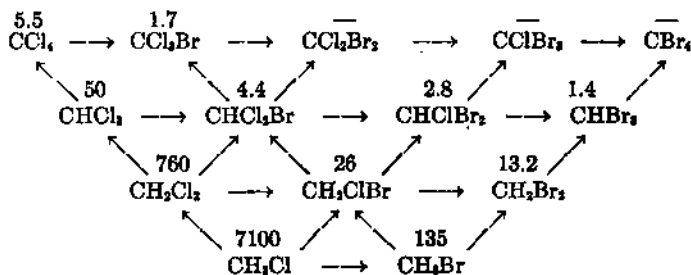


Hartel and Polanyi² investigated the reaction by the diffusion flame method. A number of experiments were made at 260° with both hydrogen and nitrogen as the carrier gas. These gave a mean value of $C = 1/5000$, corresponding to an activation energy of 8.8 kcal. They also determined the activation energy from the temperature coefficient of the rate at temperatures in the range 250° to 500°, and found $E_a = 7.5$ kcal. Measurements by the same method with greater accuracy by Heller (unpublished, quoted in reference (7)) gave a value of $C = 1/7100$. The temperature was not stated. This corresponds to $E_a = 9.7$ kcal.¹⁰

Frommer and Polanyi¹¹ by the life period method with nitrogen as a carrier found the velocity constant at 219° to be $6.0 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. This agrees well with Heller's results.

Evans and Warhurst¹¹ have estimated the activation energy of the reaction by the transition state method. Assuming a $\text{CH}_3\text{—Cl}$ bond strength of 73 kcal., reaction (23) is 24.5 kcal. exothermic. With various alternative approximations they obtained values of E_a of 12.5, 16.2, 17.7, 12, 15, and 13.5 kcal. These all appear to be at least of the right order of magnitude.

Haresnape, Stevels, and Warhurst⁴ have compared the collision yields of various halogenated methanes in the following table, which is arranged to show the various series resulting from successive substitution of one halogen for another, or for hydrogen. The numbers above each substance are the reciprocals of the collision yield, *i.e.*, the average number of collisions necessary to produce one fruitful collision. The arrows show the order of increasing reactivity.



By the diffusion flame method Hartel and Polanyi² found no appreciable reaction at 500°. This means that the collision yield is less than 10^{-7} , and corresponds to an activation energy greater than 25 kcal. Hartel, Meer, and Polanyi⁶ obtained similar results, *viz.*, $C < 10^{-6}$ at 275°.

Evans and Warhurst¹⁰ have discussed the mechanism of the reaction. If a Na—F bond strength of 126 kcal. is assumed, reaction (24) is 10 kcal.

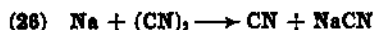
exothermic. A transition state type of calculation gives a value of E_{24} of 52.2 kcal.



Bawn and Evans¹³ investigated the reaction of sodium atoms with nitromethane by the life period method using nitrogen as a carrier. At 255° they found

$$k = 4.5 \times 10^{13} \text{ cm.}^3 \text{ mol.}^{-1} \text{ sec.}^{-1}$$

corresponding to $C = 1/10$ and an activation energy of 2.6 kcal.



Hartel and Polanyi² by the diffusion flame method with nitrogen as a carrier found a collision yield of 1/15000 at 260° corresponding to an activation energy of about 12 kcal. However the collision yield diminished somewhat on raising the temperature to 350°, instead of increasing strongly on account of the high calculated activation energy. They suggest, therefore, that in reality $E \sim 0$, and the small collision yield is due to a small steric factor. This is perhaps to be expected since the reaction involves the breaking of a C—C bond which is in the center of the molecule, *i.e.*, $\text{N}=\text{C}-\text{C}=\text{N}$.



Hartel, Meer, and Polanyi⁶ found a collision yield of 1/2600 at 275°, relative to an assumed value of $C = 1/10000$ for methyl chloride. This corresponds to $E_{27} = 8.6$ kcal.⁵

It may be remarked that the double bond produces a decided diminution in reactivity, thus for $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, $C = 1/800$. On the other hand, the presence of two halogen atoms in the molecule increases the reactivity, since the compound $\text{CH}_2=\text{CHCl}$ gives a value of C of 1/11000.



The results are similar to those for the trans-compound. (See XII-27.) The collision yield at 275° is 1/1800 relative to $C = 1/10000$ for methyl chloride (6). This corresponds to $E_{28} = 8.2$ kcal.⁵



By the diffusion flame method Evans and Walker^{3a} found a collision yield of 1/7.0 at 285°, corresponding to an activation energy of 2.2 kcal.

¹³ C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.*, **33**, 1571 (1937).



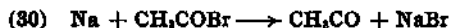
Hartel, Meer, and Polanyi⁶ found a collision yield of 1/11000 at 275° relative to an assumed value of $C = 1/10000$ for methyl chloride. This corresponds to $E_{29} = 10.1$ kcal.⁵



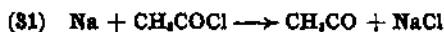
By the diffusion flame method^{5a} the collision yield was found to be 1/218 at 269°, corresponding to an activation energy of 5.8 kcal.



By the diffusion flame method Evans and Walker^{5a} found a collision yield of 1/20.0 at 263°, corresponding to $E_{29B} = 3.2$ kcal.



By the diffusion flame method Hartel and Polanyi² found a collision yield of 1/6.3 at 300°, corresponding to $E_{30} = 2.1$ kcal. This is a *higher* activation energy than that for CH_3COCl found by the same authors. This seems very unlikely and supports the higher value of E_{31} found in later work.



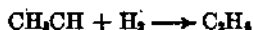
Hartel and Polanyi² by the diffusion flame method with hydrogen as a carrier found a collision yield of 1/5.0 at 270°, equivalent to $E_{31} = 1.7$ kcal. Hartel, Meer, and Polanyi⁶ state that $C \sim 1/100$ at 275° relative to $C = 1/10000$ for methyl chloride. They do not give any details of the work. This corresponds to an activation energy of ca. 5 kcal., and considering that it is a later value from the same laboratory it is probably the more reliable value.. (See XII-30.)



The luminescence accompanying the reaction of sodium atoms with CH_3CHBr_2 has been investigated,^{3,9} and it has also been found that ethylene is the sole product with either nitrogen or hydrogen as a carrier. Bawn and Dunning³ suggested that reaction (32) in which ethylene is formed directly is sufficiently exothermic to satisfy the energy requirements for luminescence. Evans¹⁴ has suggested that the ethylidene radical is formed in a singlet state, rather than the direct formation of ethylene. Bawn and Milsted,⁹ however, showed that no ethane was formed when

¹⁴ M. G. Evans, *Trans. Faraday Soc.*, 35, 193 (1939).

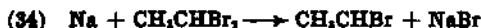
hydrogen was used as a carrier, and consider that this proves the absence of ethylidene, since if it were present the formation of ethane by the reaction



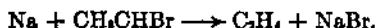
would be expected. (See also XII-34.)



Bawn and Dunning³ suggest that the luminescence observed in the reaction of sodium atoms with $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br}$ is due to the occurrence of reaction (33). (See XII-35.)

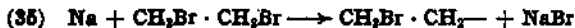


Bawn and Dunning³ investigated the luminescence produced in the reaction. As discussed in section XII-20 there seems to be no doubt that the reaction proceeds in stages, (34) being followed by

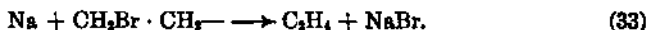


The energy required can only be obtained provided that the product of the latter reaction is not a biradical $\text{CH}_3\text{CH}=\cdot$, but is a molecule of some sort. The product is almost entirely ethylene, and Bawn and Dunning suggest that it is formed in reaction (32) in one step and not through the intermediary of ethylidene. However, the light yield of the luminescence is much less with CH_3CHBr_2 than with $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br}$, and traces of C_4 hydrocarbons were formed as well as ethylene. They therefore suggest that perhaps a certain fraction of the reaction proceeds via the ethylidene radical.

However, Bawn and Milsted⁹ in later work found no trace of C_4 hydrocarbons in the products. They also found that even with hydrogen as a carrier ethylene was the sole product. They therefore rule out the possibility of ethylidene formation, and suggest that reaction (34) is followed exclusively by (32).

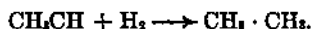


Bawn and Dunning³ found that the reaction was accompanied by luminescence, and that ethylene was the sole product. As in similar cases (see XII-20 and XII-34), they suggest that the reaction occurs in stages, (35) being followed by

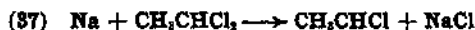


In the reaction of sodium atoms with CH_3CHCl_2 (see XII-37), the sole product is ethylene with both nitrogen and hydrogen as carriers.⁹ Bawn

and Milsted suggest that ethylene is formed directly in one step by reaction (36), and that the ethylidene radical, CH_3CH , does not occur as an intermediate stage, since otherwise it would be expected to form ethane when hydrogen is used as a carrier,



Evans¹⁴ had previously suggested that the luminescence accompanying the reaction could be explained if it were assumed that the CH_3CH radical were formed in a singlet state. He criticizes the postulation of reaction (36) on the grounds that it involves the simultaneous breaking of a C—Cl bond, the change of a C—C to a C=C bond, and the wandering of a hydrogen atom. (For a further discussion see the analogous case of CH_3CHBr_2 in sections XII-32 and XII-34.)



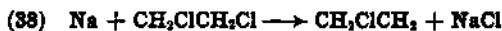
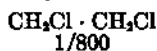
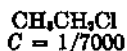
Hartel and Polanyi² by the diffusion flame method found $C = 1/71$ with nitrogen as a carrier at 230° , and $C = 1/200$ with hydrogen as a carrier at 240° . Hartel, Meer, and Polanyi⁶ found $C = 1/650$ at 275° relative to an assumed value of $C = 1/10000$ for methyl chloride. This corresponds to $E_{37} = 7.1$ kcal.⁵

Bawn and Milsted⁹ using nitrogen and hydrogen as carriers found ethylene to be the sole product. They suggest that the reaction occurs in steps, (37) being followed by

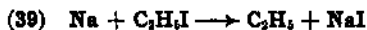


(See XII-36.)

The reactivity of chlorinated ethanes increases strongly when a second halogen atom is added, especially if both halogens are attached to the same carbon atom. This is illustrated by the series⁶



Hartel and Polanyi² by the diffusion flame method with hydrogen as a carrier found a collision yield of $1/220$ at 270° , corresponding to $E_{38} = 5.8$ kcal. Hartel, Meer, and Polanyi⁶ using the collision yield for CH_3Cl as a standard found $C = 1/800$ at 275° . The latter value corresponds to $E_{38} = 7.3$ kcal.⁵ By the same method Evans and Walker²² found a collision yield of $1/526$ at 285° , corresponding to $E_{38} = 7.0$ kcal.



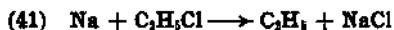
Hartel and Polanyi² by the diffusion flame method using both hydrogen and nitrogen as carriers found a collision yield of $1/6.0$ at 240° and hence

$Z39 = 1.7$ kcal. Hartel, Meer, and Polanyi⁶ found a collision yield of 1 at 275° relative to a value of 1/10000 for methyl chloride. Evans and Walker^{8a} found a collision yield of 1/2.5 at 276°, corresponding to $Z39 = 1.0$ kcal.



Hartel and Polanyi² found a collision yield of 1/75 at 240° by the diffusion flame method, and estimated EM to be 4.4 kcal. Hartel, Meer, and Polanyi⁶ found $C = 1/50$ at 275°, relative to an assumed value of $C = 1/10000$ for CH_3Cl . Evans and Walker^{8a} found $C = 1/100$ at 263°, corresponding to $Z40 = 4.9$ kcal.

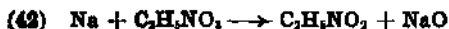
Allen and Bawn¹² have detected free radicals in the reaction by the Paneth method using antimony mirrors.



Hartel and Polanyi² using the diffusion flame method with hydrogen as a carrier found a collision yield of 1/900 at 270°, corresponding to $E41 = 7.3$ kcal. In later work by the same method with nitrogen as a carrier Hartel, Meer, and Polanyi⁶ found $C = 1/7000$ at 275° relative to an assumed value for methyl chloride of 1/10000. This is equivalent to $Ea = 9.7$ kcal.¹⁴



By the diffusion flame method Evans and Walker^{**} found a collision yield of 1/980 at 285°, corresponding to $Ea_A = 7.6$ kcal.



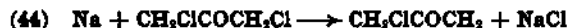
Bawn and Evans¹³ investigated the reaction by the life period method using nitrogen as a carrier. The velocity constant at 254° was $4.2 \times 10^{13} \text{ cm}^8 \text{ mol}^{-1} \text{ sec}^{-1}$, corresponding to a collision yield of 1/9.5, and to $E_{42} = 2.35$ kcal.



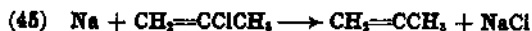
Evans and Walker⁸⁰ found a collision yield of 1/847 at 285°, corresponding to $E_{42A} = 7.5$ kcal.



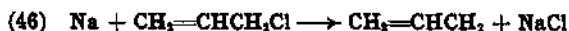
Bawn and Dunning³ observed luminescence (the sodium D-line) in the reaction of sodium atoms with $\text{CH}_2\text{ClCOCH}_2\text{Cl}$. By analogy with other similar reactions, reaction (43) probably occurs.



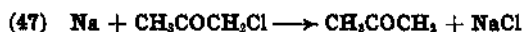
Bawn and Dunning³ observed luminescence accompanying this reaction.



Hartel, Meer, and Polanyi⁶ found $C = 1/5500$ for this reaction at 275° relative to an assumed value of $C = 1/10000$ for methyl chloride. This is equivalent to $E_{45} = 9.4$ kcal.⁵

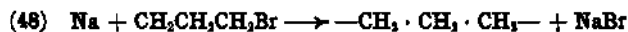


Hartel, Meer, and Polanyi⁶ found a collision yield of $1/250$ at 275° by the diffusion flame method, relative to an assumed collision yield of $1/10000$ for methyl chloride. This corresponds to an activation energy of 6.0 kcal.⁶ Evans and Walker⁸⁰ found $C = 1/143$ at 260° , corresponding to $E_{46} = 5.3$ kcal.

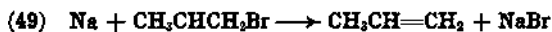


Hartel, Meer, and Polanyi⁶ by the diffusion flame method found a collision yield of $1/10$ for reaction (47) relative to an assumed value of $1/10000$ for methyl chloride. This corresponds to $E_n = 2.5$ kcal.⁵

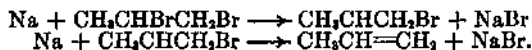
Haresnape^{14a} has identified diacetonyl as a product of the reaction, thus proving the presence of the acetonyl radical.



This reaction is presumably a step in the reaction of sodium atoms with $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$.¹⁵ The mechanism is discussed in detail in section XII-50.



In the reaction of sodium atoms with $\text{CH}_3\text{CHBrCH}_2\text{Br}$ (XII-51) luminescence occurs and propylene is the sole product.³ Bawn and Dunning suggest that the reaction occurs in steps



In order to account for the excitation energy of the luminescence (the sodium D-line has an excitation energy of 48.6 kcal.) it is necessary to assume that propylene is formed in one step in reaction (49), rather than as a biradical which later isomerizes to propylene. (See the analogous cases discussed in sections XII-20 and XII-36.)

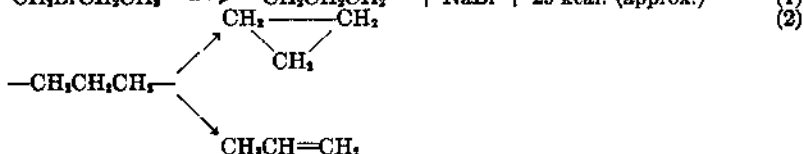
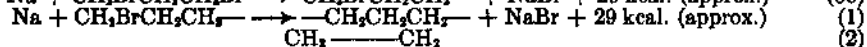


Bawn and Hunter¹⁵ investigated the reaction of sodium atoms with trimethylene bromide in an apparatus of the diffusion flame type, using

^{14a} J. N. Haresnape, *Thesis*, University of Manchester, quoted in footnote (1a).

¹⁶ C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, 34, 608 (1938).

nitrogen as a carrier gas at temperatures in the neighbourhood of 350°. The products of the reaction consisted, under normal conditions, entirely of cyclopropane and propylene, in the ratio of roughly two to one. They suggest that the reaction occurs in stages



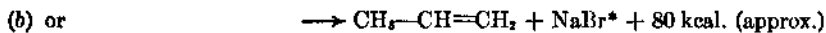
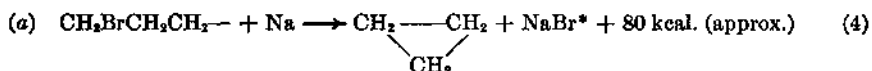
Proof of the intermediate existence of the monoradical, $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{---}$, was given by experiments with a lower concentration of sodium. This diminished the probability of reaction (1) and thus favoured the association reaction



and under these conditions the products included 1,6-dibrom hexane.

It was found that the ratio of propylene to cyclopropane in the products was decreased by increasing the pressure of the carrier gas or by decreasing the trimethylene bromide pressure. It thus appears that propylene must be formed from the biradical by a wall reaction, while cyclopropane is formed homogeneously.

The reaction is accompanied by chemiluminescence, the sodium D-line (with an excitation energy of 48.6 kcal.) being emitted. Neither reaction (50) nor (1) is sufficiently exothermic to account for the luminescence. The only possible explanation of the luminescence, therefore, appears to be the occurrence to some extent of a reaction analogous to (1) in which either propylene or cyclopropane is formed directly, without the intervention of the biradical, viz.,



followed by



By comparing the light yield with that of other reactions they conclude that between 1 and 30 per cent of the reaction must go via (4), the remainder occurring by (1).

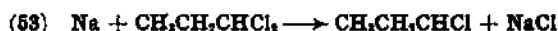
Bawn and Dunning⁸ have discussed the reaction, and conclude that since the light yield is always small in reactions involving the migration of a hydrogen atom, it is unlikely that propylene formed *hy* (4b) is the cause of the luminescence, and that cyclopropane formation by (4a) is, therefore, responsible for the light yield.



Luminescence occurs in this reaction,³ and the sole product is propylene. The mechanism of its production is discussed in section XII-49.

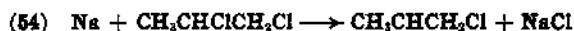
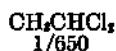
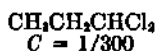


The luminescence observed by Bawn and Dunning³ in the reaction of sodium atoms with $\text{CH}_3\text{CCl}_2\text{CH}_3$ is probably due to the occurrence of reaction (52).

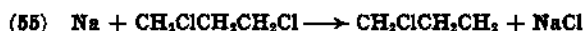


Hartel, Meer, and Polanyi⁶ by the diffusion flame method found a collision yield of 1/300 at 275° relative to $C = 1/10000$ for methyl chloride. This corresponds to $E_{53} = 6.2$ kcal.⁵

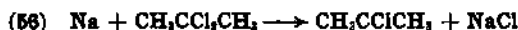
The increase in reactivity with increasing length of the hydrocarbon chain is shown by the series



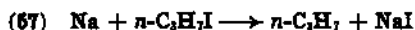
According to measurements by the diffusion flame method by Hartel, Meer, and Polanyi⁶ the collision yield of reaction (54) is 1/500 at 275° relative to $C = 1/10000$ for methyl chloride. Whence $E_{54} = 6.8$ kcal.⁵



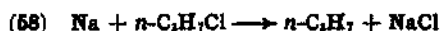
Hartel, Meer, and Polanyi⁶ by the diffusion flame method found $C = 1/1000$ at 275° relative to an assumed value of 1/10000 for methyl chloride. On this basis the activation energy of reaction (55) is 7.5 kcal.



Hartel, Meer, and Polanyi⁶ found a collision yield of 1/180 at 275°, from which E_{56} is 5.7 kcal.⁵ Bawn and Dunning³ have found that the reaction is accompanied by luminescence.

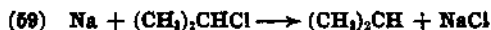


Hartel and Polanyi² by the diffusion flame method found a collision yield of 1/19 at 240°, corresponding to an activation energy of 3.0 kcal.

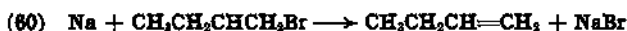


Hartel, Meer, and Polanyi⁶ investigated the reaction by the diffusion flame method at 275°. The collision yield was found to be 1/4400 relative to an assumed value of 1/10000 for methyl chloride under the same con-

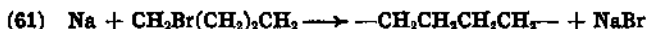
ditions. This corresponds to a value of E_{58} of 9.2 kcal.⁵ Evans and Walker⁸⁰ by the same method found a collision yield of 1/5000 at 261°, corresponding to $E_{58} = 9.0$ kcal.



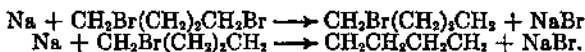
Hartel, Meer, and Polanyi⁶ by the diffusion flame method found $C = 1/3300$ at 275° relative to the assumed value of $C = 1/10000$ for CH_3Cl . Whence $E_{59} = 8.9$ kcal.⁵



Reaction (60) has been assumed by Bawn and Dunning³ as a step in the reaction of sodium atoms with $\text{CH}_2\text{BrCHBrCH}_2\text{CH}_3$. In order to account for the luminescence which accompanies the reaction it is necessary on energetic grounds to assume that butylene is formed in one step in reaction (60) rather than a biradical which later isomerizes to butylene. Bawn and Milsted⁹ also found butylene to be the sole product of the reaction.



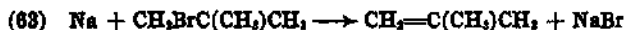
In the reaction⁹ of $\text{CH}_2\text{Br}(\text{CH}_2)_2\text{CH}_2\text{Br}$ with sodium atoms, the gaseous products are roughly 41 per cent ethylene and 59 per cent butylene. Bawn and Milsted suggest that the tetramethylene biradical is formed in stages,



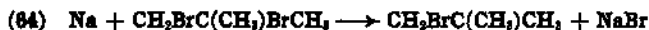
The biradical then decomposes to give the products formed experimentally, viz.,



This reaction has been assumed³ as a step in the reaction of sodium atoms with $\text{CH}_3\text{CHBrCHBrCH}_3$.



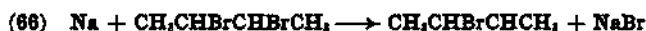
Reaction (63) has been assumed³ as a step in the reaction of sodium atoms with $\text{CH}_2\text{BrC}(\text{CH}_3)\text{BrCH}_3$.



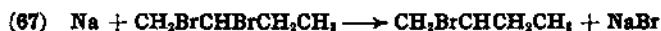
Bawn and Dunning³ found this reaction to be accompanied by luminescence (the sodium D-line). The reaction appears to proceed in stages, (64) being followed by (63).



Bawn and Milsted⁹ investigated this reaction in an apparatus of the diffusion flame type. The products were 41 per cent ethylene and 59 per cent butylene. For a discussion see XII-61.



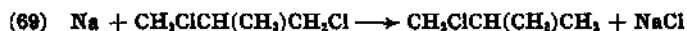
Luminescence was observed to accompany this reaction by Bawn and Dunning.³ The reaction undoubtedly occurs in stages, (66) being followed by (62).



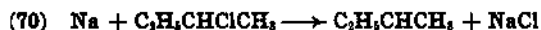
Bawn and his co-workers^{3,9} have investigated this reaction in an apparatus of the diffusion flame type. Luminescence occurs, the sodium D-line being emitted, and the sole gaseous product is butylene. The reaction unquestionably occurs in stages (67) being followed by (60). (See also XII-60.)



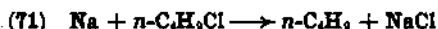
This reaction has been assumed³ as a step in the reaction of sodium atoms with $\text{CH}_2\text{ClCH}(\text{CH}_3)\text{CH}_2\text{Cl}$.



The reaction is accompanied by luminescence.³



The reaction was investigated by the diffusion flame method by Hartel, Meer, and Polanyi.⁶ At 275° the collision yield was 1/2200 relative to a value of 1/10000 for methyl chloride. This corresponds to an activation energy of 8.4 kcal.⁶

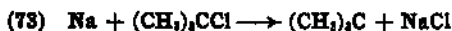


Hartel, Meer, and Polanyi⁶ by the diffusion flame method at 275° found a collision yield of 1/3300 for reaction (71) relative to an assumed value of 1/10000 for methyl chloride. This corresponds to $E_{71} = 8.8$ kcal.⁶

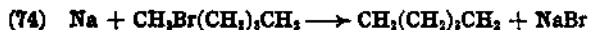


Hartel, Meer, and Polanyi⁶ by the diffusion flame method at 275° found a collision yield of 1/3500 for reaction (72) relative to an assumed value of $C = 1/10000$ for methyl chloride. This is equivalent to an activation energy of 8.9 kcal.

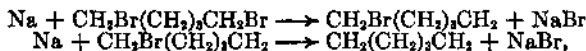
Bawn and Evans¹⁶ by the life period method at 260°, using hydrogen as a carrier, found a velocity constant of $6.4 \times 10^{10} \text{ cm.}^3 \text{ mol.}^{-1} \text{ sec.}^{-1}$. The velocity constant was found to be independent of the rate of flow and of the pressure of butyl chloride over a wide range (from 1.08 to 37.4×10^{-8} mol. per sec. flow rate, and from 0.018 to 0.115 mm. partial pressure).



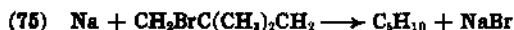
Hartel, Meer, and Polanyi⁶ by the diffusion flame method at 275° found a collision yield for reaction (73) of 1/1500, relative to $\text{C} = 1/10000$ for methyl chloride. On this basis $E_{73} = 8.0 \text{ kcal.}^{14}$



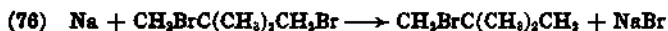
Bawn and Milsted⁹ investigated the reaction of sodium atoms with $\text{CH}_2\text{Br}(\text{CH}_2)_3\text{CH}_2\text{Br}$ in an apparatus of the diffusion flame type. There is little doubt that the reaction occurs in stages:



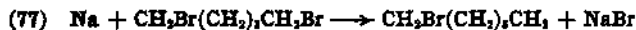
followed by the decomposition and isomerization of the pentamethylene radical. The products were found to be 10 per cent C_2H_4 , 10 per cent C_3H_6 (probably a mixture of propylene and cyclopropane), and 80 per cent C_5H_{10} (probably a mixture of amylenes and cyclopentane).



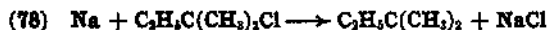
This reaction has been assumed by Bawn and Dunning³ as a step in the reaction of sodium atoms with $\text{CH}_2\text{BrC}(\text{CH}_3)_2\text{CH}_2\text{Br}$.



Bawn and Dunning³ found that the reaction was accompanied by luminescence, the sodium D-line being emitted. The reaction undoubtedly occurs in stages, (76) being followed by (75).

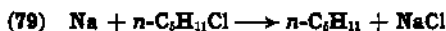


Bawn and Dunning³ found that the reaction was accompanied by luminescence (the sodium D-line). Bawn and Milsted investigated the products of the reaction.⁹ The results are discussed in section XII-74. The reaction appears to occur in stages (77) being followed by (74).



Hartel, Meer, and Polanyi⁶ by the diffusion flame method found a collision yield of 1/600 at 275°, relative to an assumed value for methyl chloride of 1/10000. This is equivalent to an activation energy of 7.0 kcal.¹⁴

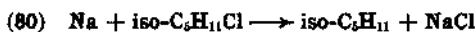
¹⁴ C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.*, **33**, 1580 (1937).



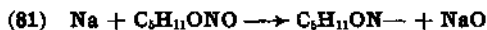
Hartel, Meer, and Polanyi⁶ found $C = 1/2200$ at 275° by the diffusion flame method relative to an assumed value of $C = 1/10000$ for CH_3Cl . This corresponds to an activation energy for reaction (79) of 8.4 kcal.⁶

An increase in the length of the hydrocarbon chain is accompanied by an increase in reaction rate, as shown by the data below:

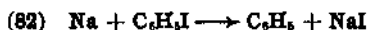
Substance	Collision yield
CH_3Cl	1/10000
$\text{C}_2\text{H}_5\text{Cl}$	1/7000
$n\text{-C}_3\text{H}_7\text{Cl}$	1/4400
$n\text{-C}_4\text{H}_9\text{Cl}$	1/3300
$n\text{-C}_5\text{H}_{11}\text{Cl}$	1/2200



Hartel and Polanyi² by the diffusion flame method with hydrogen as a carrier found a collision yield at 230° of roughly $1/234$, equivalent to $E_{50} = 5.4$ kcal. Hartel, Meer, and Polanyi⁶ by the same method found a collision yield of $1/2000$ at 275° relative to a collision yield of $1/10000$ for methyl chloride. This is probably more reliable than the result of Hartel and Polanyi, and corresponds to an activation energy of 8.3 kcal.⁶



Bawn and Evans¹³ investigated the reaction of sodium atoms with amyl nitrite by the life period method with hydrogen as a carrier gas. Their results led to a velocity constant at 251° of $3.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, corresponding to a collision yield of $1/14$ and an activation energy of 2.80 kcal.



Hartel and Polanyi² by the diffusion flame method found a collision yield at 240° of unity, corresponding to $E_{52} = 0$. This value is, however, only approximate. By the same method Hartel, Meer, and Polanyi⁶ also found a collision yield of unity at 275° , relative to an assumed value of $C = 1/10000$ for methyl chloride.

Fairbrother and Warhurst¹⁷ by the life period method using hydrogen as a carrier found a velocity constant at 227° of $2.06 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, corresponding to a collision yield of $1/2.31$ and an activation energy of 0.83 kcal. On the basis of more reliable data on the absorption of resonance radiation by sodium vapor, Tuck and Warhurst¹⁸ have corrected Fairbrother and Warhurst's data. They obtain $Jc2u = 8.90 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, $E_{52} = 1.7$ kcal.

¹⁷ F. Fairbrother and E. Warhurst, *Trans. Faraday Soc.*, 31, 987 (1935).

¹⁸ J. L. Tuck and E. Warhurst, *Trans. Faraday Soc.*, 32, 1501 (1936).

Evans and Warhurst¹⁰ have discussed the reaction theoretically. They assume a C_6H_5-I bond strength of 45 kcal., which makes reaction (82) 36.2 kcal. exothermic. By the transition state method with various approximations they obtain values of E_{82} of 0.7 and ca. 16 kcal.

(83) $Na + C_6H_5Br \longrightarrow C_6H_5 + NaBr$

Approximate results by the diffusion flame method by Hartel and Polanyi² gave a collision yield of 1/20 at 260°, and an activation energy of 3.1 kcal. Hartel, Meer, and Polanyi⁶ by the same method found $C = 1/50$ at 275°, relative to $C = 1/10000$ for CH_3Cl . Fairbrother and Warhurst¹⁷ by the life period method using hydrogen as a carrier found velocity constants of 1.62×10^{13} and $1.48 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ at 244° and 222°, and an activation energy of 3.5 kcal. Tuck and Warhurst¹⁸ investigated the absorption of resonance radiation by sodium vapor, and from their results applied a correction to the values obtained by Fairbrother and Warhurst. The corrected values are $k_{244} = 6.08 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, $E_{83} = 4.6 \text{ kcal}$.

Warhurst¹⁹ by an improved technique, using the life period method, found velocity constants of

$$\begin{aligned} k_{285} &= 2.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \\ k_{230} &= 3.1 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \end{aligned}$$

These correspond to a collision yield at 255° of 1/36, and an activation energy of 3.8 kcal. From the temperature coefficient of the collision yield he finds that the collision diameter of $35 \times 10^{-16} \text{ cm}^2$ usually assumed by workers in this field is too large, and that a value of $5.1 \times 10^{-16} \text{ cm}^2$ is a more reasonable approximation. Evans and Warhurst¹⁰ point out that if a C_6H_5-Br bond strength of 70 kcal. is assumed, reaction (83) is 28.1 kcal. exothermic. By the transition state method with alternative approximations they obtain values of E_{83} of 3.0 and 16 kcal.

(84) $Na + C_6H_5Cl \longrightarrow C_6H_5 + NaCl$

Hartel and Polanyi² by the diffusion flame method found a collision yield of 1/800 at 270°. This corresponds to $E_{84} = 7.2 \text{ kcal}$. The value is not reliable, however, since experimental conditions were somewhat uncertain and they, therefore, consider the value to be only approximate. Hartel, Meer, and Polanyi⁶ in a more reliable investigation by the same method found a collision yield of 1/10000 at 275°, relative to an assumed value of 1/10000 for methyl chloride under similar conditions.

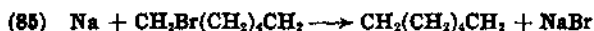
Fairbrother and Warhurst¹⁷ investigated the reaction by the life period

¹⁹ E. Warhurst, *Trans. Faraday Soc*, 35, 674 (1939).

method using hydrogen as a carrier. They found a mean value of the velocity constant at 281° of $2.65 \times 10^n \text{ cm.}^8 \text{ mol.}^{-1} \text{ sec.}^{-1}$, corresponding to a collision yield of 1/1980 and an activation energy of 8.25 kcal. Tuck and Warhurst¹⁸ have corrected the results of Fairbrother and Warhurst on the basis of more accurate information on the absorption of resonance radiation by sodium vapor. They thus obtain a velocity constant at 244° of $2.66 \times 10^{10} \text{ cm.}^3 \text{ mol.}^{-1} \text{ sec.}^{-1}$, and an activation energy of 10.2 kcal.

Evans and Warhurst¹⁰ have discussed the reaction theoretically. Assuming a $\text{C}_6\text{H}_5\text{—Cl}$ bond strength of 96 kcal., reaction (84) is 12.0 kcal. exothermic. By the transition state method with various alternative approximations they get values of E_{84} of 11.3 and 16 kcal.

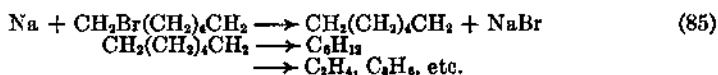
Allen and Bawn¹² have investigated the reaction by the Paneth technique. Antimony mirrors were not removed by the reaction products, but tellurium mirrors were slowly removed. The products were not identified. They suggest that the relatively slow removal of the mirror is due to a large steric factor for the attack on the metal by phenyl with the result that most phenyl radicals disappear by forming diphenyl rather than by mirror removal.



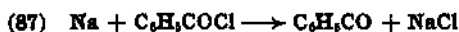
This reaction has been assumed as a step in the reaction of sodium atoms with $\text{CH}_2\text{Br}(\text{CH}_2)_4\text{CH}_2\text{Br}$.⁹ (See XII-86.)



Bawn and his co-workers^{3, 9} found this reaction to be accompanied by luminescence, the sodium D-line being emitted. The products of the reaction consisted of cyclohexane and hexenes, and a small amount (less than 5 per cent) of ethylene and propylene. There seems to be no doubt that the reaction proceeds in stages, (86) being followed by



To account for the luminescence it is necessary to assume, on energetic grounds, that a part of the reaction proceeds by the direct formation of an olefin or a cyclic compound, rather than a biradical in reaction (85), i.e.,



Hartel and Polanyi² by the diffusion flame method found an approximate collision yield of unity at 240° , i.e., $E_{87} \sim 0$. Haresnape^{14a} has identified dibenzoyl as a product of the reaction.

Hartel and Polanyi² found an approximate value of unity for the collision yield of the reaction at 240° by the diffusion flame method. A similar value was obtained by Hartel, Meer, and Polanyi⁶ at 275°, relative to a value of 1/10000 for methyl chloride. Evans and Walker⁸⁰ found $C = 1/9.4$ at 284°, corresponding to $E_{ss} = 2.5$ kcal.

The enormous increase in reactivity owing to the presence of the benzene ring is noteworthy.



Evans and Walker⁸⁰ by the diffusion flame method found a collision yield of 1/43.8 at 270°, corresponding to $E_{88A} \approx 4.1$ kcal.



Evans and Walker⁸⁰ by the diffusion flame method found $C = 1/52.0$ at 275°, corresponding to $E_{88B} = 4.3$ kcal.



Evans and Walker⁸⁰ found a collision yield of 1/13.2 at 280°, corresponding to an activation energy of 2.8 kcal.



Evans and Walker⁸⁰ found a collision yield of 1/19.2 at 285° by the diffusion flame method. This corresponds to an activation energy of 3.3 kcal.



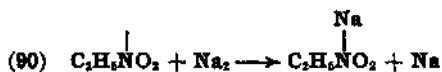
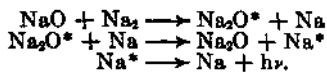
Evans and Walker⁸⁰ by the diffusion flame method found $C = 1/1.2$ at 285°, corresponding to an activation energy of 0.2 kcal.



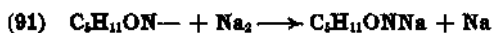
By the diffusion flame method Evans and Walker⁸⁰ found a collision yield of 1/6.4 at 275°, corresponding to an activation energy of 2.0 kcal.



Bawn and Evans¹⁸ found no chemiluminescence in the reaction of sodium atoms with CH_3NO_2 . They assume that this is due to the destruction of sodium molecules by (89), which thus inhibits possible secondary light producing reactions,



This reaction has been assumed by Bawn and Evans¹³ to explain the absence of luminescence in the reaction of sodium atoms with $\text{C}_2\text{H}_5\text{NO}_3$. (See the analogous reaction discussed in section XII-89.)



This has been assumed by Bawn and Evans¹³ as a step in the reaction of sodium atoms with $\text{C}_5\text{H}_{11}\text{ONO}$. (See section XII-89.)

Chapter XIII

Systems Containing Other Metals

Information on other metals is confined to reactions involving metal alkyls. The metal alkyls have been largely used as sources of radicals, and this use has been discussed under experimental methods. (See 11-36.) Specific information arising out of their use in this connection is given under the appropriate reaction. The photolysis of the metal alkyls has been dis-

TABLE LV. THERMAL DECOMPOSITION OF METAL ALKYLs

Substance	References
$\text{Pb}(\text{CH}_3)_4$	1, 2
$\text{Pb}(\text{C}_2\text{H}_5)_4$	3-7
$\text{Pb}(\text{C}_4\text{H}_9)_4$	8, 9
$\text{Hg}(\text{CH}_3)_2$	10, 11
$\text{Hg}(\text{C}_2\text{H}_5)_2$	12, 13
$\text{Hg}(\text{C}_4\text{H}_9)_2$	9, 14
$\text{Hg}(\text{C}_7\text{H}_{15})_2$	15
$\text{Si}(\text{CH}_3)_4$	16
$\text{Si}(\text{C}_2\text{H}_5)_4$	17
$\text{Si}(\text{C}_4\text{H}_9)_4$	17
$\text{Ge}(\text{C}_2\text{H}_5)_4$	18
$\text{Sn}(\text{CH}_3)_4$	18a
$\text{Sn}(\text{C}_6\text{H}_5 \cdot \text{CH}_2)_4$	9
$\text{Bi}(\text{CH}_3)_3$	1
$\text{Zn}(\text{CH}_3)_2$	1
$\text{Sb}(\text{CH}_3)_3$	1

¹ F. Paneth and W. Hofeditz, *Ber.*, **62B**, 1335 (1929).

² J. H. Simons, R. W. McNamee, and C. D. Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

³ P. L. Cramer, *J. Am. Chem. Soc.*, **56**, 1234 (1934).

⁴ J. A. Leermakers, *J. Am. Chem. Soc.*, **66**, 4508 (1933).

⁶ R. N. Meinert, *J. Am. Chem. Soc.*, **55**, 979 (1933).

⁶ F. Paneth and W. Lautsch, *Ber.*, **64B**, 2708 (1931).

⁷ T. G. Pearson, P. L. Robinson, and E. M. Stoddart, *Proc. Roy. Soc. (London)*, **A142**, 275 (1933).

⁸ M. F. Dull and J. H. Simons, *J. Am. Chem. Soc.*, **55**, 3898 (1933).

⁹ F. Paneth and W. Lautsch, *J. Chem. Soc.*, **1935**, 380.

¹⁰ J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.*, **6**, 359 (1938).

¹¹ J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

¹² H. S. Taylor and W. H. Jones, *J. Am. Chem. Soc.*, **52**, 1111 (1930).

¹³ W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 396 (1940).

¹⁴ F. E. Frey and H. J. Hepp, *J. Am. Chem. Soc.*, **55**, 3357 (1933).

¹⁵ F. O. Rice and O. L. Polly, *Ind. Eng. Chem.*, **27**, 915 (1935).

¹⁶ D. F. Helm and E. Mack, *J. Am. Chem. Soc.*, **69**, 60 (1937).

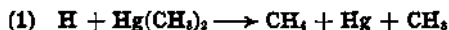
¹⁷ C. E. Waring, *Trans. Faraday Soc.*, **36**, 1142 (1940).

¹⁸ R. L. Geddes and E. Mack, *J. Am. Chem. Soc.*, **62**, 4372 (1930).

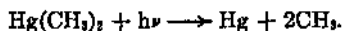
^{18a} C. E. Waring and W. S. Horton, *J. Am. Chem. Soc.*, **67**, 540 (1945).

cussed in section V-13. There is considerable information on the thermal decompositions, and references are given in Table LV. There is no doubt that in all cases the initial step involves the formation of alkyl radicals.

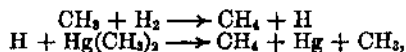
In the present chapter we will discuss only information having a bearing on their elementary reactions. In this connection most of our information comes from work on mercury dimethyl, and the general literature has been well discussed by Cunningham and Taylor.¹⁰ The reactions of mercury dimethyl have already been discussed in some detail in section VI-27.



In work on the photodecomposition of mercury dimethyl (see V-13 and VI-27), Cunningham and Taylor^{10,11} found, in agreement with others, that the primary step was the reaction



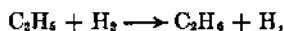
The rate of the decomposition was greatly increased by the presence of hydrogen, and they conclude that this is due to the occurrence of the reactions



which thus give the process chain characteristics.



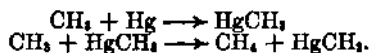
As in the case of mercury dimethyl (see XIII-1), Moore and Taylor¹³ found that the rate of the photolysis of mercury diethyl at higher temperatures was considerably increased by the presence of hydrogen, probably by the type of chain process suggested for mercury dimethyl, viz.,



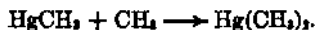
followed by (2).



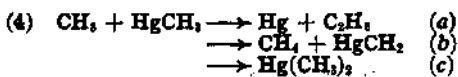
Saunders and Taylor¹⁹ investigated the photolysis of acetone in the presence of mercury. The mercury caused an increase in methane production at higher temperatures, which they attribute to the sequence



The fact that mercury vapor can be used as a detector for methyl radicals (see 11-66), shows that reaction (3) must occur readily, since the only way in which mercury dimethyl can be formed efficiently from mercury vapor and methyl radicals is by (3) followed by



¹⁹ K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, 9, 616 (1941).

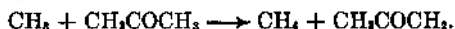


Reaction (4a) has been suggested as a step in the mechanism of the photolysis of mercury dimethyl by Linnett and Thompson.²⁰ (See XIII-5.)

Saunders and Taylor¹⁹ investigated the photolysis of acetone in the presence of mercury, as discussed in section XIII-3. They attribute the observed increase in methane production at higher temperatures in the presence of mercury to the sequence

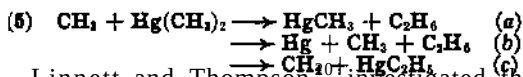


For this explanation to be valid reaction (4b) must be faster than the normal methane producing reaction

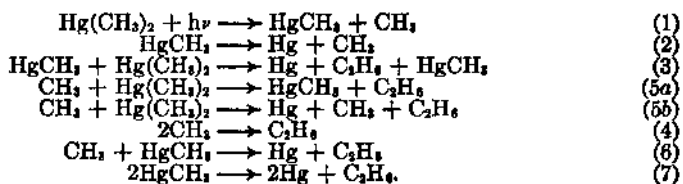


They accept a value of 16 kcal. for the latter reaction, and hence estimate the *EM* is less than 13 kcal. It may be noted that the actual difference in methane produced in the presence of mercury is very small, and the conclusions drawn are rather detailed considering the somewhat dubious nature of the evidence.

Reaction (4c) probably occurs when mercury is used as a detector for methyl radicals. (See XIII-3.)



Linnett and Thompson²⁰ investigated the photolysis of mercury dimethyl. With X2537 they found that ethane was almost the sole product at room temperature. The quantum yield was unity at room temperature, but increased at higher temperatures. Results in the presence of nitric oxide were complex, but favored a free radical mechanism. They suggested



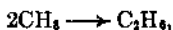
This explains the results provided it is assumed that the activation energies of reactions (3), (5a), and (5b) are high. They will thus have no effect at room temperature, and the quantum yield of unity will be due to the sequence (1), (2), and (4), or to (1), (4), (6), and (7). At higher temperatures the occurrence of (3), (5a), and (5b) will give the reaction chain

²⁰ J. W. Linnett and H. W. Thompson, *Trans. Faraday Soc.*, 33, 501, 874 (1937).

characteristics and cause the quantum yield to rise. They estimate from a "collision yield" type of calculation, and also from the temperature coefficient that the activation energy of the chain propagating reaction is 10.7 kcal., i.e., this is the activation energy of (3), (5a), or (56). Of these (5a) and (56) seem the most plausible, and are effectively the same thing. We may thus put

$$E_{5a} \sim E_{5b} \sim 10.7 \text{ kcal.}$$

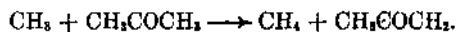
Cunningham and Taylor¹⁰ investigated the photolysis in more detail, with special emphasis on the effect of hydrogen on the reaction. (See section VI-27 for details.) Their results in the absence of hydrogen agree in general with those of Linnett and Thompson, the only important product being ethane at lower temperatures. At higher temperatures more and more methane is formed as well. At low temperatures they ascribe ethane formation to



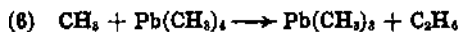
while at higher temperatures they suggest that (56) is the chain step. They ascribe the production of methane in the absence of hydrogen to (5c), viz.,



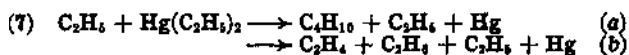
Saunders and Taylor¹⁹ investigated the photolysis of acetone in the presence of mercury, as discussed in sections XIII-3 and 4, and also in the presence of mercury dimethyl. In the presence of mercury dimethyl, as with mercury, the production of methane is increased at higher temperatures, probably by (5c). Their results indicate that (5c) is slower than (6), but faster than



They adopt a value of 16 kcal. for the activation energy of the latter reaction, and hence assign a value of 13-14 kcal. to (5c). They suggest that (5a) also occurs, and is responsible for part of the ethane production in the presence of mercury dimethyl.



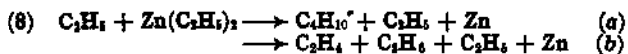
Leighton and Mortensen²¹ investigated the photolysis of lead tetramethyl, and found higher quantum yields than were obtained by Linnett and Thompson,²⁰ for mercury dimethyl. Linnett and Thompson suggest that this is due to E_6 being less than E_{5a} , and suggest $E_6 < 10$ kcal.



Moore and Taylor¹³ investigated the photolysis of mercury diethyl. The products at lower temperatures were ethylene, ethane, hydrogen, butene,

²¹ P. A. Leighton and R. A. Mortensen, *J. Am. Chem. Soc.*, 68, 448 (1936).

and a lesser amount of butane. At higher temperatures ethane increases, and hydrogen disappears as a product, and the quantum yield increases. They account for the increased quantum yield at higher temperatures by a chain mechanism similar to that for mercury dimethyl (see XIII-5), *i.e.*, one involving reactions (7a) and (7b).



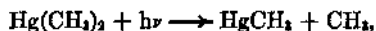
Moore and Taylor¹³ investigated the photolysis of zinc diethyl and obtained results similar to those with mercury

diethyl. (See XIII-7.)

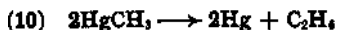
They explain the increase in quantum yield at higher temperatures in a similar way, *viz.*, by a chain mechanism involving reaction (8). The proportion of butane in the products is less at lower temperatures with zinc diethyl than with mercury diethyl, but it increases to about the same amount at higher temperatures. This is possibly due to a higher activation energy for reaction (8a), on account of the greater strength of the Zn—C bond.



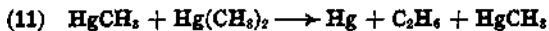
It seems certain that in the photolysis of mercury dimethyl the primary step is



and that this is followed by the rapid occurrence of (9). (See XIII-5.)



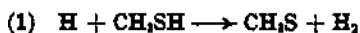
Reaction (10) is probably involved in the photolysis of mercury dimethyl. (See XIII-5.)



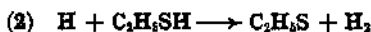
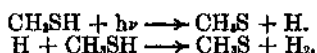
This reaction is perhaps involved in the photolysis of mercury dimethyl. (See XIII-5.) Its activation energy is probably ~ 10.7 kcal.

Chapter XIV

Systems Containing Sulfur



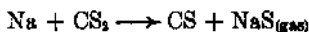
Reaction (1) has been suggested¹ as a step in the photolysis of methyl mercaptan, viz.,



This has been suggested as a step in the photolysis of ethyl mercaptan.²



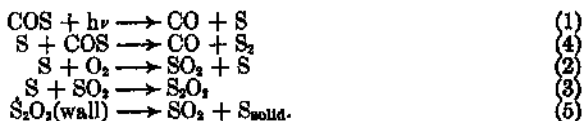
Heller and Polanyi³ investigated the reaction of sodium atoms with carbon bisulfide by the diffusion flame method. At 270° they obtained the very small collision yield of 1/207500. Since the reaction



is strongly endothermic, they consider that the reaction occurring is (3), i.e., an association. In view of the slowness of the reaction it is possible that it occurs by three-body collisions.



Kondratjew⁴ has investigated the photooxidation of COS with light in the region 2300-2550Å. The reaction was followed by the light absorption of SO_2 , the main product. He proposes the mechanism



This leads to agreement with the experimentally determined rate of SO_2 production. From it he obtains

$$E_4 - E_1 = 6 \text{ kcal.},$$

and assuming $E_3 = 0$,

$$E_4 = 6 \text{ kcal.}$$

¹ N. P. Skerrett and H. W. Thompson, *Trans. Faraday Soc.*, 37, 81 (1941).

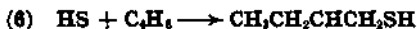
² M. Meissner and H. W. Thompson, *Trans. Faraday Soc.*, 34, 1238 (1938).

³ W. Heller and M. Polanyi, *Trans. Faraday Soc.*, 32, 633 (1936).

⁴ V. Kondratjew, *Acta Physicochimica* (U.R.S.S.), 16, 272 (1942).



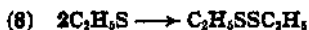
This reaction has been suggested⁵ as a step in the photoaddition of H₂S to propylene. (See XIV-11.)



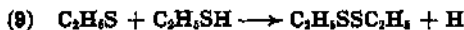
Reaction (6) has been proposed⁵ as a step in the photoaddition of H₂S to 1-butene.



Reaction (7) has been suggested as a step in the photolysis of methyl mercaptan.¹



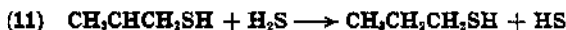
This reaction has been postulated as a step in the photolysis of ethyl mercaptan.²



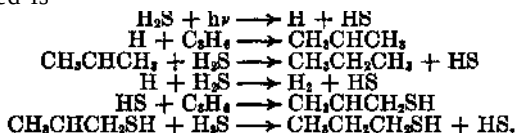
This has also been suggested as a step in the photolysis of ethyl mercaptan.²



This has been postulated⁵ as a step in the photoaddition of H₂S to propylene. (See XIV-11.)



Vaughan and Rust⁵ found that a photoaddition of H₂S to liquid propylene occurred when light of wave length below X2800 was used. The mechanism postulated is



This is quite speculative.

An acetone photosensitized reaction of a similar nature also occurs. The mechanism is presumably similar.



This reaction has been postulated⁶ as a step in the photoaddition of H₂S to 1-butene.

⁶ W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, 7, 472 (1942).

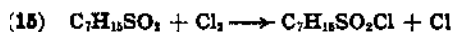


Vaughan and Rust⁵ have suggested this reaction as a step in the gas phase addition of H₂S to 1-butene. The reaction is similar to that of propylene. (See XIV-11.)



Stauff⁶ has investigated the photochemistry of mixtures of C₇H₁₆, SO₂, and Cl₂. The results are discussed in detail in section IX-44. He concludes that

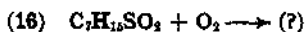
$$E_{14} \ll 5 \text{ kcal.}$$



Stauff⁶ has investigated the photoreaction between C₇H₁₆, SO₂, and Cl₂. (See IX-44.) Since the reaction is strongly inhibited by oxygen, presumably by



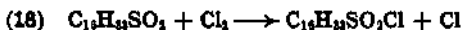
the activation energy of (15) which is competing with this must be appreciable, and E_{16} must be small.



As discussed in section XIV-15, E_{16} must be small.



Stauff⁶ has investigated the photoreaction between C₁₆H₃₄, SO₂, and Cl₂ in CCU solution. (For details see IX-46.) A comparison of the proposed mechanism with experiment leads to $E_{17} < 5 \text{ kcal.}$



Stauff⁶ has investigated the photoreaction between C₁₆H₃₄, SO₂, and da in CCU solution. (See IX-46.) The reaction is inhibited by oxygen, apparently owing to a competition between (18) and (19).



Hence E_{18} must be appreciable and E_{19} small.



As discussed in section XIV-18, E_{19} must be small.

⁶ J. Stauff, *Z. Elektrochem.*, 48, 550 (1942); H. J. Schumacher and J. Stauff, *Z. physik. Chem.* in press.

Appendix

Reaction Index and Table of Activation Energies

The following table lists all the elementary reactions discussed in Chapters VI to XIV, with their chapter, section, and page numbers. In addition, wherever possible, an attempt has been made to indicate what appears to the author to be the most reliable value of the activation energy. In some cases only a range of values can be given or an upper or lower limit to the value. In others a definite value is obtained from a mechanism which is doubtful: this is indicated by a query. Finally, in many cases insufficient evidence exists to permit any estimate. It should be emphasized that the values listed rest in many cases on uncertain evidence, but it is felt that in general they are probably correct as far as the order of magnitude is concerned.

Section	Page	Reaction	E, kcal.
VI-1	251	$H + CH_3 \rightarrow CH_3$	small
		$\rightarrow CH + H_2$	moderate
VI-2	251	$H + CH_3 \rightarrow CH_4$	small
		$\rightarrow CH_2 + H_2$	< 5
		$\rightarrow CH_3 + H$	small
VI-3	253	$H + CH_4 \rightarrow CH_4 + H_2$	13 ± 2
		$\rightarrow CH_4 + H$	~ 35
VI-4	260	$H + C_2H \rightarrow C_2H_2$	small
VI-5	260	$H + C_2H_3 \rightarrow C_2H + H_2$	< 5
		$\rightarrow C_2H_3$	< 5
VI-6	261	$H + C_2H_3 \rightarrow C_2H_2 + H_2$	< 5(?)
		$\rightarrow C_2H_4$	small
VI-7	262	$H + C_2H_4 \rightarrow C_2H_5$	< 5
		$\rightarrow C_2H_5 + H_2$	~ 10
VI-8	267	$H + C_2H_5 \rightarrow 2CH_3$	≤ 5
		$\rightarrow C_2H_6$	
		$\rightarrow C_2H_5 + H$	~ 5
		$\rightarrow C_2H_4 + H_2$	
VI-9	274	$H + C_2H_6 \rightarrow C_2H_5 + H_2$	6.7 ± 1
		$\rightarrow CH_4 + CH_3$	> 30
VI-10	280	$H + C_3H_4 \rightarrow C_3H_7$	≤ 5
VI-11	282	$H + C_3H_7 \rightarrow C_3H_8$	
		$\rightarrow CH_3 + C_2H_5$	5
VI-12	282	$H + C_3H_8 \rightarrow C_3H_7 + H_2$	10 ± 2
		$\rightarrow C_3H_8 + CH_4$	large
		$\rightarrow C_3H_7 + CH_3$	large
		$\rightarrow C_3H_8 + H$	large
VI-12A	286	$H + C_4H_8 \rightarrow C_4H_9$	small
VI-12B	286	$H + C_4H_7 \rightarrow C_4H_8$	small
VI-13	286	$H + C_4H_8 \rightarrow C_4H_9$	small
VI-14	286	$H + C_4H_8 \rightarrow C_3H_7 + CH_3$	≤ 5
		$\rightarrow 2C_2H_5$	≤ 5
VI-15	287	$H + n-C_4H_{10} \rightarrow C_4H_9 + H_2$	10 ± 1.5

Section	Page	Reaction	E, kcal.
VI-16	288	$H + \text{iso-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2$	10.5 ± 1.5
VI-17	290	$H + \text{C}_4\text{H}_{12} \rightarrow \text{C}_4\text{H}_{11} + \text{H}_2$	≤ 10
VI-18	290	$H + \text{C}_4\text{H}_6 \rightarrow \text{C}_4\text{H}_5 + \text{H}_2$	≤ 10
		$\rightarrow \text{C}_4\text{H}_7$	
VI-19	291	$H + \text{C}_4\text{H}_{18} \rightarrow \text{C}_4\text{H}_{17} + \text{H}_2$	~ 10
VI-20	291	$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4$	
		$\rightarrow \text{CH}_3 + \text{H}$	
VI-21	293	$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	
VI-22	293	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	
VI-23	293	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	
		$\rightarrow 2\text{CH}_4$	
VI-24	294	$\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_6$	small
VI-25	294	$\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_6$	
VI-26	294	$\text{CH}_3 + \text{C}_4\text{H}_{10} \rightarrow \text{CH}_3 + \text{C}_4\text{H}_9$	15 ± 5
VI-27	294	$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$	9 ± 2
VI-28	303	$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	small
		$\rightarrow \text{C}_2\text{H}_5 + \text{H}$	
		$\rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	
		$\rightarrow \text{CH}_4 + \text{CH}_2$	~ 14
VI-28A	311	$2\text{CH}_3 + \text{H}_2 \rightarrow 2\text{CH}_4$	large
VI-29	311	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{H}$	> 40
VI-30	312	$\text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3$	small
		$\rightarrow \text{CH}_4 + \text{C}_2\text{H}$	
VI-31	312	$\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_6$	1-2
		$\rightarrow \text{CH}_4 + \text{C}_2\text{H}_2$	> 10
VI-32	313	$\text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3$	small
VI-33	313	$\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5$	8
VI-34	314	$\text{CH}_3 + \text{C}_3\text{H}_8 \rightarrow \text{C}_4\text{H}_{10}$	
VI-35	314	$\text{CH}_3 + \text{C}_3\text{H}_8 \rightarrow \text{CH}_4 + \text{C}_3\text{H}_7$	3.1
		$\rightarrow \text{C}_4\text{H}_9$	
VI-36	318	$\text{CH}_3 + \text{C}_3\text{H}_7 \rightarrow \text{C}_4\text{H}_{10}$	small
VI-37	318	$\text{CH}_3 + \text{C}_3\text{H}_8 \rightarrow \text{CH}_4 + \text{C}_3\text{H}_7$	6-8
VI-38	319	$\text{CH}_3 + \text{C}_4\text{H}_{10} \rightarrow \text{C}_5\text{H}_{12}$	
VI-39	320	$\text{CH}_3 + \text{C}_4\text{H}_{10} \rightarrow \text{C}_5\text{H}_{12}$	small
VI-40	320	$\text{CH}_3 + n\text{-C}_4\text{H}_{10} \rightarrow \text{CH}_4 + \text{C}_4\text{H}_9$	5.5
		$\text{CH}_3 + \text{iso-C}_4\text{H}_{10} \rightarrow \text{CH}_4 + \text{C}_4\text{H}_9$	4.2
VI-41	320	$\text{CH}_3 + \text{C}(\text{CH}_3)_4 \rightarrow \text{CH}_4 + \text{C}_5\text{H}_{11}$	8.3
VI-42	320	$\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5$	> 10
VI-43	320	$\text{CH}_3 + \text{C}_2\text{H}_5\text{CH}_3 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5\text{CH}_3$	5.6
VI-44	321	$\text{CH}_3 + (\text{C}_2\text{H}_5)_2\text{CH}_2 \rightarrow \text{CH}_4 + (\text{C}_2\text{H}_5)_2\text{CH}$	< 5.6
VI-45	321	$\text{CH}_3 + \text{higher hydrocarbons}$	
VI-46	323	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_4$	
VI-46A	323	$\text{C}_2\text{H}_5 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3$	> 8
VI-47	323	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_6$	
VI-48	323	$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	38-43
VI-49	325	$\text{C}_2\text{H}_5 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}$	~ 9
VI-50	328	$\text{C}_2\text{H}_5 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3$	
VI-51	328	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_4$	small
VI-52	328	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_6$	< 5
		$\rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_3$	> 10
VI-53	329	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_4$	small
		$\rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$	small (?)
VI-54	336	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_6 \rightarrow \text{C}_4\text{H}_{10}$	
		$\rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_5$	
VI-55	336	$\text{C}_2\text{H}_5 + \text{C}_4\text{H}_{10} \rightarrow \text{C}_6\text{H}_{14}$	
VI-56	337	$\text{C}_2\text{H}_5 + \text{other hydrocarbons}$	
VI-57	338	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_4$	
VI-58	338	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_3 \rightarrow \text{C}_3\text{H}_8$	
		$\rightarrow \text{CH}_3 + \text{C}_2\text{H}_5$	large
VI-59	339	$\text{C}_2\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$	25-40
		$\rightarrow \text{C}_2\text{H}_6 + \text{H}$	large
VI-60	342	$\text{C}_2\text{H}_7 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}$	~ 9
VI-61	343	$\text{C}_2\text{H}_7 + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_{10}$	< 5

Section	Page	Reaction	E, kcal.
VI-62	343	$2C_2H_7 \rightarrow C_6H_{14}$	small
VI-62A	345	$C_4H_7 + C_4H_9 \rightarrow C_8H_{16}$	small (?)
VI-63	345	$CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \rightarrow C_4H_8$	small
		$\rightarrow 2C_2H_4$	
VI-64	345	$C_4H_9 \rightarrow C_2H_5 + C_2H_4$	
		$\rightarrow CH_3 + C_3H_6$	
		$\rightarrow H + C_4H_9$	
VI-65	346	$2C_4H_9 \rightarrow C_8H_{18}$	small
		$\rightarrow C_4H_9 + C_4H_{10}$	
VI-66	347	$C_6H_9 + C_8H_{17} \rightarrow C_{14}H_{26}$	
VI-67	348	$C_4H_9 + C_8H_{18} \rightarrow C_4H_{10} + C_8H_{17}$	
VI-68	349	$CH_3(CH_2)_2CH_2 \rightarrow C_2H_4 + C_3H_6$	
		$\rightarrow C_6H_{10}$	
VI-69	349	$C_6H_{11} \rightarrow CH_2 + C_5H_8$	
		$\rightarrow C_2H_5 + C_4H_6$	
VI-70	349	$2C_6H_5 \rightarrow (C_6H_5)_2$	small (?)
VI-70A	350	$2C_6H_5CH_3 \rightarrow (C_6H_5 \cdot CH_3)_2$	small (?)
VI-71	350	$CH_2(CH_2)_4CH_3 \rightarrow C_6H_{12}$	
		$\rightarrow 2C_3H_6$	
		$\rightarrow 3C_2H_4$	
VI-72	350	$C_7H_{13} \rightarrow C_6H_{12} + CH_3$	
VI-73	351	$C_8H_{17} \rightarrow C_4H_9 + C_4H_8$	
VI-74	351	$C_{10}H_{22} \rightarrow (?)$	
VII-1	352	$H + CO \rightarrow CHO$	
VII-2	353	$H + CHO \rightarrow H_2 + CO$	~ 5
VII-3	353	$H + HCHO \rightarrow H_2 + CHO$	5-16
VII-4	354	$H + HCOOH \rightarrow (?)$	7-8
VII-5	354	$H + CH_3OH \rightarrow (?)$	≤ 10
VII-6	354	$H + CH_3COO \rightarrow CH_4 + CO_2$	
VII-7	355	$H + CH_3CHO \rightarrow H_2 + CH_3CO$	~ 7
VII-8	356	$H + CH_3COOH \rightarrow CH_4 + COOH$	7-10(?)
		$\rightarrow H_2 + CH_3COO$	7-10(?)
VII-9	357	$H + CH_3OCH_3 \rightarrow H_2 + CH_3OCH_3$	
VII-9A	357	$H + CH_3COCH_3 \rightarrow CH_3CO + CH_3$	
VII-9B	357	$H + CH_3COCH_2 \rightarrow CH_3COCH_2 + H_2$	9
VII-10	357	$H + C_2H_5COOH \rightarrow (?)$	7-9
VII-11	358	$H + C_6H_5CHO \rightarrow C_6H_5 + CHO$	
VII-12	358	$O + HCHO \rightarrow OH + CHO$	≤ 8
VII-13	358	$O + HCOOH \rightarrow CO_2 + H_2O$	6-7(?)
		$\rightarrow OH + CO_2 + H$	6-7(?)
VII-14	359	$O + CH_4 \rightarrow CH_2 + H_2O$	8(?)
		$\rightarrow HCHO + H_2$	
VII-15	360	$O + CH_3OH \rightarrow OH + CH_2O$	≤ 4
VII-16	360	$O + C_2H_2 \rightarrow C_2H + OH$	$\leq 4(?)$
		$\rightarrow C_2H_2O$	$\leq 4(?)$
VII-17	360	$O + C_2H_4 \rightarrow C_2H_2O$	small
VII-18	361	$O + C_2H_6 \rightarrow OH + C_2H_5$	7(?)
VII-19	361	$O + C_2H_5OH \rightarrow OH + C_2H_5O$	≤ 4
VII-20	361	$O + C_6H_5 \rightarrow OH + C_6H_5$	~ 5
VII-21	361	$O + C_6H_6 \rightarrow OH + C_6H_5$	≤ 4
		$\rightarrow C_6H_6O$	small
VII-22	361	$O + C_6H_{11} \rightarrow OH + C_6H_{11}$	~ 5
VII-23	362	$OH + CH_4 \rightarrow CH_3 + H_2O$	8.5(?)
VII-24	362	$HO_2 + CH_4 \rightarrow (?)$	small
VII-25	362	$HO_2 + C_2H_6 \rightarrow (?)$	small
VII-26	362	$HO_2 + C_6H_6 \rightarrow (?)$	small
VII-27	362	$CHO \rightarrow CO + H$	~ 26
VII-28	364	$2CHO \rightarrow 2CO + H_2$	
		$\rightarrow HCHO + CO$	
		$\rightarrow CHO \cdot CHO$	

APPENDIX

Section	Page	Reaction	E, kcal.
VII-29	365	$\text{CHO} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{CO}$	small
VII-30	365	$\text{CHO} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO} + \text{CHO}$	$\geq 10(?)$
		$\rightarrow \text{CH}_3\text{CO} + \text{H}_2 + \text{CO}$	
VII-31	366	$\text{CHO} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{CO}$	
		$\rightarrow \text{C}_2\text{H}_5\text{CHO}$	
VII-32	366	$\text{COOH} \rightarrow \text{CO} + \text{OH}$	
VII-33	367	$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$	1.9
VII-34	367	$\text{CH}_2 + \text{CO} \rightarrow \text{CH}_2\text{CO}$	
VII-35	367	$\text{CH}_2 + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_4 + \text{CO}$	large
VII-36	368	$\text{CH}_3 + (\text{CH}_3)_2\text{O} \rightarrow 2\text{CH}_3 + \text{CO}$	
VII-37	368	$\text{CH}_2 + -\text{CH}_2 \cdot \text{CH}_2\text{O}- \rightarrow \text{CH}_2\text{O} + \text{C}_2\text{H}_4$	8(?)
VII-38	368	$\text{CH}_2 + \text{C}_4\text{H}_8\text{O}_2 \text{ (dioxane)} \rightarrow \text{HCHO} + \text{C}_2\text{H}_4 + \text{CH}_2\text{CH}_2\text{O}$	23(?)
VII-39	368	$\text{CH}_3 + (\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	15 ± 5
VII-40	369	$\text{CH}_2 + \text{O}_2 \rightarrow (?)$	small
VII-41	370	$\text{CH}_2 + \text{CO} \rightarrow \text{CH}_2\text{CO}$	
VII-42	370	$\text{CH}_3 + \text{HCHO} \rightarrow \text{CH}_4 + \text{CHO}$	
VII-43	370	$\text{CH}_2 + \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{CH}_2\text{O}$	
VII-44	371	$\text{CH}_3 + \text{CH}_3\text{CO} \rightarrow \text{C}_2\text{H}_6 + \text{CO}$	$\sim 8(?)$
		$\rightarrow \text{CH}_3\text{COCH}_3$	$\sim 8(?)$
VII-45	372	$\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$	8-10
VII-46	374	$\text{CH}_2 + \text{HCOOCH}_3 \rightarrow (?)$	
VII-47	375	$\text{CH}_3 + \text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_3\text{OC}_2\text{H}_5$	
VII-48	375	$\text{CH}_2 + \text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{OCH}_3$	~ 15
VII-49	375	$\text{CH}_3 + \text{CH}_2\text{COCH}_3 \rightarrow \text{CH}_3\text{COC}_2\text{H}_5$	
VII-50	375	$\text{CH}_3 + \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_4 + \text{CH}_3\text{COCH}_3$	~ 7
		$\rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CO}$	
VII-51	376	$\text{CH}_2 + \text{CH}_2\text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	
VII-52	376	$\text{CH}_3 + \text{CH}_2\text{OC}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{CH}_3\text{OC}_2\text{H}_5$	
		$\rightarrow \text{C}_2\text{H}_6 + \text{CH}_2\text{OCH}_3$	
VII-53	377	$\text{CH}_2 + \text{CH}_2\text{COCOC}_2\text{H}_5 \rightarrow \text{CH}_2\text{COCOC}_2\text{H}_5$	
VII-54	377	$\text{CH}_3 + (\text{CH}_2=\text{CH})_2\text{O} \rightarrow (?)$	
VII-55	377	$\text{CH}_3 + \text{CH}_2\text{COCOC}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{CH}_2\text{COCOC}_2\text{H}_5$	~ 13
		$\rightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{CO}$	
VII-56	378	$\text{CH}_2 + \text{CH}_2\text{COC}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{CH}_2\text{COC}_2\text{H}_5$	
VII-57	378	$\text{CH}_3 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	
VII-58	378	$\text{CH}_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	
		$\rightarrow \text{C}_2\text{H}_6 + \text{CH}_2\text{OC}_2\text{H}_5$	
VII-59	378	$\text{CH}_2\text{O} \rightarrow \text{HCHO} + \text{H}$	
VII-60	378	$\text{CH}_2\text{O} + \text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_2\text{OH} + \text{CH}_2\text{OCH}_3$	
VII-60A	378	$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow (?)$	
VII-61	379	$\text{CH}_2\text{CO} \rightarrow \text{CH}_2 + \text{CO}$	18
VII-62	382	$2\text{CH}_2\text{CO} \rightarrow (\text{CH}_2\text{CO})_2$	small
VII-63	383	$\text{CH}_2\text{CO} + \text{CH}_2\text{COCH}_3 \rightarrow \text{CH}_2\text{COCH}_2\text{COCH}_3$	
VII-64	383	$\text{CH}_3\text{CHO} \rightarrow \text{H} + \text{CH}_3\text{CO}$	
		$\rightarrow \text{CH}_2\text{CO}$	
		$\rightarrow \text{CH}_3 + \text{CO}$	
VII-65	383	$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2$	
VII-66	383	$\text{C}_2\text{H}_5 + \text{CH}_3\text{CHO} \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CO}$	
VII-67	383	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{CHO} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{CO}$	6.5(?)
VII-68	384	$\text{C}_2\text{H}_5 + \text{CH}_2\text{COC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_2\text{COC}_2\text{H}_5$	
VII-69	384	$\text{CH}_2\text{COO} \rightarrow \text{CH}_2 + \text{CO}_2$	large
VII-70	385	$\text{CH}_2\text{CH}_2\text{O} \rightarrow \text{CH}_2 + \text{HCHO}$	28-34
VII-71	385	$\text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_2 + \text{HCHO}$	~ 35
VII-72	385	$\text{CH}_2\text{OCH}_3 + \text{CH}_2\text{OCH}_3 \rightarrow (\text{CH}_2\text{OCH}_3)_2$	
VII-73	386	$\text{CH}_2\text{OCH}_3 + \text{CH}_2\text{COCH}_3 \rightarrow (?)$	~ 10
VII-73A	386	$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow (?)$	
VII-74	386	$\text{CH}_2\text{CH}_2\text{CHO} \rightarrow \text{C}_2\text{H}_4 + \text{CHO}$	
VII-75	386	$\text{C}_2\text{H}_5\text{CO} \rightarrow \text{C}_2\text{H}_5 + \text{CO}$	< 17
VII-76	387	$\text{CH}_2\text{COCH}_3 \rightarrow \text{CH}_2 + \text{CH}_2\text{CO}$	large
VII-77	387	$\text{CH}_2\text{COCH}_3 + \text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_2\text{COCH}_3 + \text{CH}_2\text{OCH}_3$	20(?)
VII-78	387	$\text{CH}_2\text{COCH}_3 + \text{CH}_2\text{COCH}_3 \rightarrow \text{CH}_2\text{COCH}_2\text{CH}_2\text{COCH}_3$	
VII-79	387	$\text{C}_2\text{H}_7 + \text{C}_2\text{H}_7\text{CHO} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_7\text{CO}$	5.6(?)
VII-80	387	$\text{CH}_2\text{OC}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{CH}_3\text{CHO}$	

Section	Page	Reaction	E, kcal.
VII-81	388	$\text{CH}_3\text{COCOCH}_3 \rightarrow \text{CH}_3\text{CO} + \text{CH}_3\text{CO}$	
VII-81A	388	$\text{C}_2\text{H}_7 + \text{O}_2 \rightarrow (?)$	
VII-82	388	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5$	
VIII-1	389	$\text{H} + \text{HCN} \rightarrow \text{H}_2 + \text{CN}$	
VIII-2	389	$\text{H} + \text{CH}_3\text{NH} \rightarrow \text{CH}_3\text{NH}_2$	
VIII-3	389	$\text{H} + \text{CH}_3\text{NH}_2 \rightarrow \text{H}_2 + \text{CH}_3\text{NH}$	
VIII-4	390	$\text{H} + (\text{CN})_2 \rightarrow \text{HCN} + \text{CN}$	small
VIII-5	390	$\text{H} + \text{CH}_3\text{NNCH}_3 \rightarrow \text{CH}_3\text{NHNCH}_3$	~ 0
		$\rightarrow \text{CH}_4 + \text{CH}_3\text{N}_2$	8
VIII-6	391	$\text{H} + (\text{CH}_3)_2\text{NH} \rightarrow (\text{CH}_3)_2\text{N} + \text{H}_2$	
VIII-7	391	$\text{H} + \text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{C}_2\text{H}_5\text{NH} + \text{H}_2$	
VIII-8	392	$\text{H} + \text{CH}_3\text{NHNHCH}_3 \rightarrow \text{CH}_3\text{NH}_2 + \text{CH}_3\text{NH}$	8(?)
		$\rightarrow \text{H}_2 + \text{R}$	
VIII-9	392	$\text{H} + \text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{C}_2\text{H}_5\text{NH} + \text{H}_2$	
VIII-10	392	$\text{H} + \text{C}_2\text{H}_{11}\text{NH}_2 \rightarrow \text{C}_2\text{H}_{11}\text{NH} + \text{H}_2$	
VIII-11	392	$\text{O} + \text{HCN} \rightarrow (?)$	7-8
VIII-12	392	$\text{O} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_2\text{O}$	~ 0
VIII-13	393	$\text{O} + (\text{CN})_2 \rightarrow (?)$	7-8
VIII-14	393	$\text{O} + (\text{CH}_3)_3\text{N} \rightarrow (\text{CH}_3)_3\text{NO}$	~ 0
VIII-15	393	$\text{CN} + \text{CN} \rightarrow (\text{CN})_2$	~ 0
VIII-16	393	$\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}$	~ 7
VIII-17	394	$\text{CH}_2 + \text{CH}_2\text{N}_2 \rightarrow \text{C}_2\text{H}_4 + \text{N}_2$	small
VIII-18	395	$\text{CH}_3 + \text{NO} \rightarrow \text{CH}_3\text{NO}$	6.5
VIII-19	396	$\text{CH}_2 + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_4 + \text{CH}_3\text{NH}$	
VIII-20	396	$\text{CH}_2 + \text{CH}_3\text{CH}_2\text{ONO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CHONO}$	< 10
VIII-21	397	$\text{CH}_3 + \text{CH}_3\text{NNCH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{N}_2$	
		$\rightarrow \text{C}_2\text{H}_6 + \text{CH}_3 + \text{N}_2$	
		$\rightarrow (\text{CH}_3)_2\text{NNCH}_3$	
VIII-22	398	$\text{CH}_3 + \text{CH}_3\text{NHNHCH}_3 \rightarrow \text{CH}_4 + \text{R}$	
VIII-23	398	$\text{CH}_3 + \text{C}_2\text{H}_7\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_2 + \text{C}_2\text{H}_7$	large
VIII-24	398	$\text{CH}_3 + (\text{CH}_3)_2\text{N} \rightarrow \text{CH}_4 + \text{CH}_3\text{N}(\text{CH}_3)_2$	
VIII-25	398	$\text{CH}_3 + (\text{CH}_3)_2\text{NNCH}_3 \rightarrow \text{C}_2\text{H}_6 + (\text{CH}_3)_2\text{N}_2$	
		$\rightarrow (\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$	
VIII-25A	399	$\text{CH}_2\text{NH} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_2=\text{NCH}_3 + \text{NH}_3$	
VIII-26	399	$\text{CH}_3\text{N}_2 \rightarrow \text{CH}_3 + \text{N}_2$	
VIII-27	399	$\text{CH}_3\text{NO} \rightarrow \text{CH}_3=\text{NOH}$	
VIII-27A	399	$\text{CH}_3\text{NH} \rightarrow \text{CH}_2=\text{NH} + \text{H}$	
VIII-28	399	$\text{CH}_2\text{NH} + \text{CH}_3\text{NH} \rightarrow \text{CH}_2\text{N}=\text{CH}_2 + \text{NH}_3$	
VIII-29	399	$\text{CH}_3\text{CO} + \text{NO} \rightarrow (?)$	> 6.5
VIII-30	399	$\text{CH}_3\text{CHONO} \rightarrow \text{CH}_3\text{CHO} + \text{NO}$	
VIII-31	399	$\text{C}_2\text{H}_5 + \text{NO} \rightarrow (?)$	
VIII-32	400	$\text{C}_2\text{H}_5 + \text{CH}_3\text{NNCH}_3 \rightarrow (?)$	
VIII-33	400	$\text{CH}_3\text{CH}_2\text{O} + \text{CH}_3\text{CH}_2\text{ONO} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CHONO}$	12-18
VIII-33A	400	$\text{CH}_2=\text{NCH}_3 \rightarrow \text{C}_2\text{H}_5\text{N} + \text{H}_2$	
VIII-34	400	$(\text{CH}_3)_2\text{N} + (\text{CH}_3)_2\text{N} \rightarrow (\text{CH}_3)_3\text{NH} + \text{CH}_3\text{NCH}_3$	
VIII-35	401	$\text{C}_2\text{H}_5\text{NH} + \text{C}_2\text{H}_5\text{NH} \rightarrow \text{C}_2\text{H}_5\text{NCHCH}_3 + \text{NH}_3$	
VIII-36	401	$\text{CH}_3\text{NHNCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{NHNHCH}_3 + \text{H}$	3-4
VIII-37	401	$\text{CH}_3\text{N}(\text{CH}_3)_2 \rightarrow \text{CH}_3 + \text{CH}_2\text{N}=\text{CH}_2$	
VIII-38	401	$2(\text{CH}_3)_2\text{NNCH}_3 \rightarrow ((\text{CH}_3)_2\text{NNCH}_3)_2$	
VIII-39	401	$\text{C}_2\text{H}_5\text{N} \rightarrow \text{C}_2\text{H}_5 + \text{HCN}$	
VIII-40	401	$2\text{C}_2\text{H}_5\text{NH} \rightarrow \text{C}_2\text{H}_5=\text{N}-\text{C}_2\text{H}_5 + \text{NH}_3$	
		$\rightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{C}_2\text{H}_5\text{N}=\text{}$	
VIII-41	402	$2(\text{C}_2\text{H}_5)_3\text{N} \rightarrow (\text{C}_2\text{H}_5)_3\text{NH} + \text{C}_2\text{H}_5\text{NC}_2\text{H}_5$	
VIII-42	402	$2\text{C}_2\text{H}_{11}\text{NH} \rightarrow \text{C}_2\text{H}_{11}\text{NCHC}_2\text{H}_5 + \text{NH}_3$	
IX-1	403	$\text{H} + \text{CH}_3\text{F} \rightarrow \text{HF} + \text{CH}_3$	> 9
IX-2	403	$\text{H} + \text{CCl}_4 \rightarrow \text{HCl} + \text{CCl}_3$	3.5
IX-3	404	$\text{H} + \text{CHCl}_3 \rightarrow \text{CH}_2\text{Cl}_2$	small

Section	Page	Reaction	E, kcal.
IX-4	404	$H + CHCl_3 \rightarrow HCl + CHCl_2$ $\rightarrow H_2 + CCl_3$	< 4.3
IX-5	404	$H + CH_2Cl \rightarrow CH_2Cl$	small
IX-6	405	$H + CH_2Cl_2 \rightarrow HCl + CH_2Cl$ $\rightarrow H_2 + CHCl_2$	~ 6 ~ 6
IX-7	405	$H + CH_3Cl \rightarrow HCl + CH_3$ $\rightarrow H_2 + CH_2Cl$	7-9
IX-8	405	$H + C_2H_5Cl \rightarrow C_2H_5 + HCl$	8
IX-9	406	$O + CCl_4 \rightarrow COCl_2 + Cl_2$	7-8
IX-10	406	$O + CHCl_3 \rightarrow COCl_2 + HCl$	≤ 4
IX-11	406	$O + CH_2Cl_2 \rightarrow (?)$	≤ 4
IX-12	406	$O + CH_3Cl \rightarrow (?)$	5-6
IX-13	406	$Cl + CCl_4 \rightarrow CCl_4$	
IX-14	406	$Cl + CCl_4 \rightarrow CCl_3 + Cl_2$	> 12
IX-15	407	$Cl + CO \rightarrow COCl$	small
IX-16	407	$Cl + COCl \rightarrow CO + Cl_2$	1.9
IX-17	407	$Cl + COCl_2 \rightarrow COCl + Cl$	23
IX-18	408	$Cl + CHCl_3 \rightarrow HCl + CCl_3$	8 ± 1
IX-19	409	$Cl + CH_2Cl_2 \rightarrow CHCl_2 + HCl$	< 8
IX-20	410	$Cl + HCHO \rightarrow CHO + HCl$	
IX-21	410	$Cl + HCOOH \rightarrow COOH + HCl$	
IX-22	411	$Cl + CH_3 \rightarrow CH_3Cl$	
IX-23	411	$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	< 8
IX-24	411	$Cl + CH_4 \rightarrow CH_3 + HCl$ $\rightarrow CH_2Cl + H$	< 8
IX-25	413	$Cl + C_2Cl_4 \rightarrow C_2Cl_5$	<< 8
IX-26	414	$Cl + C_2HCl_3 \rightarrow C_2HCl_4$	small
IX-27	414	$Cl + C_2HCl_3 \rightarrow C_2H_2 + HCl$	5-8
IX-28	415	$Cl + CCl_3CHO \rightarrow CCl_3CO + HCl$	< 6
IX-29	415	$Cl + C_2H_2 \rightarrow C_2HCl + H$ $\rightarrow C_2H_2Cl$	
IX-30	416	$Cl + C_2H_2Cl_2 \rightarrow C_2H_2Cl_3$ $\rightarrow C_2H_2Cl_2 + Cl$	
IX-31	416	$Cl + C_2H_3Cl \rightarrow C_2H_3Cl_2$	
IX-32	416	$Cl + C_2H_4 \rightarrow C_2H_4Cl$ $\rightarrow C_2H_3 + HCl$	~ 0
IX-33	418	$Cl + C_2H_4Cl \rightarrow C_2H_4 + Cl_2$	1-2
IX-34	418	$Cl + C_2H_4Cl_2 \rightarrow C_2H_4Cl + Cl_2$ $\rightarrow C_2H_4 + Cl_3$	
IX-35	418	$Cl + C_2H_5 \rightarrow C_2H_5Cl$	
IX-36	418	$Cl + C_2H_5 \rightarrow C_2H_6 + HCl$	
IX-37	419	$Cl + C_2H_5 \rightarrow C_2H_5Cl$ $\rightarrow C_2H_6 + HCl$	
IX-38	420	$Cl + C_3H_8 \rightarrow C_3H_7 + HCl$	
IX-39	420	$Cl + C_3H_8 \rightarrow C_3H_8Cl$ $\rightarrow C_3H_7 + HCl$	
IX-40	420	$Cl + C_3H_{10} \rightarrow C_3H_{10}Cl$	
IX-41	420	$Cl + C_3H_9Cl \rightarrow C_3H_9Cl_2$	
IX-42	421	$Cl + C_3H_7Cl_2 \rightarrow C_3H_7Cl + Cl_2$	
IX-43	421	$Cl + C_3H_8 \rightarrow C_3H_8Cl$ $\rightarrow C_3H_7 + HCl$	
IX-44	421	$Cl + C_7H_{16} \rightarrow C_7H_{15} + HCl$	6
IX-45	422	$Cl + C_{10}H_{22} \rightarrow C_{10}H_{21}Cl$	~ 0
IX-46	422	$Cl + C_{10}H_{22} \rightarrow C_{10}H_{21} + HCl$	6
IX-47	424	$Cl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + Cl$	
IX-47A	424	$ClO + CO_2Cl_2 \rightarrow COCl_2 + O_2 + Cl_2$	
IX-47B	424	$ClO + CHCl_3 \rightarrow HCl + COCl_2 + Cl$	
IX-47C	424	$ClO + C_2HCl_3 \rightarrow CCl_2COCl + HCl + Cl$	
IX-47D	424	$ClO + CCl_3CHO \rightarrow COCl_2 + HCl + Cl$	
IX-48	424	$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl$	~ 8
IX-49	424	$CCl_3 + O_2 \rightarrow COCl_2 + ClO$	1-2
IX-50	425	$CCl_3 + HCl \rightarrow Cl + CHCl_3$	21(7)
IX-51	425	$CCl_3 + CCl_3 \rightarrow C_2Cl_6$	

Section	Page	Reaction	E, kcal.
IX-52	425	$2\text{CCl}_3 + \text{Cl}_2 \rightarrow 2\text{CCl}_4$	~ 0
IX-53	425	$\text{COCl} \rightarrow \text{CO} + \text{Cl}$	5.6
IX-54	425	$\text{COCl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl}$	2.6
IX-55	425	$\text{COCl}_2 + \text{COCl}_2 \rightarrow 2\text{COCl}_2 + \text{Cl}_2$	small
IX-56	426	$\text{CO}_2\text{Cl}_2 \rightarrow \text{COCl}_2 + \text{ClO}$	15(?)
IX-57	426	$\text{CHCl}_2 + \text{Cl}_2 \rightarrow \text{CHCl}_3 + \text{Cl}$	< 5
IX-58	426	$\text{CHO} + \text{Cl}_2 \rightarrow \text{CHOC}_2\text{Cl} + \text{Cl}$	
IX-59	426	$\text{COOH} + \text{Cl}_2 \rightarrow \text{ClCOOH} + \text{Cl}$	
IX-60	426	$\text{CH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{Cl}$	< 5
IX-61	426	$\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}$	< 5
IX-62	427	$\text{CH}_3 + \text{HCl} \rightarrow \text{CH}_4 + \text{Cl}$	
IX-63	427	$\text{C}_2\text{Cl}_5 + \text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6 + \text{Cl}$	~ 8
IX-64	428	$\text{C}_2\text{Cl}_5 + \text{O}_2 \rightarrow (?)$	< 5
IX-65	429	$\text{C}_2\text{Cl}_5 + \text{C}_2\text{Cl}_6 \rightarrow 2\text{C}_2\text{Cl}_4 + \text{Cl}_2$	~ 0
		$\rightarrow \text{C}_2\text{Cl}_4 + \text{C}_2\text{Cl}_4$	~ 0
IX-66	429	$\text{CCl}_3\text{CO} \rightarrow \text{CCl}_2 + \text{CO}$	> 22
IX-67	429	$\text{CCl}_3\text{CO} + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{CO} + \text{Cl}$	~ 6
IX-68	429	$\text{CCl}_3\text{CO} + \text{O}_2 \rightarrow \text{Peroxide}$	small
IX-69	430	$2\text{CCl}_3\text{CO} \rightarrow \text{C}_2\text{Cl}_6 + 2\text{CO}$	1-2
IX-70	430	$\text{CCl}_3\text{CO} + \text{CCl}_3\text{CHO} \rightarrow \text{CHCl}_2 + 2\text{CO} + \text{CCl}_4$	
IX-70A	430	$\text{CCl}_3\text{CO} + \text{CCl}_3\text{CHO} \rightarrow \text{CHCl}_2 + 2\text{CO} + \text{CCl}_4$	
IX-71	430	$\text{C}_2\text{HCl}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{HCl}_3 + \text{Cl}$	5.5
IX-72	430	$\text{C}_2\text{HCl}_4 + \text{O}_2 \rightarrow \text{Peroxide}$	~ 0
IX-73	431	$2\text{C}_2\text{HCl}_4 \rightarrow 2\text{C}_2\text{HCl}_3 + \text{Cl}_2$	~ 0
		$\rightarrow \text{C}_2\text{HCl}_3 + \text{C}_2\text{HCl}_3$	~ 0
IX-74	431	$\text{C}_2\text{H}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_4 + \text{Cl}$	3.5
IX-75	432	$2\text{C}_2\text{H}_2\text{Cl}_2 \rightarrow 2\text{C}_2\text{H}_2\text{Cl}_3 + \text{Cl}_2$	~ 0
		$\rightarrow \text{C}_2\text{H}_2\text{Cl}_3 + \text{C}_2\text{H}_2\text{Cl}_3$	~ 0
IX-76	432	$\text{C}_2\text{H}_3 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{Cl}$	
IX-77	432	$\text{C}_2\text{H}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_3 + \text{Cl}$	≥ 6
IX-78	432	$\text{C}_2\text{H}_3\text{Cl}_2 + \text{O}_2 \rightarrow (?)$	small
IX-79	433	$2\text{C}_2\text{H}_3\text{Cl}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl}_3 + \text{C}_2\text{H}_3\text{Cl}$	≥ 10
IX-80	433	$\text{C}_2\text{H}_3\text{Cl} \rightarrow \text{Cl} + \text{C}_2\text{H}_4$	8 ± 5
IX-81	433	$\text{C}_2\text{H}_3\text{Cl} + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl}_2 + \text{Cl}$	7 ± 3
IX-82	434	$\text{C}_2\text{H}_4\text{Cl} + \text{O}_2 \rightarrow (?)$	small
IX-83	434	$\text{C}_2\text{H}_5 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}$	small
IX-84	434	$\text{C}_2\text{H}_5 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}$	
IX-85	434	$\text{C}_2\text{H}_5\text{Cl} + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl}_2 + \text{Cl}$	
IX-86	434	$\text{C}_2\text{H}_7 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_7\text{Cl} + \text{Cl}$	small
IX-87	435	$\text{C}_4\text{H}_7 + \text{Cl}_2 \rightarrow \text{C}_4\text{H}_7\text{Cl} + \text{Cl}$	
IX-88	435	$\text{C}_4\text{H}_8\text{Cl} + \text{Cl}_2 \rightarrow \text{C}_4\text{H}_8\text{Cl}_2 + \text{Cl}$	
IX-89	435	$\text{C}_6\text{H}_5\text{Cl}_2 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl}_3 + \text{Cl}$	
IX-90	435	$\text{C}_7\text{H}_{15} + \text{Cl}_2 \rightarrow \text{C}_7\text{H}_{15}\text{Cl} + \text{Cl}$	~ 5
IX-91	435	$\text{C}_{10}\text{H}_{21} + \text{Cl}_2 \rightarrow \text{C}_{10}\text{H}_{21}\text{Cl} + \text{Cl}$	9
X-1	436	$\text{H} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3 + \text{HBr}$	3-7
X-2	436	$\text{H} + \text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_5 + \text{HBr}$	~ 6
X-3	437	$\text{Cl} + \text{CCl}_3\text{Br} \rightarrow \text{CCl}_2 + \text{BrCl}$	< 8
X-4	438	$\text{ClO} + \text{CCl}_3\text{Br} \rightarrow \text{COCl}_2 + \text{Cl}_2 + \text{Br}$	0(?)
X-5	438	$\text{Br} + \text{CBr}_4 \rightarrow \text{CBr}_3 + \text{Br}_2$	$< 5(?)$
X-6	439	$\text{Br} + \text{CCl}_3\text{Br} \rightarrow \text{CCl}_2 + \text{Br}_2$	6(?)
X-7	439	$\text{Br} + \text{CHCl}_3 \rightarrow \text{CCl}_2 + \text{HBr}$	10 ± 1
X-8	440	$\text{Br} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Br}$	0
X-8A	441	$\text{Br} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Br} + \text{HBr}$	15.6
X-9	441	$\text{Br} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HBr}$	17.8
X-10	443	$\text{Br} + \text{C}_2\text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_2\text{Br}$	
X-11	443	$\text{Br} + \text{C}_2\text{Cl}_4 \rightarrow \text{C}_2\text{Cl}_4\text{Br}$	
X-12	444	$\text{Br} + \text{C}_2\text{Cl}_4\text{Br}_2 \rightarrow \text{C}_2\text{Cl}_4\text{Br} + \text{Br}_2$	
X-13	444	$\text{Br} + \text{CCl}_3\text{CHO} \rightarrow \text{CCl}_3\text{CO} + \text{HBr}$	< 8
X-14	445	$\text{Br} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2\text{Br}$	~ 0
X-15	447	$\text{Br} + \text{C}_2\text{H}_2\text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_3\text{Br}$	~ 0
X-16	447	$\text{Br}_2 + \text{C}_2\text{H}_2\text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_3\text{Br}$	

Section	Page	Reaction	E, kcal.
X-17	447	$\text{Br} + \text{C}_2\text{H}_5\text{ClBr} \rightarrow \text{C}_2\text{H}_5\text{ClBr}_2$	~ 0
X-18	448	$\text{Br} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{Br}$	~ 0
X-19	448	$\text{Br} + \text{C}_2\text{H}_4\text{Br}_2 \rightarrow \text{C}_2\text{H}_4\text{Br} + \text{Br}_2$	
		$\rightarrow \text{C}_2\text{H}_4 + \text{Br}_2$	
X-20	448	$\text{Br} + \text{C}_2\text{H}_5\text{Cl}_2\text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl}_2\text{Br} + \text{Br}_2$	$> 11(?)$
X-21	448	$\text{Br} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{Br}$	~ 0
X-22	448	$\text{Br} + \text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr}$	
		$\rightarrow \text{C}_2\text{H}_5\text{Br} + \text{Br}$	large
X-23	448	$\text{Br} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HBr}$	13.8
X-24	449	$\text{Br} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{Br}$	$\ll 17.3$
X-25	450	$\text{Br} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$	
X-26	450	$\text{Br} + \text{C}_2\text{H}_{12} \rightarrow \text{C}_2\text{H}_{11} + \text{HBr}$	
X-27	450	$\text{Br}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{Br}_2 + \text{Br}$	
X-28	451	$\text{BrO} + \text{CCl}_3\text{Br} \rightarrow \text{COCl}_2 + \text{Br}_2$	small
X-28A	451	$\text{BrO} + \text{CCl}_3\text{CHO} \rightarrow \text{COCl}_2 + \text{CO} + \text{HCl} + \text{Br}$	
X-29	451	$\text{CBBr}_3 + \text{Br}_2 \rightarrow \text{CBBr}_4 + \text{Br}$	
X-30	451	$\text{CBBr}_3 + \text{O}_2 \rightarrow (?)$	
X-31	451	$\text{CCl}_4 + \text{Br}_2 \rightarrow \text{CCl}_3\text{Br} + \text{Br}$	6-7(?)
X-32	451	$\text{CCl}_4 + \text{HBr} \rightarrow \text{CHCl}_3 + \text{Br}$	6-7
X-33	451	$\text{COBr} \rightarrow \text{CO} + \text{Br}$	
X-33A	452	$\text{CH}_2\text{Br} + \text{Br}_2 \rightarrow \text{CH}_2\text{Br}_2 + \text{Br}$	small
X-33B	452	$\text{CH}_2\text{Br} + \text{HBr} \rightarrow \text{CH}_3\text{Br} + \text{Br}$	
X-34	452	$\text{CH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{Br}$	small
X-35	452	$\text{CH}_3 + \text{HBr} \rightarrow \text{CH}_4 + \text{Br}$	1.5 ± 1
X-36	454	$\text{CH}_3 + \text{CH}_3\text{Br} \rightarrow \text{C}_2\text{H}_6 + \text{Br}$	
		$\rightarrow \text{CH}_4 + \text{CH}_2\text{Br}$	≈ 7
X-37	455	$\text{C}_2\text{Cl}_2\text{Br} \rightarrow \text{C}_2\text{Cl}_2 + \text{Br}$	
X-38	455	$\text{C}_2\text{Cl}_2\text{Br} + \text{Br}_2 \rightarrow \text{C}_2\text{Cl}_2\text{Br}_2 + \text{Br}$	
X-39	455	$\text{C}_2\text{Cl}_4\text{Br} \rightarrow \text{C}_2\text{Cl}_4 + \text{Br}$	
X-40	455	$\text{C}_2\text{Cl}_4\text{Br} + \text{Br}_2 \rightarrow \text{C}_2\text{Cl}_4\text{Br}_2 + \text{Br}$	small
X-41	456	$\text{CCl}_3\text{CO} + \text{Br}_2 \rightarrow \text{CCl}_3\text{Br} + \text{CO} + \text{Br}$	> 16
X-41A	456	$\text{CCl}_3\text{CO} + \text{HBr} \rightarrow \text{CHCl}_3 + \text{CO} + \text{Br}$	
X-42	456	$\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_5 + \text{Br}$	14 ± 3
X-43	456	$\text{C}_2\text{H}_5\text{Br} + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br}_2 + \text{Br}$	5-10
X-44	456	$\text{C}_2\text{H}_5\text{Cl}_2\text{Br} \rightarrow \text{C}_2\text{H}_5\text{Cl}_2 + \text{Br}$	14 ± 3
X-45	456	$\text{C}_2\text{H}_5\text{Cl}_2\text{Br} + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl}_2\text{Br}_2 + \text{Br}$	~ 5
X-46	457	$\text{C}_2\text{H}_5\text{ClBr} \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Br}$	
X-47	457	$\text{C}_2\text{H}_5\text{ClBr} + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{ClBr}_2 + \text{Br}$	≥ 7
X-48	458	$\text{C}_2\text{H}_5\text{ClBr} + \text{O}_2 \rightarrow (?)$	small
X-49	458	$\text{CH}_3\text{CO} + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{CO} + \text{Br}$	
X-50	458	$\text{C}_2\text{H}_4\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{Br}$	13 ± 2
X-51	459	$\text{C}_2\text{H}_4\text{Br} + \text{Br}_2 \rightarrow \text{C}_2\text{H}_4\text{Br}_2 + \text{Br}$	> 5
X-52	460	$\text{C}_2\text{H}_4\text{Br} + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{Br}$	
X-53	461	$\text{C}_2\text{H}_4\text{Br} + \text{O}_2 \rightarrow (?)$	~ 0
X-54	461	$\text{C}_2\text{H}_4\text{Br} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{Br}$	
X-54A	461	$\text{C}_2\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{Br}$	small
X-55	461	$\text{C}_2\text{H}_5 + \text{HBr} \rightarrow \text{C}_2\text{H}_6 + \text{Br}$	~ 2
X-56	461	$\text{C}_2\text{H}_5\text{Br} + \text{HBr} \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{Br}$	
X-57	461	$2\text{CH}_3\text{BrCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{Br}(\text{CH}_2)_2\text{CH}_2\text{Br}$	
X-58	461	$\text{C}_4\text{H}_9 + \text{Br}_2 \rightarrow \text{C}_4\text{H}_9\text{Br} + \text{Br}$	
X-59	461	$\text{C}_4\text{H}_{11} + \text{Br}_2 \rightarrow \text{C}_4\text{H}_{11}\text{Br} + \text{Br}$	
XI-1	462	$\text{H} + \text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{HI}$	< 5
XI-2	462	$\text{H} + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5 + \text{HI}$	< 5
XI-3	463	$\text{OH} + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{OH} + \text{I}$	
XI-4	463	$\text{I} + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{I}_2$	
XI-5	463	$\text{I} + \text{CH}_4 \rightarrow \text{CH}_3\text{I}$	~ 0
XI-6	465	$\text{I} + \text{CCl}_3\text{CHO} \rightarrow \text{CCl}_3 + \text{CO} + \text{HI}$	
XI-7	465	$\text{I} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{I}$	~ 0
XI-8	465	$\text{I} + \text{CH}_3\text{COI} \rightarrow \text{I}_2 + \text{CH}_3\text{CO}$	small
XI-9	466	$\text{I} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{I}$	
XI-10	466	$\text{I} + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5\text{I}_2$	

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Section	Page	Reaction	E, kcal.
XI-11	466	$I + C_2H_5I_2 \rightarrow C_2H_5I + I_2$	12 ± 3
		$\rightarrow C_2H_4 + I_2$	large
XI-12	469	$I + C_2H_4 \rightarrow C_2H_5I$	~ 0
XI-13	469	$I + C_2H_2 \rightarrow C_2H_3I$	~ 0
XI-14	470	$I + C_3H_6(\text{cyclopropane}) \rightarrow C_3H_7I$	17
XI-15	471	$I + C_3H_6(\text{propylene}) \rightarrow C_3H_7I$	
XI-16	471	$I + n\text{-}C_3H_7 \rightarrow n\text{-}C_3H_7I$	small
		$I + \text{iso-}C_3H_7 \rightarrow \text{iso-}C_3H_7I$	small
XI-17	472	$I + n\text{-}C_4H_9 \rightarrow \text{iso-}C_4H_9 + I_2$	$20 \pm 2(?)$
		$I + \text{iso-}C_4H_9 \rightarrow \text{iso-}C_4H_9 + I_2$	
XI-18	474	$I + C_4H_8 \rightarrow C_4H_9I$	
XI-19	475	$I + \text{sec-}C_4H_9 \rightarrow C_4H_9I + I$	13.8
		$\rightarrow C_4H_8 + I_2$	16.8
XI-20	475	$I_2 + C_2H_4 \rightarrow C_2H_5I_2 + I$	
XI-21	475	$CHO + I_2 \rightarrow HI + I + CO$	small
XI-22	476	$CH_3 + CH_3I \rightarrow C_2H_5I$	
XI-23	476	$CH_3I \rightarrow CH_2 + I$	
XI-24	477	$CH_3I + CH_3 \rightarrow C_2H_5I$	
XI-25	477	$CH_3I + CH_3I \rightarrow CH_3I_2 + CH_3$	
XI-26	477	$CH_3 + I_2 \rightarrow CH_3I + I$	0.5 ± 0.5
XI-27	478	$CH_3 + HI \rightarrow CH_4 + I$	small
XI-28	479	$CH_3 + CH_3I \rightarrow CH_4 + CH_2I$	$12(?)$
		$\rightarrow CH_3I + CH_3$	
		$\rightarrow C_2H_5I + H$	
		$\rightarrow C_2H_4 + I$	
XI-29	479	$CH_3 + CH_3COI \rightarrow CH_4 + CH_3COI$	~ 8
XI-30	480	$CH_3COI \rightarrow CH_3CO + I$	$43(?)$
XI-31	480	$CH_3CO + I_2 \rightarrow CH_3COI + I$	small
XI-32	480	$C_2H_5I \rightarrow C_2H_4 + I$	$13.4(?)$
XI-33	481	$C_2H_5I + I_2 \rightarrow C_2H_5I_2 + I$	~ 12
XI-34	481	$C_2H_5I + C_2H_5I \rightarrow C_2H_5I_2 + C_2H_6$	
XI-35	481	$C_2H_5 + I_2 \rightarrow C_2H_5I + I$	~ 0
XI-36	482	$C_2H_5 + HI \rightarrow C_2H_6 + I$	
XI-37	482	$C_2H_5 + C_2H_5I \rightarrow C_4H_{10} + I$	
		$\rightarrow C_2H_6 + C_2H_4I$	
		$\rightarrow C_2H_6 + C_2H_4 + I$	
XI-38	482	$CH_3CHCH_3I \rightarrow C_3H_8 + I$	~ 13
		$CH_3CH_2CH_2I \rightarrow C_3H_8(\text{cyclopropane}) + I$	$27(?)$
XI-39	482	$CH_3CH_2CH_2I + I_2 \rightarrow CH_3I + CH_2CH_2I + I$	$12(?)$
XI-40	483	$C_2H_7 + I_2 \rightarrow C_2H_7I + I$	$12.6(?)$
XI-41	483	$C_2H_7 + HI \rightarrow C_2H_8 + I$	
XI-42	483	$C_2H_7 + C_2H_7I \rightarrow C_2H_8 + C_2H_7I$	
XI-43	483	$C_4H_9 + I_2 \rightarrow C_4H_9I + I$	~ 14
XI-44	484	$C_4H_9 + C_4H_9I \rightarrow C_4H_{10} + C_4H_9 + I$	
XII-1	485	$Na + CCl_3 \rightarrow CCl_2 + NaCl$	
		$Na + CCl_3 \rightarrow CCl + NaCl$	
		$Na + CCl \rightarrow C + NaCl$	
XII-2	485	$Na + CCl_3Br \rightarrow CCl_2 + NaBr$	0.5
XII-3	486	$Na + CCl_4 \rightarrow CCl_3 + NaCl$	1.7
XII-4	486	$Na + CFBBr_3 \rightarrow CFBBr_2 + NaBr$	0.9
XII-5	486	$Na + CNBr \rightarrow CN + NaBr$	1.6
		$\rightarrow Br + NaCN$	
XII-6	487	$Na + CNCl \rightarrow CN + NaCl$	1.7
		$\rightarrow Cl + NaCN$	
XII-7	487	$Na + COCl_2 \rightarrow COCl + NaCl$	2.3
XII-8	487	$Na + CHBr_3 \rightarrow CHBr_2 + NaBr$	0.3
XII-9	487	$Na + CHClBr_2 \rightarrow CHClBr + NaBr$	1.0
XII-10	487	$Na + CHCl_2 \rightarrow CHCl + NaCl$	
XII-11	488	$Na + CHCl_2Br \rightarrow CHCl_2 + NaBr$	1.5
XII-12	488	$Na + CHCl_3 \rightarrow CHCl_2 + NaCl$	4.0
XII-13	488	$Na + CHFBr_2 \rightarrow CHFBr + NaBr$	2.5

APPENDIX

Section	Page	Reaction	E, kcal.
XII-14	488	$\text{Na} + \text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{NaI}$	
XII-15	489	$\text{Na} + \text{CH}_3\text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{NaI}$	
XII-16	489	$\text{Na} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3 + \text{NaBr}$	
XII-17	489	$\text{Na} + \text{CH}_3\text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{NaBr}$	2.6
XII-18	489	$\text{Na} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3 + \text{NaCl}$	
XII-19	490	$\text{Na} + \text{CH}_2\text{ClBr} \rightarrow \text{CH}_2\text{Cl} + \text{NaBr}$	3.3
XII-20	490	$\text{Na} + \text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl} + \text{NaCl}$	6.8
XII-21	491	$\text{Na} + \text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{NaI}$	2.5
XII-22	492	$\text{Na} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3 + \text{NaBr}$	5.0
XII-23	493	$\text{Na} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3 + \text{NaCl}$	9.7
XII-24	493	$\text{Na} + \text{CH}_3\text{F} \rightarrow \text{CH}_3 + \text{NaF}$	> 25
XII-25	494	$\text{Na} + \text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3\text{NO} + \text{NaO}$	2.3
XII-26	494	$\text{Na} + (\text{CN})_2 \rightarrow \text{CN} + \text{NaCN}$	~ 0(?)
XII-27	494	$\text{Na} + \text{CHCl}=\text{CHCl}(\text{trans}) \rightarrow \text{CHCl}=\text{CH} + \text{NaCl}$	8.6
XII-28	494	$\text{Na} + \text{CHCl}=\text{CHCl}(\text{cis}) \rightarrow \text{CHCl}=\text{CH} + \text{NaCl}$	8.2
XII-28A	494	$\text{Na} + \text{CNCH}_2\text{Cl} \rightarrow \text{CNCH}_2 + \text{NaCl}$	2.2
XII-29	495	$\text{Na} + \text{CH}_2=\text{CHCl} \rightarrow \text{CH}_2=\text{CH} + \text{NaCl}$	10.1
XII-29A	495	$\text{Na} + \text{CH}_2=\text{CHBr} \rightarrow \text{CH}_2=\text{CH} + \text{NaBr}$	5.8
XII-29B	495	$\text{Na} + \text{CH}_2=\text{CHI} \rightarrow \text{CH}_2=\text{CH} + \text{NaI}$	3.2
XII-30	495	$\text{Na} + \text{CH}_3\text{COBr} \rightarrow \text{CH}_3\text{CO} + \text{NaBr}$	2.
XII-31	495	$\text{Na} + \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{CO} + \text{NaCl}$	~15
XII-32	495	$\text{Na} + \text{CH}_3\text{CHBr} \rightarrow \text{C}_2\text{H}_4 + \text{NaBr}$	
XII-33	496	$\text{Na} + \text{CH}_3\text{CH}_2\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{NaBr}$	
XII-34	496	$\text{Na} + \text{CH}_3\text{CHBr}_2 \rightarrow \text{CH}_3\text{CHBr} + \text{NaBr}$	
XII-35	496	$\text{Na} + \text{CH}_3\text{BrCH}_2\text{Br} \rightarrow \text{CH}_3\text{BrCH}_2 + \text{NaBr}$	
XII-36	496	$\text{Na} + \text{CH}_3\text{CHCl} \rightarrow \text{C}_2\text{H}_4 + \text{NaCl}$	
XII-37	497	$\text{Na} + \text{CH}_3\text{CHCl}_2 \rightarrow \text{CH}_3\text{CHCl} + \text{NaCl}$	7.1
XII-38	497	$\text{Na} + \text{CH}_3\text{ClCH}_2\text{Cl} \rightarrow \text{CH}_3\text{ClCH}_2 + \text{NaCl}$	7.0
XII-39	497	$\text{Na} + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5 + \text{NaI}$	1.0
XII-40	498	$\text{Na} + \text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_5 + \text{NaBr}$	4.9
XII-41	498	$\text{Na} + \text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_5 + \text{NaCl}$	9.7
XII-41A	498	$\text{Na} + \text{ClCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaCl}$	7.6
XII-42	498	$\text{Na} + \text{C}_2\text{H}_5\text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{NO}_2 + \text{NaO}$	2.4
XII-42A	498	$\text{Na} + \text{CH}_3\text{ClCH}_2\text{CN} \rightarrow \text{CH}_3\text{CH}_2\text{CN} + \text{NaCl}$	7.5
XII-43	498	$\text{Na} + \text{CH}_3\text{ClCOCH}_3 \rightarrow \text{CH}_3\text{COCH}_3 + \text{NaCl}$	
XII-44	498	$\text{Na} + \text{CH}_3\text{ClCOCH}_2\text{Cl} \rightarrow \text{CH}_3\text{ClCOCH}_2 + \text{NaCl}$	
XII-45	499	$\text{Na} + \text{CH}_2=\text{CClCH}_3 \rightarrow \text{CH}_2=\text{CCH}_3 + \text{NaCl}$	9.4
XII-46	499	$\text{Na} + \text{CH}_2=\text{CHCH}_2\text{Cl} \rightarrow \text{CH}_2=\text{CHCH}_2 + \text{NaCl}$	5.3
XII-47	499	$\text{Na} + \text{CH}_3\text{COCH}_2\text{Cl} \rightarrow \text{CH}_3\text{COCH}_2 + \text{NaCl}$	2.5
XII-48	499	$\text{Na} + \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2 + \text{NaBr}$	
XII-49	499	$\text{Na} + \text{CH}_3\text{CHCH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{NaBr}$	
XII-50	499	$\text{Na} + \text{CH}_3\text{BrCH}_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{BrCH}_2\text{CH}_2 + \text{NaBr}$	
XII-51	501	$\text{Na} + \text{CH}_3\text{CHBrCH}_2\text{Br} \rightarrow \text{CH}_3\text{CHCH}_2\text{Br} + \text{NaBr}$	
XII-52	501	$\text{Na} + \text{CH}_3\text{CClCH}_3 \rightarrow \text{CH}_3=\text{CHCH}_3 + \text{NaCl}$	
XII-53	501	$\text{Na} + \text{CH}_3\text{CH}_2\text{CHCl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHCl} + \text{NaCl}$	6.2
XII-54	501	$\text{Na} + \text{CH}_3\text{CHClCH}_2\text{Cl} \rightarrow \text{CH}_3\text{CHCH}_2\text{Cl} + \text{NaCl}$	6.8
XII-55	501	$\text{Na} + \text{CH}_3\text{ClCH}_2\text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{ClCH}_2\text{CH}_2 + \text{NaCl}$	7.5
XII-56	501	$\text{Na} + \text{CH}_3\text{CCl}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CClCH}_3 + \text{NaCl}$	5.7
XII-57	501	$\text{Na} + n\text{-C}_4\text{H}_9\text{I} \rightarrow n\text{-C}_4\text{H}_9 + \text{NaI}$	3.0
XII-58	501	$\text{Na} + n\text{-C}_4\text{H}_9\text{Cl} \rightarrow n\text{-C}_4\text{H}_9 + \text{NaCl}$	9.0
XII-59	502	$\text{Na} + (\text{CH}_3)_2\text{CHCl} \rightarrow (\text{CH}_3)_2\text{CH} + \text{NaCl}$	8.9
XII-60	502	$\text{Na} + \text{CH}_3\text{CH}_2\text{CHCH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{NaBr}$	
XII-61	502	$\text{Na} + \text{CH}_3\text{Br}(\text{CH}_2)_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 + \text{NaBr}$	
XII-62	502	$\text{Na} + \text{CH}_3\text{CHBrCHCH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CHCH}_3 + \text{NaBr}$	
XII-63	502	$\text{Na} + \text{CH}_3\text{BrC}(\text{CH}_3)_2\text{CH}_3 \rightarrow \text{CH}_3=\text{C}(\text{CH}_3)_2 + \text{NaBr}$	
XII-64	502	$\text{Na} + \text{CH}_3\text{BrC}(\text{CH}_3)_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{BrC}(\text{CH}_3)_2 + \text{NaBr}$	
XII-65	503	$\text{Na} + \text{CH}_3\text{Br}(\text{CH}_2)_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{Br}(\text{CH}_2)_2\text{CH}_2 + \text{NaBr}$	
XII-66	503	$\text{Na} + \text{CH}_3\text{CHBrCHBrCH}_3 \rightarrow \text{CH}_3\text{CHBrCHCH}_3 + \text{NaBr}$	
XII-67	503	$\text{Na} + \text{CH}_3\text{BrCHBrCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{BrCHCH}_2\text{CH}_3 + \text{NaBr}$	
XII-68	503	$\text{Na} + \text{CH}_3\text{ClCH}(\text{CH}_3)_2 \rightarrow \text{C}_4\text{H}_9 + \text{NaCl}$	
XII-69	503	$\text{Na} + \text{CH}_3\text{ClCH}(\text{CH}_3)\text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{ClCH}(\text{CH}_3)\text{CH}_2 + \text{NaCl}$	
XII-70	503	$\text{Na} + \text{C}_2\text{H}_5\text{CHClCH}_3 \rightarrow \text{C}_2\text{H}_5\text{CHCH}_3 + \text{NaCl}$	8.4
XII-71	503	$\text{Na} + n\text{-C}_4\text{H}_9\text{Cl} \rightarrow n\text{-C}_4\text{H}_9 + \text{NaCl}$	8.8

Section	Page	Reaction	E, kcal.
XII-72	503	$\text{Na} + \text{iso-C}_4\text{H}_9\text{Cl} \rightarrow \text{iso-C}_4\text{H}_9 + \text{NaCl}$	8.9
XII-73	504	$\text{Na} + (\text{CH}_3)_3\text{CCl} \rightarrow (\text{CH}_3)_3\text{C} + \text{NaCl}$	8.0
XII-74	504	$\text{Na} + \text{CH}_2\text{Br}(\text{CH}_2)_3\text{CH}_2 \rightarrow \text{CH}_2(\text{CH}_2)_3\text{CH}_2 + \text{NaBr}$	
XII-75	504	$\text{Na} + \text{CH}_2\text{BrC}(\text{CH}_3)_2\text{CH}_2 \rightarrow \text{C}_3\text{H}_7 + \text{NaBr}$	
XII-76	504	$\text{Na} + \text{CH}_2\text{BrC}(\text{CH}_3)_2\text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{BrC}(\text{CH}_3)_2\text{CH}_2 + \text{NaBr}$	
XII-77	504	$\text{Na} + \text{CH}_2\text{Br}(\text{CH}_2)_3\text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{Br}(\text{CH}_2)_3\text{CH}_2 + \text{NaBr}$	
XII-78	504	$\text{Na} + \text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2\text{Cl} \rightarrow \text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2 + \text{NaCl}$	7.0
XII-79	505	$\text{Na} + n\text{-C}_6\text{H}_{11}\text{Cl} \rightarrow n\text{-C}_6\text{H}_{11} + \text{NaCl}$	8.4
XII-80	505	$\text{Na} + \text{iso-C}_6\text{H}_{11}\text{Cl} \rightarrow \text{iso-C}_6\text{H}_{11} + \text{NaCl}$	8.3
XII-81	505	$\text{Na} + \text{C}_6\text{H}_{11}\text{ONO} \rightarrow \text{C}_6\text{H}_{11}\text{ON} + \text{NaO}$	2.8
XII-82	505	$\text{Na} + \text{C}_6\text{H}_5\text{I} \rightarrow \text{C}_6\text{H}_5 + \text{NaI}$	1.7
XII-83	506	$\text{Na} + \text{C}_6\text{H}_5\text{Br} \rightarrow \text{C}_6\text{H}_5 + \text{NaBr}$	3.8
XII-84	506	$\text{Na} + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{C}_6\text{H}_5 + \text{NaCl}$	10.2
XII-85	507	$\text{Na} + \text{CH}_2\text{Br}(\text{CH}_2)_4\text{CH}_2 \rightarrow \text{CH}_2(\text{CH}_2)_4\text{CH}_2 + \text{NaBr}$	
XII-86	507	$\text{Na} + \text{CH}_2\text{Br}(\text{CH}_2)_4\text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{Br}(\text{CH}_2)_4\text{CH}_2 + \text{NaBr}$	
XII-87	507	$\text{Na} + \text{C}_6\text{H}_5\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{CO} + \text{NaCl}$	~ 0
XII-88	508	$\text{Na} + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{NaCl}$	2.5
XII-88A	508	$\text{Na} + \text{C}_6\text{H}_5\text{CH}=\text{CHBr} \rightarrow \text{C}_6\text{H}_5\text{CH}=\text{CH} + \text{NaBr}$	4.1
XII-88B	508	$\text{Na} + \text{C}_6\text{H}_5\text{CH}=\text{CHCl} \rightarrow \text{C}_6\text{H}_5\text{CH}=\text{CH} + \text{NaCl}$	4.2
XII-88C	580	$\text{Na} + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{NaBr}$	2.8
XII-88D	508	$\text{Na} + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{NaCl}$	3.3
XII-88E	508	$\text{Na} + \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{Br} \rightarrow \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2 + \text{NaBr}$	0.2
XII-88F	508	$\text{Na} + \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2 + \text{NaCl}$	2.0
XII-89	508	$\text{CH}_3\text{NO} + \text{Na}_2 \rightarrow \text{CH}_3\text{NONa} + \text{Na}$	
XII-90	509	$\text{C}_2\text{H}_5\text{NO}_2 + \text{Na}_2 \rightarrow \text{C}_2\text{H}_5\text{NO}_2\text{Na} + \text{Na}$	
XII-91	509	$\text{C}_6\text{H}_{11}\text{ON} + \text{Na}_2 \rightarrow \text{C}_6\text{H}_{11}\text{ONNa} + \text{Na}$	
XIII-1	511	$\text{H} + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{CH}_4 + \text{Hg} + \text{CH}_3$	
XIII-2	511	$\text{H} + \text{Hg}(\text{C}_2\text{H}_5)_2 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_5 + \text{Hg}$	
XIII-3	511	$\text{CH}_3 + \text{Hg} \rightarrow \text{HgCH}_3$	
XIII-4	512	$\text{CH}_3 + \text{HgCH}_3 \rightarrow \text{Hg} + \text{C}_2\text{H}_6$	
		$\rightarrow \text{CH}_4 + \text{HgCH}_2$	<13(?)
		$\text{CH}_3 + \text{HgCH}_3 \rightarrow \text{Hg}(\text{CH}_3)_2$	
XIII-5	512	$\text{CH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{HgCH}_3 + \text{C}_2\text{H}_6$	
		$\rightarrow \text{Hg} + \text{CH}_3 + \text{C}_2\text{H}_6$	
		$\rightarrow \text{CH}_4 + \text{HgC}_2\text{H}_5$	13-14(?)
XIII-6	513	$\text{CH}_3 + \text{Pb}(\text{CH}_3)_4 \rightarrow \text{Pb}(\text{CH}_3)_3 + \text{C}_2\text{H}_6$	<10(?)
XIII-7	513	$\text{C}_2\text{H}_5 + \text{Hg}(\text{C}_2\text{H}_5)_2 \rightarrow \text{C}_4\text{H}_{10} + \text{C}_2\text{H}_5 + \text{Hg}$	
		$\rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{C}_2\text{H}_5 + \text{Hg}$	
XIII-8	514	$\text{C}_2\text{H}_5 + \text{Zn}(\text{C}_2\text{H}_5)_2 \rightarrow \text{C}_4\text{H}_{10} + \text{C}_2\text{H}_5 + \text{Zn}$	
		$\rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{C}_2\text{H}_5 + \text{Zn}$	
XIII-9	514	$\text{HgCH}_3 \rightarrow \text{Hg} + \text{CH}_3$	
XIII-10	514	$2\text{HgCH}_3 \rightarrow 2\text{Hg} + \text{C}_2\text{H}_6$	
XIII-11	514	$\text{HgCH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{Hg} + \text{C}_2\text{H}_6 + \text{HgCH}_3$	
XIV-1	515	$\text{H} + \text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{S} + \text{H}_2$	
XIV-2	515	$\text{H} + \text{C}_2\text{H}_5\text{SH} \rightarrow \text{C}_2\text{H}_5\text{S} + \text{H}_2$	
XIV-3	515	$\text{Na} + \text{CS}_2 \rightarrow \text{CS}_2\text{Na}$	large
XIV-4	515	$\text{S} + \text{COS} \rightarrow \text{CO} + \text{S}_2$	6
XIV-5	516	$\text{HS} + \text{C}_2\text{H}_5 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$	
XIV-6	516	$\text{HS} + \text{C}_4\text{H}_9 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$	
XIV-7	516	$2\text{CH}_3\text{S} \rightarrow \text{CH}_3\text{SSCH}_3$	
XIV-8	516	$2\text{C}_2\text{H}_5\text{S} \rightarrow \text{C}_2\text{H}_5\text{SSC}_2\text{H}_5$	
XIV-9	516	$\text{C}_2\text{H}_5\text{S} + \text{C}_2\text{H}_5\text{SH} \rightarrow \text{C}_2\text{H}_5\text{SSC}_2\text{H}_5 + \text{H}$	
XIV-10	516	$\text{C}_4\text{H}_9 + \text{H}_2\text{S} \rightarrow \text{C}_4\text{H}_9 + \text{HS}$	
XIV-11	516	$\text{CH}_3\text{CHCH}_3\text{SH} + \text{H}_2\text{S} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{SH} + \text{HS}$	
XIV-12	516	$\text{C}_4\text{H}_9 + \text{H}_2\text{S} \rightarrow \text{C}_4\text{H}_{10} + \text{HS}$	

Section	Page	Reaction	E, kcal.
XIV-13	517	$\text{CH}_3\text{CH}_2\text{CHCH}_2\text{SH} + \text{H}_2\text{S} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH} + \text{HS}$	
XIV-14	517	$\text{C}_7\text{H}_{15} + \text{SO}_2 \longrightarrow \text{C}_7\text{H}_{15}\text{SO}_2$	$\ll 5$
XIV-15	517	$\text{C}_7\text{H}_{15}\text{SO}_2 + \text{Cl}_2 \longrightarrow \text{C}_7\text{H}_{15}\text{SO}_2\text{Cl} + \text{Cl}$	
XIV-16	517	$\text{C}_7\text{H}_{15}\text{SO}_2 + \text{O}_2 \longrightarrow (?)$	small
XIV-17	517	$\text{C}_{15}\text{H}_{33} + \text{SO}_2 \longrightarrow \text{C}_{15}\text{H}_{33}\text{SO}_2$	$\ll 5$
XIV-18	517	$\text{C}_{15}\text{H}_{33}\text{SO}_2 + \text{Cl}_2 \longrightarrow \text{C}_{15}\text{H}_{33}\text{SO}_2\text{Cl} + \text{Cl}$	
XIV-19	517	$\text{C}_{15}\text{H}_{33}\text{SO}_2 + \text{O}_2 \longrightarrow (?)$	small

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Subject Index

NOTE: Since elementary reactions are indexed in the Appendix, they are not included here. For example, the decomposition of formaldehyde is listed in the subject index under "Formaldehyde, decomposition." The decomposition of formyl, however, is not listed in the subject index but will be found in the Reaction Index in the Appendix under " $\text{CHO} + \text{H}.$ "

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