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THE THEORY OF ORGANIC CHEMISTRY

An Advanced Course

BY

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PREFACE

THE STRUCTURAL THEORY of Kekule has been the growth hormone of organic chemistry. This theory used the atom and the bond as its fundamental concepts. It assumed no knowledge of either the composition of the atom or the nature of the bond. In recent years, however, modern theories of atoms and bonds have nearly filled these lacunae.

The deduction of the contents of organic chemistry from first principles with the aid of quantum mechanics is a goal to be reached; not an actual attainment. A simpler procedure is to incorporate G. N. Lewis' ideas of atoms and bonds with the classical structural theory. The result of this alliance is a structural theory whose fundamental concepts are valence electrons and atomic kernels. This electronic structural theory, and its application to organic chemistry, is the subject matter of this book.

We believe that a chemist can attain a fruitful knowledge of electronic structural theory without the ability to perform quantum mechanical calculations. However, quantum mechanics has contributed greatly to the development of the electronic structural theory. We have, therefore, included some digressions into quantum mechanics—notably in considering such fundamental concepts as the shared electron bond and molecular resonance.

We have attempted to keep a uniform point of view throughout rather than to produce a collection and evaluation of the mass of existing theories. This policy necessitates giving our opinions undue prominence. Ideas have been ignored on the slight grounds that we do not agree with them. Controversial points have been left without any decision because we have not reached one. Nevertheless we believe our policy to be the correct one in dealing with so live a subject.

The language of the new theories of organic chemistry has not had time to become uniform. The same ideas are expressed in different words by different authorities. C. K. Ingold, whose contributions to electronic structural theory are second to none, has developed a language to express his ideas. We have given scant recognition to this language, and have even taken certain liberties with it.

Actually we are in very close agreement with Professor Ingold's theories.

In the course of the preparation of the manuscript, we have had occasion to refer frequently to a number of very useful existing texts, chief among which are Gilman's *Organic Chemistry*, Watson's *Modern Theories of Organic Chemistry*, Pauling's *The Nature of the Chemical Bond*, and Freudenberg's *Stereochemie*. Special thanks are due to Professor Pauling for the original of Figure 9.

It is indeed a pleasure to acknowledge the co-operation of our colleagues, Professor Gilbert N. Lewis, Professor K. S. Pitzer, Dr. R. S. Halford, and Dr. David Lipkin, in the reading and discussion of manuscript and proof; and of Mrs Gerald Branch, to whose patience and understanding this book owes its existence.

G. E. K. B.
M. C.

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PREFACE

The use of synthetic adjuncts in foods has progressed so rapidly within recent years that there is little question of the need for a book in this field. I trust that this text represents an adequate contribution

Though many color and flavor compositions are detailed in this text, it is not intended that this book be used as a formulary. Some of these formulas are illustrative of trade practice; others are of an experimental nature. These formulations are included to serve as operating suggestions. Those well versed in the art of flavor manufacture may improve them by the application of their own skill and art. For others, these compositions may serve as a basis of instruction.

I am grateful for the assistance rendered in the preparation of this text by Mr. William E. Wilmore and thanks are due to Mr. W. C. Bainbridge and Mr. Louis Koch of H. Kohnstamm & Co., for reviewing the chapters dealing with synthetic coloring matters.

MORRIS B. JACOBS

Brooklyn, New York, 1946

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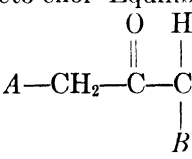
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10. THE LEWIS ATOM

The construction of an electrical model of an atom naturally led to the hope that chemical behavior could be explained or deduced from the classical laws of electricity. But it was soon apparent that these laws were inadequate to explain even how such atoms could exist, much less the complex facts of chemistry. The field was open to the introduction of new assumptions about the behavior of positive and negative electricity in the narrow confines of an atom. Speculators were free to base their assumptions on the chemical behavior of elements and compounds as well as the phenomena arising from widely separated atoms.

Lewis[3] assumed that the laws of electricity and magnetism are such that in the narrow space of an atom the electrons assume certain definite configurations. These configurations are concentric shells of electrons. As one goes from member to member of the series of elements, the added electron goes into a shell already occupied until an especially stable configuration has been reached, after which the added electron starts a new shell. An atom which is just short of the electrons required for one of these stable configurations has a tendency to acquire the necessary electrons and thereby the stable configuration, whereas one which has a slight excess of electrons over the stable configuration readily loses them. Hence in the series of elements a strongly negative element is followed by an inert element and the latter by a strongly positive element. This transition must be repeated every time a new shell is started. Consequently the elements show a marked periodicity of chemical properties when arranged according to their atomic numbers. Also, any property which depends either on the number of shells or on the number of electrons in an incomplete shell shows a corresponding periodicity. This periodicity in the chemical and physical properties of the elements is the reason for the ordering of the elements and the construction of periodic tables. Lewis' stable electron configurations must be identified with those of the noble gases. The atomic numbers of these elements are 2, 10, 18, 36, 54, and 86. The periods are then 2, 8, 8, 18, 18, and 32. The periodic table natural to the Lewis theory has only the above periods and hence belongs to the extended type rather than to the older condensed type.

[3] Lewis, G. N., *J. Am. Chem. Soc.*, **38**, 762 (1916). Almost identical suggestions were made by Kossel, W., *Ann. Physik*, **49**, 229 (1916). See also Lewis, *Valence and the Structure of Atoms and Molecules* (Chemical Catalog Co., 1923); and Kossel, *Valenzkräfte und Röntgenspektren* (Springer, 1927).

Lewis further assumes on the basis of chemical evidence that, except for the first one consisting of only two electrons, the stable arrangements all have an outermost shell of eight electrons, consisting of four pairs situated at the corners of a regular tetrahedron. Since the atomic number of a noble gas may differ by more than eight from that of the next one, a new shell may start in the series of elements before the inner ones are full.

Having obtained this picture of the structure of the atom, Lewis built up a theory of the chemical bond and molecular structure which is considered in the next chapter.

11. THE QUANTUM THEORY OF THE ATOM

11a. The Bohr atom. The first attempt to formulate the laws of motion for atomic systems, some of the results of which were contained in the Lewis postulates, was made by Bohr[4] (1913). He applied the concept of quanta first enunciated by Planck[5] (1900) to explain black-body radiation and used by Einstein[6] to interpret the photoelectric effect and the specific heats of solids, to the nuclear atom described by Rutherford. Bohr assumed that an electron can move about the nucleus only in one of a series of discrete states, each state of motion having a definite energy, and that the electron could be converted from one state of motion into another only by the emission or absorption of a definite quantity of energy equal to the difference in energy between these two states. If this energy were in the form of electromagnetic radiation, it would have a frequency given by the relation

$$\nu = \frac{E_2 - E_1}{h} \tag{1}$$

where h is Planck's constant of action having the value 6.55×10^{-27} erg sec. and E_1 and E_2 are the energies of the initial and final states, respectively. If E_1 is greater than E_2, the energy is emitted; if E_1 is less than E_2, the energy is absorbed. Further, he was able to calculate the energies of these states for the hydrogen atom by using the classical laws of electrodynamics upon which were superimposed the quantizing condition that for circular orbits of the motion of the electron about the nucleus, only those orbits were possible for which the angular momentum was an integral multiple, n, of $h/2\pi$. This

[4] Bohr, N., *The Theory of Spectra and Atomic Constitution.* Cambridge University Press, 1924.

[5] Planck, M., *Thermodynamics.* Longmans, Green & Co., New York, 1927.

[6] Einstein, A., *Ann. Physik,* **17**, 132 (1905); **37**, 832; **38**, 881 (1912).

was extended by Sommerfeld for all kinds of orbits by quantizing separately and in the same way each of the three components of the momentum of the electron and thus obtaining three related quantum numbers.[7] In the absence of any external disturbances such as other atoms, electric or magnetic fields, the energy of the atom depended only on the sum of these quantum numbers, and so it was possible to have several slightly different states of motion all having the same energy. In the presence of an external field, these different states of motion acquire different energy values. This form of the theory, however, was soon found to be inadequate in many respects; for example, it failed to give the energy states necessary to obtain the observed spectrum of the very next element of the periodic system, Helium, so that in 1926 Schrödinger[8] introduced a new law for describing atomic systems.

11b. The wave mechanical atom. Schrödinger used the de Broglie concept that a wave of wave length $\lambda = h/mv$ was associated with a moving particle. By combining this value of the wave length with the classical equation for wave motion, he obtained an expression representing the motions of atomic particles. This law has since been developed and expressed in the form of a differential equation

$$(H - W)\Psi = 0 \qquad (2)$$

together with the limiting condition that the solution of this equation must be such that the variable Ψ must be continuous, single valued, and finite for all possible co-ordinates of the system. H is an expression obtained from the Hamiltonian function of classical mechanics by means of a certain set of rules whose only justification is that they give results in agreement with experiment. It contains the co-ordinates of the particles in the system, the first and second differentials with respect to these co-ordinates, and the Planck constant. (This new law, which we shall henceforth call the Schrödinger equation, contains classical mechanics as the special case of $h = 0$.) W is the energy of the system, for which this equation has an allowed solution. It gives the values of Ψ as a function of the co-ordinates of the system, and the energy can be calculated by the relation

$$W = \int \Psi H \Psi \, d\tau, \qquad (3)$$

---

[7] An excellent and brief exposition of all of these concepts is to be found in *Atomic Spectra and Atomic Structure*, by G. Herzberg (Prentice-Hall, Inc., New York, 1937).

[8] Schrödinger, E., *Ann. Physik*, **79**, 361, 489; **80**, 437; **81**, 109 (1926). Suggested also by Heisenberg in a different form. Heisenberg, *Zeit. f. Phys.*, **33**, 879 (1925). Born, M., *Problems of Atomic Dynamics*, Cambridge, Mass., 1926.

which is a rearrangement of equation (2) where $d\tau$ is the differential of volume in phase space and the integral is taken over all the phase space for the system. Ψ is known as the wave function for the system. The solution of a differential equation for a system of particles, set up according to the law of classical mechanics, gives us directly the co-ordinates in space of these particles and their momenta as a function of these co-ordinates and time. This, however, is not true of the Schrödinger equation. The analogous process in quantum mechanics is an explicit solution for Ψ, from which the energy of the system and its distribution in space may be calculated.

The only atom for which the Schrödinger equation has been completely solved is the simplest one, the hydrogen atom, consisting of a positively charged nucleus around which a single electron is moving. The solution giving ψ explicitly as a function of the co-ordinate (r, θ, ϕ, in polar co-ordinates) of the electron about the nucleus as origin contains three parameters, n, l, and m, which can have only certain integral numerical values, and the solution is usually represented by $\psi_{n,l,m}(r, \theta, \phi)$. These parameters are known as the total quantum number n, the azimuthal quantum number l, and the magnetic quantum number m. The values which they are permitted to have in order that the wave equation and its limiting conditions be fulfilled are:

$$\begin{aligned} n &= 1, 2, 3, \cdots \\ l &= 0, 1, 2, \cdots n-1, \\ m &= -l, -l+1, \cdots 0, 1, 2, \cdots +l-1, +l. \end{aligned}$$

Thus for any given set of values of n, l, m, there exists a ψ describing a particular mode of motion of the electron, one of Bohr's orbits. Two of these ψ functions which are frequently used are those for which $n = 1$, $l = 0$, $m = 0$, and $n = 2$, $l = 1$, $m = \pm 1$ or 0; they are given explicitly by

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \tag{4}$$

$$\left.\begin{aligned} \psi_{210} &= \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta \\ \psi_{2,1,\pm 1} &= \begin{cases} \dfrac{1}{4\sqrt{2\pi a_0^3}} \dfrac{r}{a_0} e^{-r/2a_0} \sin\theta \cos\phi \\ \dfrac{1}{4\sqrt{2\pi a_0^3}} \dfrac{r}{a_0} e^{-r/2a_0} \sin\theta \sin\phi \end{cases} \end{aligned}\right\} \tag{5}$$

The energy of the electron in the state represented by $\psi_{n,l,m}(r, \theta, \phi)$ is given by

$$W = \frac{2\pi^2 \mu Z^2 e^4}{h^2 n^2} \tag{6}$$

where Ze is the charge on the nucleus, $-e$ the charge on the electron, μ the reduced mass of the system given by $\frac{m_{\text{electron}} \times m_{\text{nucleus}}}{m_{\text{electron}} + m_{\text{nucleus}}}$, h the Planck constant, and n the total quantum number. Just as n determines the energy of the electron, l determines the angular momentum of the electron and m determines how this angular momentum is to be oriented in space. It is thus apparent m plays no part in describing the electron in an atom unless some particular direction in space is specified by means of an external field, electric or magnetic, or by the presence of other atoms. Since these theories were first developed with special reference to spectroscopic data, the language of spectroscopy has been maintained in their use. An electronic wave function for which $n = 1$, $l = 0$, is written ψ_{1s}, for which $n = 2$, $l = 1$, ψ_{2p}, etc., where the letters s, p, d, f, g, h correspond to the l values, 0, 1, 2, 3, 4, and 5, respectively. Such a wave function, describing a possible mode of motion of a single electron, has been called an orbital. From the above-mentioned relationships between the permitted values of n, l, and m, it may be seen that for each value of n there exist n^2 such orbitals. Since the energy of a state is determined only by the value of n, there will be n^2 modes of motion for each energy level.

To complete the description of the atom, a way must be found to obtain from the ψ function[9] the actual position of the electron with respect to the nucleus. This has been done by attributing to $\bar{\psi}^2$ the value of a probability so that $\bar{\psi}^2 d\tau$ becomes the probability that an electron will be found in the element of volume $d\tau$. If the probability for each of the volume elements is added for all space, the sum must be unity, i.e. $\int \bar{\psi}^2 d\tau = 1$. This is simply saying that the electron must be somewhere in space around the nucleus. The ground state (most stable state) of the hydrogen atom is represented by ψ_{1s}, which is independent of θ and ϕ, i.e., it is spherically symmetrical about the nucleus and depends only on the distance from the nucleus (r). If, for such an orbital, the probability of finding the electron in a

[9] Henceforth we will omit all of the subscripts necessary to describe ψ unless some specific set is required.

spherical shell, whose internal radius is r and whose external radius is $r + dr$, is plotted against r, the result shown in Figure 1 is obtained.

The point of maximum probability is at $r_0 = 0.529$ Å, which corresponds exactly with the radius of the first Bohr orbit for hydrogen. Therefore we must now relinquish the idea that it is possible to state precisely where an electron will be, or exactly how fast it will be moving. This is to be replaced by the idea that an electron has a finite probability of being anywhere outside the nucleus, but that this probability is appreciable only for positions very close to that of maximum probability. The same argument holds for the distribution of velocity of the electron. Since most observable processes in which atoms take part are very slow compared to the most probable velocity of the electron, the atom can be considered as a

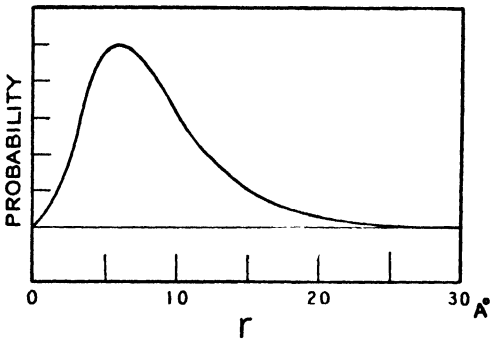


Figure 1. The probability distribution of the electron in the ground state of the hydrogen atom (s orbital).

positive nucleus surrounded by a distribution of negative charge whose density variation corresponds with the probability distribution. In Figure 2 are shown three-dimensional solid figures whose surfaces correspond to the maxima in the angular probability distribution for the two most important types of orbitals of the hydrogen atom, that for which $l = 0$ (s orbital) and those for which $l = 1$ (p orbitals). The s orbital figure represents the radial distribution as well. The value of n is left unspecified, since the symmetry of these figures is independent of n. There is only one possible s orbital ($m = 0$) but there are three mutually perpendicular p orbitals corresponding to $m = \pm 1$ or 0.

As a result of the study of the fine structure of certain atomic spectra, especially those of the alkali metals, Uhlenbeck and Gouds-

mit[10] found it necessary to ascribe to the valence electron a half unit of angular momentum in addition to its orbital angular momentum. Thus, in order to describe an electron completely, it is now necessary to give its intrinsic angular momentum (spin) in addition to its other three quantum numbers. This spin quantum number can have only the values $+\frac{1}{2}$ or $-\frac{1}{2}$. Further, no two electrons can have the identical set of all four quantum numbers. This is one form of expression for the Pauli Exclusion Principle,

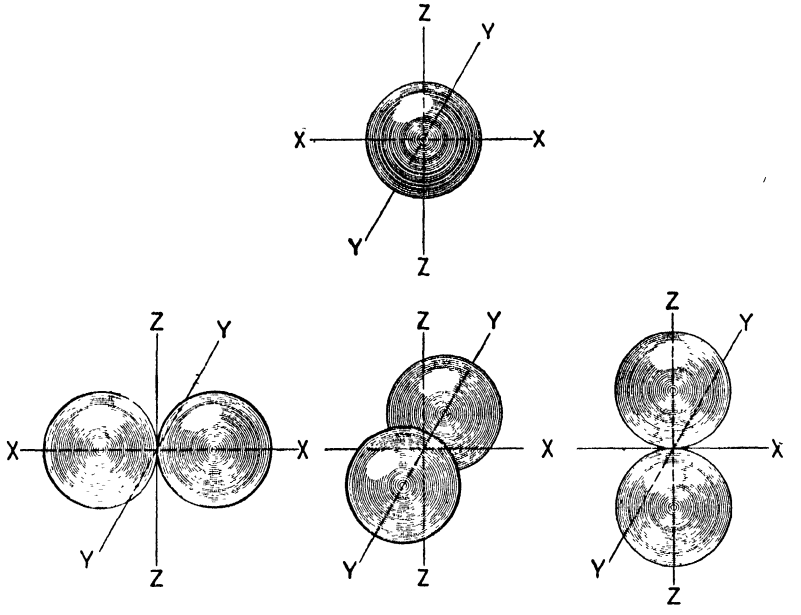


Figure 2. Surfaces of maximum probability for an s orbital (upper figure) and p orbitals, p_x, p_y, p_z (lower figures). The p orbitals give only the angular distribution.

which is really a statement of experimental fact. It is equivalent to saying that no two electrons can occupy the same place at the same time.

All of the characteristics of the possible electronic motions in the hydrogen atom, which we have described, remain valid for the possible motions of an electron in any spherically symmetrical field. Neglecting for the moment the interactions of the electrons among themselves, there exist about any nucleus, for each value of n, n^2

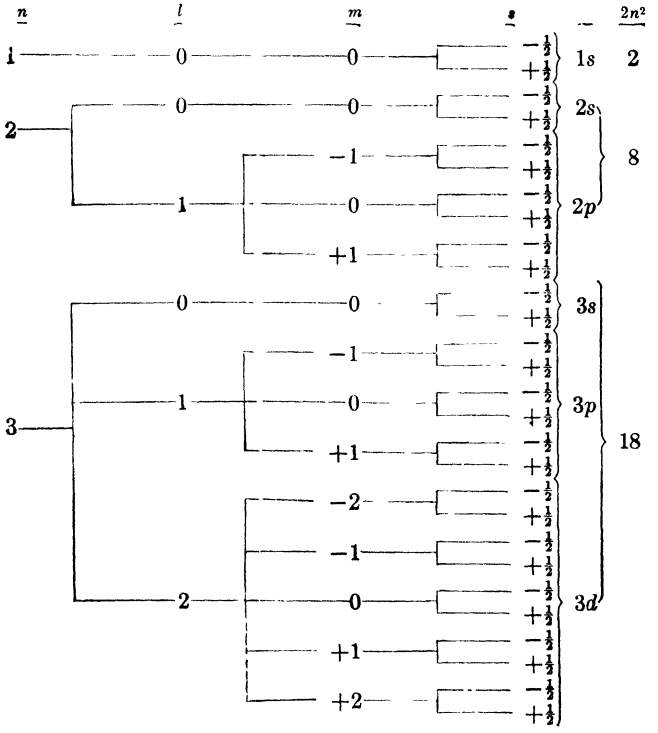
[10] Uhlenbeck, G. E., and Goudsmit, S., *Naturwiss.*, **13**, 953 (1925); *Nature*, **117**, 264 (1926).

orbitals (tracks, or modes of motion) into each of which not more than two electrons can be placed, and if there are two they must have opposite spins. Table 1 shows the possible conditions of an electron about a nucleus.

By taking a series of nuclei with increasing positive charges, the neutral atoms may be constructed by adding the equivalent number of electrons into the possible orbitals in their order of increasing

Table 1

QUANTUM NUMBERS FOR ORBITAL ELECTRONS



energy. This order of increasing energy of the orbitals must be determined experimentally from optical and X-ray spectra, and it appears that the order is that of increasing n and l up to the point at which the $3p$ shell is filled, i.e. Ar. The next electron goes into the $4s$ orbital instead of the $3d$ and gives potassium. From this point, then, the electronic interaction is sufficient to make the energy of a state of a given value of n and a high value of l greater than that of the state $n + 1$, but with a low value of l. Long before this

point, however, it had become possible to distinguish energy differences between different values of l for the same value of n.

Table 2 gives the electronic distributions of the atoms. An ex-

TABLE 2

THE ELECTRON DISTRIBUTION IN ATOMS

Atomic Number	Element	Ionization Potential (volts)	K $n=1$	L 2	M 3			N 4				O 5			P 6			Q 7
			$l=0$ s	0 1 s p	0 1 2 s p d			0 1 2 3 s p d f				0 1 2 s p d			0 1 2 s v d			0 s
1	H	13.539	1																
2	He	24.46	2																
3	Li	5.37	2	1															
4	Be	9.281	2	2															
5	B	8.28	2	2 1															
6	C	11.217	2	2 2															
7	N	14.47	2	2 3															
8	O	13.550	2	2 4															
9	F	18.6	2	2 5															
10	Ne	21.47	2	2 6															
11	Na	5.12	Neon Configuration		1														
12	Mg	7.61			2														
13	Al	5.96			2 1														
14	Si	8.12			2 2														
15	P	10.3			2 3														
16	S	10.31			2 4														
17	Cl	12.96			2 5														
18	Ar	15.69			2 6														
19	K	4.32	Argon Configuration					1											
20	Ca	6.09						2											
21	Sc	6.57					1	2											
22	Ti	6.80					2	2											
23	V	6.76					3	2											
24	Cr	6.74					5	1											
25	Mn	7.40					5	2											
26	Fe	7.83					6	2											
27	Co	7.81					7	2											
28	Ni	7.606					8	2											
29	Cu	7.69					10	1											
30	Zn	9.35					10	2											
31	Ga	5.97					10	2 1											
32	Ge	8.09					10	2 2											
33	As	9.4					10	2 3											
34	Se	9.5					10	2 4											
35	Br	11.80					10	2 5											
36	Kr	13.940					10	2 6											

TABLE 2 (*Cont.*)

Atomic Number	Element	Ionization Potential (volts)	*K* $n=1$	*L* 2	*M* 3	*N* 4	*O* 5	*P* 6	*Q* 7
			$l=0$ *s*	0 1 *s p*	0 1 2 *s p d*	0 1 2 3 *s p d f*	0 1 2 *s p d*	0 1 2 *s p d*	0 *s*
37	Rb	4.16					1		
38	Sr	5.67					2		
39	Y	6.5				1	2		
40	Zr	6.92				2	2		
41	Nb					4	1		
42	Mo	7.35				5	1		
43	Ma					6	1		
44	Ru	7.7	Krypton			7	1		
45	Rh	7.7	Configuration			8	1		
46	Pd	8.3				10			
47	Ag	7.54				10	1		
48	Cd	8.96				10	2		
49	In	5.76				10	2 1		
50	Sn	7.30				10	2 2		
51	Sb	8.5				10	2 3		
52	Te					10	2 4		
53	I	10				10	2 5		
54	X	12.078				10	2 6		
55	Cs	3.87						1	
56	Ba	5.19						2	
57	La						1	2	
58 to	Rare					1 to	1	2	
71	earths					14	1	2	
72	Hf					14	2	2	
73	Ta					14	3	2	
74	W					14	4	2	
75	Re		Xenon			14	5	2	
76	Os		Configuration including 8			14	6	2	
77	Ir		electrons in 5*s* and 5*p*			14	7	2	
78	Pt	8.9	shells, but none in 4*f* shell.			14	9	1	
79	Au	9.20				14	10	1	
80	Hg	10.39				14	10	2	
81	Tl	6.08				14	10	2 1	
82	Pb	7.39				14	10	2 2	
83	Bi	8.0				14	10	2 3	
84	Po					14	10	2 4	
85						14	10	2 5	
86	Rn	10.689				14	10	2 6	
87									1
88	Ra								2
89	Ac		Radon					1	2
90	Th		Configuration					2	2
91	Pa							3	2
92	U							5	1

amination of the table will show that the rare gases, with the exception of He, have an external electron configuration of eight electrons existing in four orbitals each containing a pair of electrons with opposite spins. Helium has only the stable single pair. It should be noted that the next electron added after a rare gas configuration has been completed always appears in the shell with the succeeding value of n. These atoms following the rare gases are thus the ones which begin the periods. To this must be added the experimental rule of Hund, that for any given value of l the electrons will tend to have the same spin so long as there are orbitals available which will permit them to do so. For example, there are three possible p orbitals and the three p electrons of nitrogen can remain unpaired by having each occupy a different p orbital. In oxygen, however, there are four p electrons and hence two of them must be paired in the same orbital, leaving only two unpaired electrons.

The wave mechanics contains in it the Lewis concepts of atomic structure, of the rule of eight, of the rule of two, and of the valence property of the unpaired electron. How these atoms can be combined to form the molecules of Chapter I with their localized bonds, geometrical arrangements, and free or restricted rotations, etc., will be taken up in the following chapter.

Chapter III

MOLECULAR STRUCTURE

12. ELECTRONIC STRUCTURAL FORMULAS

The properties of substances depend on the composition and structure of their molecules. These consist of atoms held together by chemical affinity. In classical chemistry the origin of affinity is not stated, but rules governing it are developed from observed facts. For instance, an atom is assumed to have definite valences, because substances are preparable only when their formulas can be made to agree with the assigned valences of the component atoms. Practically all known hydrocarbons have empirical formulas that could result from the assumptions of tetravalence of carbon and monovalence of hydrogen. Similarly the theory that the four valences of a carbon atom are directed to the corners of a tetrahedron is based on the facts of stereochemistry and is quite independent of any theory as to the origin of affinity.

Just as the periodic classification of the elements was developed before we had any knowledge of the composition of atoms, so the whole system of structural chemistry preceded all theories of the origin of the binding forces in a molecule. The atomic theory has increased our understanding and accuracy of the application of the periodic system. The development of bond theory, in its turn, may be expected to lead to marked advances in structural theory.

When atoms were found to be made of positive and negative charges, it was assumed that affinity was electrical in character. It was supposed either that an electron passed from one of a pair of bonded atoms to the other, the electrostatic attraction between the oppositely charged atoms constituting the binding force, or that electrons assumed a position between bonded atoms, the attraction of the intermediate electrons for each of the atoms constituting the binding force. The Lewis theory presupposes the latter condition.

Electrons in pairs are assumed to be able to belong to two atoms at the same time. The two shared electrons contribute to the valence electron shell of each of the atoms. Whenever the electron configurations of the bonded atoms are more stable than those of the

individual atoms, energy is needed to separate the atoms and a bond specific to the two atoms results. Similarly, two pairs or three pairs may be shared, resulting in double or triple bonds. Since Lewis assumes that the arrangement of the electrons in a noble gas is particularly stable, bonds will be formed when atoms can achieve these configurations by sharing their electrons. Thus fluorine atoms have seven valence electrons; by sharing a pair they can each have eight valence electrons and the stable arrangement of a neon atom. Even when an atom has enough bonds to fill its valence shell, it can still form bonds if it still has pairs of electrons not shared with other atoms, by sharing one of these pairs of electrons with an atom lacking valence electrons. Thus a nitrogen atom, which has five valence electrons, can use three of them to form bonds with hydrogen atoms. The other two electrons can be shared with a hydrogen ion, which is two electrons short of a helium electron configuration. The result is ammonium ion.

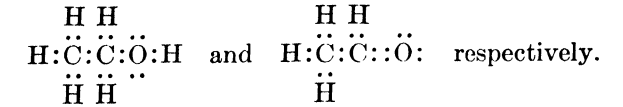
Lewis assumed that the pair of electrons was one of the stable arrangements, so that apart from the formation of noble gas electron arrangements, atoms having unpaired electrons would form bonds. This he calls the rule of two, to distinguish it from the rule of eight. Both rules are explicit in his theory.

It must not be assumed that these two rules exhaust the possibilities of bond formation. Thus mercuric ion combines with chloride ions to form mercuric chloride in which the mercury atom is bonded to the two chlorine atoms. In this process the mercury atom does not acquire an octet, and the chlorine atoms have the same octets in the chloride ions as in mercuric chloride. The bonds in this case may arise from a specific instability of the electron configuration of the mercuric ion. But the bonds which maintain themselves through the greatest vicissitudes are those in which the atoms have achieved noble-gas electron configurations.

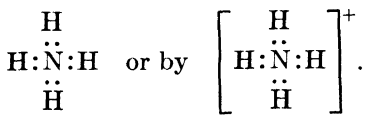
Atoms can also achieve noble-gas electron arrangements by the transfer of electrons from one atom to another. This process is also an integral part of Lewis' theory. The process produces opposite charges on the atoms and an attractive force between them. This force is not specific between the two atoms; the ion attracts all neighboring ions of opposite charge. Thus a sodium atom can give up an electron to a fluorine atom, both atoms achieving neon electron arrangements. The resulting ions attract each other and, if in profusion, will arrange themselves in a lattice so that ions will be surrounded by oppositely charged ions as far as possible. The existence

of the two types of binding has long been recognized, and they have been distinguished by various names. Perhaps the simplest nomenclature is to call the shared electron binding a chemical bond and the other type an ionic binding.

The Lewis theory readily allows the graphic representation of molecular structures. Since, in general, only the valence electrons are involved in bonds, electrons of inner shells need not be depicted. The symbol of the element represents the atom without its outermost shell of electrons; this part of the atom is known as the kernel. The electrons are shown as dots about the symbols, those electrons that are shared as bonds being placed between the appropriate symbols, the others around the symbol of the atom to which they belong. Electrons that are paired are placed close to each other. Thus the alcohol and acetaldehyde molecules are represented by



As the elementary symbols represent positively charged kernels and the dots electrons, it is not necessary to include any special sign for the charge on an ion, though this is sometimes done for convenience. Thus the ammonium ion is represented by



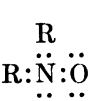
In the former graphic formula the letter N implies five units of positive charge and the letter H one. Since there are eight electrons, and since one N and four H's are shown, the charge is +1.

A system of structural formulas very similar to that of organic chemistry can be constructed from Lewis' atom and bond theory. In many instances an electron formula is assigned to a molecule for the same reasons that are used to assign the bond formula. Often the two types of formulas are used for the same purposes and in the same way. However, the two systems of structural formulas are not quite equivalent. In general, the Lewis theory has implications that are absent from classical structure theory, and in most cases—perhaps not in all—these implications are substantiated by the facts.

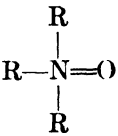
The rule of eight may replace the old rules of valence to predict the modes of combination of the elements, more especially for those that are not far from some noble gas in the series of elements. The valence rules used in building up bond formulas require that the

valence of a nitrogen atom be either three or five without any restrictions on the method of combination. If we assume that a nitrogen atom in a stable compound shall have an electron configuration like that of neon, the modes of combination allowed to nitrogen are three negative charges, two negative charges and a bond, one negative charge and two bonds, three bonds, and finally, one positive charge and four bonds. Although these modes can be identified with the tri- and pentavalence of the older theory, they are really more restrictive. Thus in an ionizable compound (salt) of trivalent nitrogen, the Lewis theory requires that the nitrogen is part of the anion. Generally the differences between the octet rule and the older valence rules are most marked in the higher valences. Thus the octet rule requires that pentavalent nitrogen can be obtained only when there is an atom or group that can acquire a negative charge to balance the positive charge of the nitrogen atom. A compound with the formula NH_4Cl is to be expected but not one with the formula NH_5. Further, if the combination is one with only monovalent atoms or groups, the pentavalent nitrogen compound must be a salt. The old valence rules make no restriction as to the types of atoms or groups in a pentavalent nitrogen compound, and say nothing as to the nature of the compound.

In many cases double bonds shown in the older formulas must be replaced by single bonds in electron structures to maintain the rule of eight. Thus an amine oxide is represented by the formula



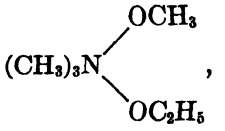
while the older formula



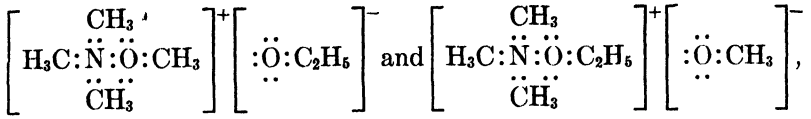
has a double bond.

Generally in these cases the single bond fits the properties of the substance better than the double bond.

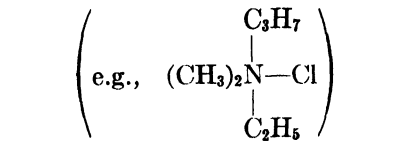
The old bond theory makes no implication as to the equivalence of the bonds of pentavalent nitrogen and implies that its stereochemistry would correspond to the geometry of some five-pointed object. The electron formula requires that four of the valences be equivalent, that one be an undirected electrostatic attraction, and that the stereochemistry would correspond to the geometry of a tetrahedron. The existence of two isomers of



as shown by the Lewis formulas,



and the lack of isomerism in compounds in which only one of the five groups would be likely to have a negative charge



confirms the idea of equivalence in four of the valences but not in all five. The stereochemistry of pentavalent nitrogen and of any atom having a noble-gas electron configuration agrees with that deducible from tetrahedral atoms.

12a. Co-ordination number. We have used nitrogen to exemplify the difference between the older and the new valence theory. In this case the new theory is entirely borne out by the facts, but this is not true for all elements. For instance, if the phosphorus atom in PCl_5 has an octet, the substance would be a salt, whereas the properties indicate that the five chlorine atoms are all attached by non-polar bonds to the phosphorus atom, as the bond structure would have implied. This is not a unique case. The formation of an octet does not exhaust the bond-forming possibilities. Even after octets have been formed they may be destroyed by the formation of extra bonds. Usually this occurs when the extra bonds are between oppositely charged ions (e.g., $PCl_4^+ + Cl^- \rightarrow PCl_5$). The maximum number of bonds possible to an atom of any element is known as its co-ordination number. Experimentally it is found that the co-ordination number is determined by the number of electron shells, as shown in the table.

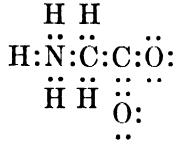
TABLE 3[1]

CO-ORDINATION NUMBERS

No. of Electron Shells	Co-ordination No.
1	2
2	4
3	6
4	6
5	8
6	8

[1] Sidgwick, Ref. (1), Chapter I.

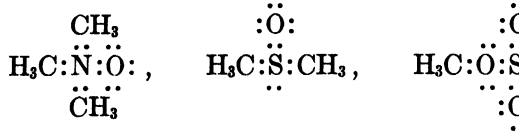
12b. Charge distribution. An electron formula depicts an arrangement of positive and negative charges, while a bond formula depicts one of neutral atoms. Consequently electron formulas should often directly show properties of compounds that are not implied by bond formulas. In an electron formula it is not possible to draw a boundary that separates the atoms from each other, because some of the electrons belong to two atoms. If we arbitrarily draw a boundary so as to separate the charge of shared electrons equally between the bonded atoms, each atom will either be neutral or have an integral number of electronic charges. This number is the same as the electrovalence of Sidgwick; we shall call it the formal charge of the atom. It must approximately represent the charges associated with regions of the molecules. Thus in



a boundary line drawn according to the above specification about the nitrogen atom will include four electrons and the letter N, which implies five positive charges. The region included has a net positive charge. Similarly the boundary around the singly bonded oxygen atom includes seven electrons and the six positive charges of the oxygen kernel, and is negatively charged. Boundaries around the other atoms represent neutral regions. The molecule as a whole is neutral but has an excess of positive charge at one point and negative charge at another, and should represent a molecule with a large dipole moment. It is natural to assume that this method will give larger dipoles than those actually found; for the electrons will tend to distribute themselves in the bonds so as partially to neutralize the charges. Actually the molecules of such substances as glycine have large dipole moments.

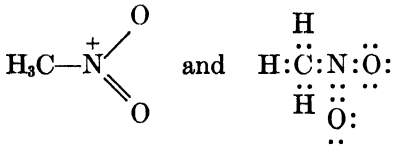
The existence of this separation of charge was known before the development of electron formulas. It was arrived at by chemical reasoning. A compound such as NH_2CH_2COOH is both a base and an acid, as it has an amino and a carboxyl group. It must neutralize itself, forming oppositely charged portions in the same molecule. These substances are known as zwitter ions, or better, inner salts.

A special type of inner salt is that in which the positively and negatively charged atoms are bonded to each other: e.g.,



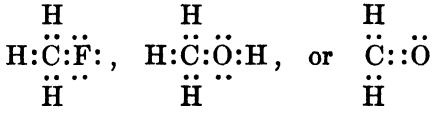
Sugden[2] has called this type of union a semipolar double bond. In old bond formulas a double bond connected the positively and negatively charged atoms.

By adding the formal charges of the atoms to the bond formulas, structures can be evolved that are practically equivalent to electron formulas. The bond formula of this type corresponding to any electron formula can be obtained by calculating the formal charges of the atoms and representing them by plus and minus signs, replacing all shared electron pairs by bonds, and ignoring all other electrons. The reverse process consists of replacing all bonds by a pair of dots and then adding unshared electrons so as to make the formal charges correspond to those given in the bond formula. Thus the formulas



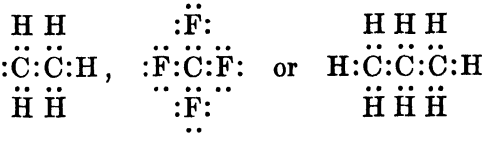
are equivalent and easily changed from one form to the other.

If one accepts tetrahedral symmetry for the electron pairs in a noble-gas configuration other than that of helium, a molecule whose atoms have noble-gas configurations is a structure built up of tetrahedra terminating either in hydrogen atoms or in unshared electron pairs. The kernels of atoms other than hydrogen are at the centers of their respective tetrahedra. If it is assumed that the hydrogen nuclei and their bonding pairs of electrons have coincident centers of gravity (by analogy to helium), a neutral molecule lacking balance among its hydrogen terminals has an electric dipole. Thus in



[2] Sugden, S., *The Parachor and Valency*. G. Routledge & Sons, London, 1930.

the center of gravity of the electrons should be displaced away from the center of gravity of the kernel charges and in the direction of the atoms of higher kernel charge. On the other hand, in

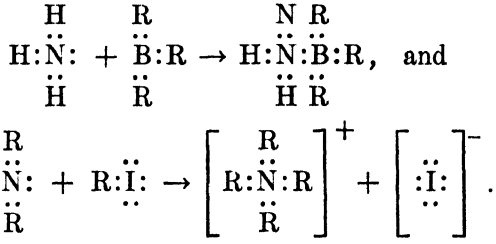


there should be no electric dipole. (See section 18, Chapter V.)

Many structures show electrical balance or the lack of it according to the degree of freedom of rotation permitted about the bonds. Thus for Cl—CH_2—CH_2—Cl a fixed position with the chlorine atoms *trans* to each other is balanced, but a fixed position with these atoms *cis* to each other is unbalanced. Free rotation permits a distribution between these two conditions. The dipole moment can be used to determine to what extent the rotation is hindered and what spatial configuration is stable. For ethylene dichloride, the dipole moment shows the *trans* configuration to be slightly more stable than the *cis*.

We shall not use this theory of dipole moment, for there are theoretical reasons to believe that the electrons of a bond are not equally shared between two atoms. The electrons belong more to the atoms with the greater electron affinities and higher ionization potentials. In consequence there is a dipole associated with each bond, and the resulting moment of the molecule is the vector sum of these bond dipoles.

12c. Acids, bases, and free radicals. Unshared electron pairs or lack of electrons shows the possibility of further reaction either in additions or in metatheses; e.g.,



These possibilities are not shown by older formulas unless the reactants are ions. Often more than one unshared electron pair exists in an ion, and it is not necessary to assume a tautomerism of the ion when it can give two sets of derivatives. Thus, because cyanides form nitriles and isonitriles, it is not necessary to assume tautomerism

between cyanide and isocyanide ion; the formula :C⁝⁝N: is the ion of both hydrocyanic and isohydrocyanic acids and shows a reactive point on both the carbon and the nitrogen atoms. The atom with an unshared pair of electrons is unsaturated with respect to an atom capable of increasing its valence electrons by two. The two classes of unsaturated atoms are basic and acidic, respectively.

Lewis assumed that an electron in an atom or molecule has a magnetic moment, but an electron pair has none; that most organic compounds therefore must be diamagnetic, as all of their electrons are paired; but that all atoms and molecules which have an odd electron must be paramagnetic. This has been found to be correct. But further, if a substance is found to be paramagnetic, a formula showing only paired electrons must be erroneous. Thus he gave oxygen the formula $:\dot{\underset{\cdot\,\cdot}{O}}:\dot{\underset{\cdot\,\cdot}{O}}:$ instead of $:\underset{\cdot\,\cdot}{O}::\underset{\cdot\,\cdot}{O}:$ (equivalent to the previously accepted formula O=O). Many of the chemical properties of oxygen (e.g., its rapid addition to free radicals) correspond more closely to the structure $:\dot{\underset{\cdot\,\cdot}{O}}:\dot{\underset{\cdot\,\cdot}{O}}:$ than to the structure $:\underset{\cdot\,\cdot}{O}::\underset{\cdot\,\cdot}{O}:$.

13. THE ELECTRON PAIR BOND IN QUANTUM MECHANICS

We see then, that there are at least two extreme ways in which atoms may be held together to form a molecule: namely, the shared electron pair bond and the ionic link. The background for an understanding of the ionic linkage had been at hand for a long time in the form of the coulombic laws of electrostatic attraction and repulsion, and there was little difficulty in conceiving a mechanism by which such a binding could come about. But the mechanism of the shared electron pair bond remained completely in the dark until the advent of the quantum mechanics. Just as the chemist's ideas concerning atomic structure and the periodic system were confirmed and extended, so did his conception of the chemical bond and molecular structure receive a theoretical background and at least something of a start toward a quantitative formulation. Most of the concepts of the structure and behavior of molecules which have emerged from the quantum mechanics had been known to the organic chemists in a qualitative way for a long time, together with many ramifications and extensions which have not yet been subjected to any kind of mathematical treatment. It is our task at this point to provide a sort of dictionary for the interconversion of the two vocabularies insofar as this can be done, so that the quantitative relationships

existing among the terms of the one language may be made use of in the other and the very much greater extension of qualitative relationships existing in chemical terminology may be of some guiding service to the theoretician.

As has already been said,[3] the complete solution of the Schrödinger equation, the law which governs the motions of atomic systems, has been accomplished in only the simplest case even for a single atom. The equation may be set up for the simplest of all molecules, H_2, but it cannot be directly solved because of the mathematical difficulties. These mathematical difficulties are introduced largely because of the necessity for considering the interaction of the electrons among themselves, i.e. by terms of the type e^2/r_{12} where e is the electronic charge and r_{12} is the distance between electrons 1 and 2. It is this very interaction which permits the beginning of new shells before old ones are completely full, in building up the atoms. In this difficulty lies the source of much misunderstanding concerning the nature of molecular structures and the properties which they represent. There is a tendency to attribute to these structures characteristics which are really the result of the inadequacy of our methods of representation. This appears in both the quantitative and the qualitative aspects of the theory, and will appear again later in connection with specific cases.

13a. Methods of approximation. Since the problem of two nuclei and two electrons, the hydrogen molecule, cannot be solved directly, we must seek methods of approximation to this solution. The true solution of the equation would yield in the first instance a wave function Ψ for the system, from which all its other properties, such as energy, spatial arrangement, excited states, etc., could be derived. So we must set about to find approximate wave functions which would represent the system as truly as possible. There are two very general methods of doing this, both of which depend on the mathematical theorem that under certain conditions any function may be represented by a linear combination of another set of functions. Thus the unknown wave function Ψ could be represented as a linear combination of a set of known functions, ψ_1, ψ_2, ψ_3, etc., with a set of constant coefficients, c_1, c_2, c_3, etc.: $\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 \cdots c_n\psi_n$. The problem thus becomes the one of selecting the proper set of known wave functions, ψ_1, ψ_2, etc., and determining the values of their coefficients, c_1, c_2, etc. The two methods which have been most frequently used to determine these coefficients are known

[3] See section 11, Chapter II.

as the perturbation method and the variational method. The type of problem to be solved will determine which method is most directly applicable. The case of the hydrogen molecule was first solved by Heitler and London[4] using the perturbation method, but the best solution has more recently been obtained by James and Coolidge[5] using a variational method, and so we shall give here a very brief account of the variational method. Detailed accounts may be found elsewhere.[6]

Let us suppose that for a given problem we have selected a certain set of wave functions which are known to represent the system in some extreme configuration. For the hydrogen molecule we might choose a set of hydrogen-atom wave functions which would represent the molecule when the two atoms are very widely separated. We can then approximate the unknown wave function as a linear combination of these known functions

$$\phi = \sum_n c_n \psi_n \tag{1}$$

where the ψ_n's are the known wave function and the c_n's are a series of constants whose values are to be determined. The energy of the system represented by ϕ will then be given by

$$E = \int \phi H \phi \, d\tau \tag{2}$$

where H is the complete Hamiltonian of the system obtained by the set of rules mentioned in Chapter II. Now it can be shown that E must be an upper limit to the energy, W_0, of the ground state of the system. If the ψ_n's and the c_n's are so chosen as to make ϕ the true wave function of the system, then $E = W_0$; if, however, this has not been done, then $E > W_0$. The problem then becomes one of adjusting the values of the c_n's for a given set of ψ_n's so as to make E

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[4] Heitler, W., and London, F., *Z. Physik*, **44**, 455 (1927).

[5] James, H. M., and Coolidge, A. S., *J. Chem. Phys.*, **1**, 825 (1933); **3**, 129 (1935).

[6] For a more detailed exposition of the quantum mechanical parts of this book the reader is referred to:

Dushman, S., *Elements of Quantum Mechanics*. John Wiley & Sons, New York, 1938.

Pauling, L., and Wilson, E. B., *Introduction to Quantum Mechanics*. McGraw-Hill Book Co., New York, 1935.

Hellman, H., *Einführung in die Quantenchemie*. Franz Deuticke, Leipzig u. Wien, 1937.

Van Vleck, J. H., and Sherman, A., "The Quantum Theory of Valence," *Rev. Mod. Phys.*, **7**, 167 (1935).

a minimum and then revising the selection of the ψ_n's and repeating the adjustment of the c_n's to a new minimum value of E which should be lower than the first. This process is to be repeated until this minimum value of E can no longer be reduced. It should then be a fairly close approximation to the ground state energy of the system. The adjustment of the c_n values for a given selection of ψ_n's (i.e. for a given ϕ, called a variation function) is accomplished in a straightforward way by setting the first derivative of E with respect to c_n equal to zero for each value of n and solving the resulting system of n simultaneous equations for the same number of values of c_n. In the course of the solution of this set of n simultaneous equations, a determinantal equation of nth order for the value of E is obtained. From this result n values of E, some or all of which may be the same. The lowest value corresponds to the most stable state. The others may be excited states of the system. The selection and revision of the ψ_n's, however, is not such a simple and straightforward procedure. So far, here again, two points of view have been developed: the method of molecular orbitals of Hund, Mulliken, *et al.*, and the method of atomic orbitals of Heitler, London, Slater, and Pauling.[7] In the method of molecular orbitals, the wave function of a molecule may be set up as a product of molecular orbitals, a molecular orbital being the wave function of a single electron in the molecular field of the fixed nuclei. This implies that the electrons have no interaction with each other and that their states are entirely determined by their interaction with the nuclei. Thus the complete wave function of a molecule containing n electrons is given by

$$\Psi = \psi_1(1)\psi_2(2)\psi_3(3) \ldots . \psi_n(n) \tag{3}$$

where $\psi_1(1)$ is molecular orbital number 1 containing electron 1. Each molecular orbital can be considered as made up of a linear combination of the atomic orbitals. Take for example two atoms A and B, each with a single valence electron in equivalent states (e.g., s states); then $\psi_1(1)$ could be represented by

$$\psi_1(1) = a\psi_A(1) + b\psi_B(1) \tag{4}$$

and $\psi_2(2)$ would be

$$\psi_2(2) = a\psi_A(2) + b\psi_B(2). \tag{4a}$$

The wave function of the molecule is then

$$\Psi = [a\psi_A(1) + b\psi_B(1)][a\psi_A(2) + b\psi_B(2)],$$

[7] For a critique of these methods, see Van Vleck and Sherman, Ref. (6).

which leads to

$$\Psi = a^2\psi_A(1)\psi_A(2) + b^2\psi_B(1)\psi_B(2) + ab[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)]. \quad (5)$$

In this expression, for the wave function of the molecule AB, the term $\psi_A(1)\psi_A(2)$ is taken to represent a state in which both electrons are associated with atom A, i.e. an ionic state such as might be represented by A^-B^+. In the same manner $\psi_B(1)\psi_B(2)$ would correspond to a state A^+B^-, while $\psi_A(1)\psi_B(2)$ would represent a purely homopolar state A^0B^0 in which the electrons are evenly distributed between the two atoms. The state represented by $\psi_B(1)\psi_A(2)$ is one of identical energy with $\psi_A(1)\psi_B(2)$, since the electrons are so far indistinguishable. Thus the molecule AB should exhibit the properties of the structures A^-B^+, A^+B^-, and A^0B^0, and the relative extent to which these properties will be exhibited will depend on the relative values of the coefficients a and b. Let us suppose for the moment that the atoms A and B are identical, say two hydrogen atoms. Then $a^2 = b^2 = ab$, and the two ionic states should contribute equally and to the same extent as each of the homopolar states. The electronic distribution would be symmetrical and there would be no permanent dipole, which is actually the case. But the hydrogen molecule certainly exhibits very little or nothing of the properties of H^+H^-. This state must be of considerably higher energy than the purely homopolar state (the ionization potential of H is 13.5 volts, while its electron affinity is only 0.7). This same overemphasis on the ionic contributions appears in other symmetrical molecules such as methane. This is due to the complete neglect of the interaction between the electrons, the repulsion represented by the e^2/r_{12} term in the Hamiltonian.

The method of Heitler and London, on the other hand, neglects the ionic terms completely and represents the wave function of the molecule AB by

$$\Psi = c[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)], \quad (6)$$

that is, in terms of the homopolar states alone, assuming that the electronic repulsion will never permit the two electrons to be associated with the same atom. This is clearly not true for such a molecule as HCl, which certainly exhibits something of the properties which would be expected of H^+Cl^-.

In general, we can say that the method of molecular orbitals will be more nearly applicable to cases of atoms of higher nuclear charge and smaller internuclear distances where the electron-nuclear inter-

action will be large compared to the electronic repulsions, while the Heitler-London method will more nearly approximate the truth for larger distances and smaller nuclear charge. The intermediate cases, which after all are the ones most frequently met in chemistry, can be approximated by including both types of terms with independent coefficients which are to be determined by one of the previously mentioned methods.

13b. The hydrogen molecule. Since the solution of the problem of the ground state of the hydrogen molecule involves most of the ideas concerning valence and the electron pair bond with which we will be concerned, we will examine this case a little more closely. The system, consisting of two protons and two electrons, is shown in Figure 3.

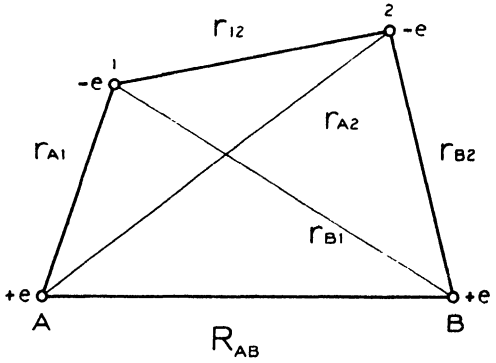


Figure 3. Internuclear and electronic distances in the hydrogen molecule

When the two atoms A and B are far apart, the wave function of the system can be taken as the product of two normal hydrogen atom functions: $\Psi_{\mathrm{I}} = \psi_{1s_A}(1)\psi_{1s_B}(2)$, i.e. electron No. 1 in a $1s$ orbital on nucleus A and electron No. 2 in a $1s$ orbital on nucleus B. But since the electrons are as yet identical, an equally good wave function would be $\Psi_{\mathrm{II}} = \psi_{1s_A}(2)\psi_{1s_B}(1)$. So we can take as a first approximation some linear combination of these two to represent the system as the distance R_{AB} grows smaller:

$$\Psi = c_{\mathrm{I}}\Psi_{\mathrm{I}} + c_{\mathrm{II}}\Psi_{\mathrm{II}}. \tag{7}$$

In the course of the solution for c_{I} and c_{II} by one of the aforementioned methods (Heitler and London used the perturbation method)

a quadratic equation is obtained which yields two values of the energy

$$W_S = \frac{H_{I\,I} + H_{I\,II}}{1 + \Delta^2} \tag{8}$$

and

$$W_A = \frac{H_{I\,I} - H_{I\,II}}{1 - \Delta^2} \tag{8a}$$

corresponding to two possible sets of the constants:

$$c_I = c_{II} = \frac{1}{\sqrt{2 + 2\Delta^2}} \tag{9}$$

and

$$c_I = -c_{II} = \frac{1}{\sqrt{2 - 2\Delta^2}} \tag{9a}$$

giving the two wave functions

$$\Psi_S = \frac{1}{\sqrt{2 + 2\Delta^2}} (\psi_{1s_A}(1)\psi_{1s_B}(2) + \psi_{1s_A}(2)\psi_{1s_B}(1)) \tag{10}$$

and

$$\Psi_A = \frac{1}{\sqrt{2 - 2\Delta^2}} (\psi_{1s_A}(1)\psi_{1s_B}(2) - \psi_{1s_A}(2)\psi_{1s_B}(1)) \tag{10a}$$

where

$$H_{I\,I} = \int \Psi_I H \Psi_I \, d\tau \tag{11}$$

$$H_{I\,II} = \int \Psi_I H \Psi_{II} \, d\tau \tag{12}$$

$$\Delta^2 = \int \Psi_I \Psi_{II} \, d\tau \tag{13}$$

$$H_{I\,I} = H_{II\,II}\,; \; H_{I\,II} = H_{II\,I} \tag{14}$$

The energies W_S and W_A are shown in Figure 4 (curves **S** and **A** respectively), plotted as a function of the internuclear distance R_{AB}.

The two isolated hydrogen atoms are taken as the zero of energy. A system whose energy is less than this (i.e. negative) would be more stable, and a system whose energy is greater than this (i.e. positive) would be less stable, than two isolated atoms. The curve showing a minimum (**S**) then represents the stable hydrogen molecule whose wave function is Ψ_S. The subscripts **A** and **S** indicate states which are antisymmetric and symmetric, respectively, with respect to the

co-ordinates of the electron. A wave function is said to be symmetric if interchanging the electrons leaves the wave function unchanged, and antisymmetric if the sign is changed upon interchange of the electrons. Another statement of the Pauli principle is that a wave function which represents a possible state must be completely antisymmetric in the electrons. So far we have not yet considered the effect that the electron spin will have on these wave functions. In order that these wave functions satisfy the Pauli

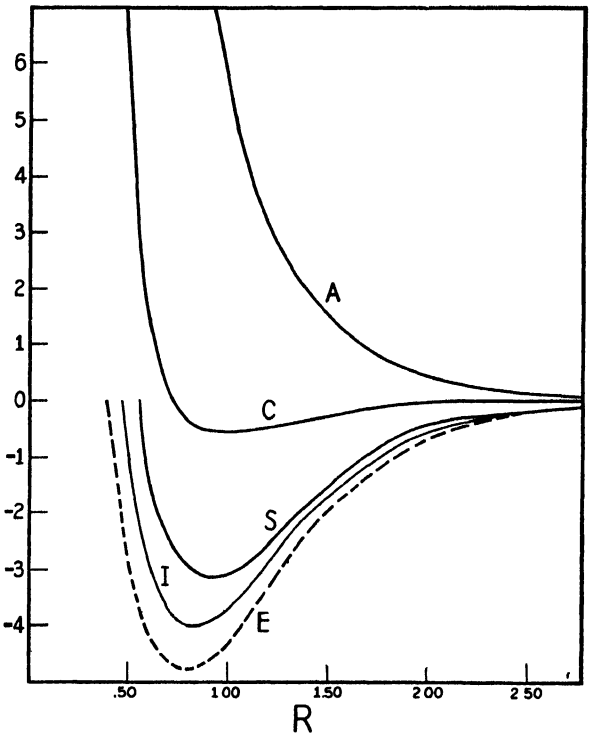


Figure 4. Potential energy curves for the hydrogen molecule.

principle, they must be antisymmetric when the spin functions are introduced. This requires that the state which is symmetric with respect to the positional co-ordinates of the electron, Ψ_S, must be antisymmetric with respect to the spins so that the final wave function including spin will be antisymmetric. For the antisymmetric orbital wave function Ψ_A, the spin function must be symmetric. This brings us to the important conclusion that the spins of each of the pair of electrons must be opposite if the two atoms are to come

together to form a bond (curve **S**, Figure 4). If the spins are the same, the two atoms will not form a bond but will repel each other at all distances (curve **A**, Figure 4).

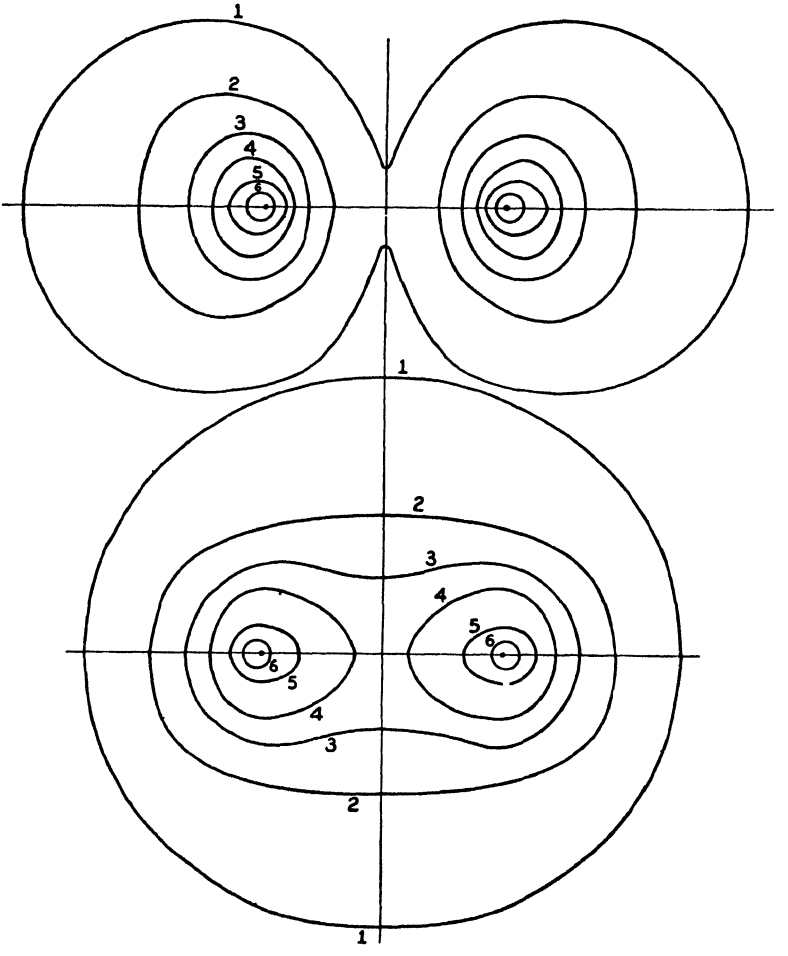


Figure 5. Electron distributions in the repulsive state (upper figure) and attractive state (lower figure) of the hydrogen molecule. Each line represents a contour of constant electronic density increasing with the numbers (after London).

Recalling the interpretation which has been placed on ψ^2, we can now examine the negative charge distribution in the two states of the hydrogen molecule represented by Ψ_A and Ψ_S. This is shown in Figure 5, in which each contour line is drawn through all the points

of constant density given by the number (in arbitrary units) associated with that line. These represent the charge distribution in any plane through the molecule, including both nuclei. In the attractive state (Ψ_S) there is a piling up of charge between the two atoms, whereas in the repulsive state (Ψ_A) the reverse is true (the electrons tend to stay away from the region between the atoms).

The experimental value for the internuclear distance in the hydrogen molecule is $R = 0.74$ Å with a dissociation energy of $D = 4.72$ e.v. The values obtained from the above calculation of Heitler-London-Sugiura are 0.80 Å and 3.14 e.v., which is not a bad agreement. But it should be remembered that in the approximate wave function (equation 10) only purely homopolar terms were used with an effective nuclear charge of 1. On the other hand, the extreme molecular orbital approximation for the wave function, in which the ionic terms are given equal weight with the homopolar ones, gives even poorer agreement. From the previous discussion we have seen that, since both of these methods are only approximations, we are not forced to use either one to the complete exclusion of the other. In fact, the variational method permits the use of any functions whatever with as many adjustable parameters as we need to achieve the minimization of the energy. This in fact has been done by James and Coolidge,[8] as we shall see later, but first we shall consider other approximate wave functions obtained by less radical adjustments of the ones we have already used. Three changes have been made in the Heitler-London wave function, Ψ_S, independently and together, which have produced dissociation energies and internuclear distances of different degrees of agreement with the experimental values. In the first place, when the nuclei are close together the electrons will be moving in a positive field somewhat different from that of a single nucleus. This difference was introduced into the calculation by allowing the effective nuclear charge to become one of the variable parameters in the variational calculation. This was done by replacing Ze by $Z'e$ in all the hydrogen atom wave functions that are used. Secondly, as the two atoms approach each other, they will mutually polarize each other; i.e. the electronic cloud of one atom will be distorted in the direction of the other. This effect is simply due to the polarizability of an atom which is observed experimentally in terms of the index of refraction, and as the van der Waal's force. It is introduced into the calculation by allowing the $2p$ orbital

[8] Ref. (5), Chapter III.

to contribute to the state of the atom. This is accomplished by using as the atomic wave function a combination of $1s$ and $2p$ orbitals, $\psi_{1s} + \sigma\psi_{2p}$ in place of just the $1s$ orbital ψ_{1s}, where σ is a parameter determining the extent of the $2p$ contribution. And, finally, the ionic terms mentioned earlier are introduced with the coefficient C, which determines the extent of their contribution. The entire bonding wave function Ψ_S, including these additional terms, can then be written analogous to equation (5):

$$\Psi_S = N\{\underbrace{[\psi_{1s_A}(1)\psi_{1s_B}(2) + \psi_{1s_A}(2)\psi_{1s_B}(1)]}_{\text{I}}$$

$$+ \underbrace{\sigma[\psi_{2p_A}(1)\psi_{1s_B}(2) + \psi_{1s_A}(1)\psi_{2p_B}(2) + \psi_{1s_B}(1)\psi_{2p_A}(2) + \psi_{2p_B}(1)\psi_{1s_A}(2)]}_{\text{II}}$$

$$+ \underbrace{\sigma^2[\psi_{2p_A}(1)\psi_{2p_B}(2) + \psi_{2p_A}(2)\psi_{2p_B}(1)]}_{\text{III}}$$

$$+ \underbrace{C[\psi_{1s_A}(1)\psi_{1s_A}(2) + \psi_{1s_B}(1)\psi_{1s_B}(2)]}_{\text{IV}}\} \qquad (15)$$

The constant N is the normalization factor which is adjusted so as to make Ψ_S satisfy the relation $\int \Psi_S^2 \, d\tau = 1$. Each of the atomic orbitals appearing in this expression is now to be considered as a function of an effective atomic number Z' instead of $Z = 1$. The energy will now be minimized with respect to each of the three variational parameters, Z', σ, and C, and thus their best values determined. This function will reduce to the original Heitler-London approximation if $Z' = 1$, $\sigma = 0$, and $C = 0$; i.e. term I represents the purely homopolar bond without distortion. If $Z' = 1$, $C = 1$, and $\sigma = 0$, the extreme molecular orbital approximation will result, in which the ionic terms, represented by IV, are given equal weight with the homopolar terms. Term II represents the mutual distortion of the two atoms in the homopolar state by permitting the electron on one nucleus to be in a $2p$ state while that on the other is in a $1s$ state. Term III is a second-order distortion effect in which both electrons are in $2p$ states on either nucleus. The distortion effects in the ionic terms which would be represented by functions like $\psi_{2p_A}(1)\psi_{2p_A}(2)$ are terms of even smaller order since they would represent both electrons on one nucleus and in excited (higher) states at that, so they have been omitted. The results obtained by assuming various values for one, two, or all three of these parameters and performing the varia-

tion calculation on the remaining ones are given in Table 4, together with the values assumed or obtained for the several parameters.

In Figure 4, curve **S** corresponds to approximation (1) of Table 4 and curve **I** to approximation (9). Curve **E** is experimentally deduced from spectroscopic evidence and accepted as the true repre-

TABLE 4

APPROXIMATIONS FOR THE H_2 MOLECULE

No.	Author	Z'	σ	C	D(e.v.)	R(Å)
(1)	Heitler-London-Sugiura	1	0	0	3.14	0.80
(2)	Extreme molecular orbital	1	0	1	~2.65	~.80
(3)	Wang	1.166	0	0	3.76	.76
(4)	Molecular orbital	1.193	0	1	3.47	.73
(5)	Rosen	1	0.10	0	3.35	.88
(6)	Rosen	1.19	0.10	0	4.02	.75
(7)	Weinbaum	1	0	0.158	3.22	.88
(8)	Bethe	1.19	0	1	3.46	.73
(9)	Weinbaum	1.193	0	0.256	4.00	.76
(10)	Weinbaum	1.190	0.07	0.176	4.10	.77
(11)	James and Coolidge				4.722	.74
(12)	Experiment				4.72	.7395

REFERENCES

(1) Sugiura, Y., *Z. Physik*, **45**, 484 (1927).
(2) Hellman, H., Ref. (6), Chapter III.
(3) Wang, S. C., *Phys. Rev.*, **31**, 579 (1928).
(4) Pauling, L., and Wilson, E. B., Ref. (6), Chapter III.
(5) and (6) Rosen, N., *Phys. Rev.*, **38**, 2099 (1931).
(7), (9), and (10) Weinbaum, S., *J. Chem. Phys*, **1**, 593 (1933).
(8) Bethe, H., "Quantenmechanik der Ein- und Zweielektronprobleme," *Handbuch d. Physik*, **24**, 1 Teil, 273 (1933).
(11) James, H. M., and Coolidge, A. S., Ref. (5), Chapter III.

sentation of the hydrogen molecule. Curve **C** represents the result which is obtained for a wave function of the type

$$\Psi_S = \psi_{1s_A}(1)\psi_{1s_B}(2), \tag{16}$$

the energy of which is given by H_{II} (equation 11). This represents the hydrogen molecule without the possibility of interchange of the electrons which is permitted by the wave function of equation 10 and which has as a consequence an additional energy H_{III} (equation 12). H_{II} is called a coulombic integral because it represents the purely coulombic interaction of the two atoms, while H_{III} is called an exchange integral because it results from the possibility of the interchange or exchange of the positional co-ordinates of the electrons. This phenomenon of exchange of co-ordinates is known as resonance, and the difference in energy between a pure state [repre-

sented by curve **C**, Figure 4 (equation 16)] and one permitting this resonance, curve **S**, Figure 4 (equation 10), is called the resonance energy, *R.E.* If we desire a more detailed picture of this resonance, we must imagine the electrons exchanging places with a frequency given by $2\ R.E./h$, which is of the order of 10^{16} sec.$^{-1}$. When it is possible to describe a system by more than one state of the same energy, such as $\psi_{1s_A}(1)\psi_{1s_B}(2)$ and $\psi_{1s_A}(2)\psi_{1s_B}(1)$ for the hydrogen molecule, it is said to be degenerate, and the degree of degeneracy is measured by the number of such states which are possible, all having an identical energy. The best resonance occurs only among totally degenerate states; however, it is possible to have states whose energies are only slightly different (nearly degenerate) also in resonance. Their participation and the resulting energy differences are considerably smaller than for totally degenerate states. This is exemplified in the case of the hydrogen molecule by the large difference between curves **C** and **S**, which is the *R.E.* introduced by the equivalent contributions of the totally degenerate states Ψ_{I} and Ψ_{II} (equation 7) and the much smaller *R.E.* introduced by the small contribution of the ionic states $\psi_{1s_A}(1)\psi_{1s_A}(2)$ and $\psi_{1s_B}(1)\psi_{1s_B}(2)$ given by the difference between curves **S** and **I**.

It must be remembered that, fundamental as this phenomenon of exchange is, it appears only as a result of the necessity and the methods of approximation. James and Coolidge, by changing the system of co-ordinates and including the r_{12} terms of electron repulsion, obtained the best solution of the H_2 molecule. Their curve corresponds almost exactly with the experimental one, and no exchange integrals of the type of $H_{\mathrm{I\,II}}$ appear in their calculation.

Thus we have from the quantum mechanics a mechanism for the Lewis shared-electron-pair bond: a pair, because of the Pauli principle, which permits only two electrons with opposite spins to occupy a single orbital, and shared because of the simultaneous interaction of each electron with both nuclei.

13c. The one-electron bond. There is another type of bond which is possible in certain special cases and which also owes its stability to the phenomenon of exchange degeneracy. This is the single electron bond which is responsible for the existence of H_2^+, the hydrogen molecule ion,[9] in gas discharge tubes. Here we have a single electron which can exist in an atomic orbital on either nucleus. This one state would be simply ψ_{1s_A} and proton *B*. But an equally good

[9] A third type, called the three-electron bond, has been observed in He_2^+.

state would be ψ_{1s_B} and proton A. The coulombic energy corresponding to either of these states is identical and gives repulsion at all distances. (The corresponding pure state of the H_2 molecule gave a very weak bond, curve C, Figure 4.) If, however, one constructs a linear symmetric combination of these two totally degenerate states—

$$\Psi_S = \frac{1}{\sqrt{2 + 2\Delta^2}} (\psi_{1s_A} + \psi_{1s_B}) \tag{17}$$

—the resulting energy-internuclear distance plot shows a minimum at $R_{AB} = 1.32$ Å to a depth of 1.77 e.v. The experimental values are $R_{AB} = 1.06$ Å and $D = 2.78$ e.v. This wave function has been improved in much the same way as was done for the hydrogen molecule, and complete agreement has been obtained. In this case we see that practically the entire bond energy can be attributed to *R.E.*, but it is a considerably weaker bond than the electron-pair bond. In addition, there is a fundamental difference in the nature of the two degeneracies. In the H_2^+ ion the two states are totally degenerate only if the orbitals on the two nuclei are of identical energy. This is generally the case only if the two nuclei themselves are identical. And so we may not expect one-electron bonds between any but identical nuclei. The electron-pair degeneracy, however, is not subject to this limitation. Since in either of the two constituent states, Ψ_I or Ψ_{II}, there is always an electron in each orbital; and since the electrons are indistinguishable (except for spin), the energies of the two states will be identical even if the two orbitals have different energies, and we may thus expect strong electron-pair bonds even between dissimilar atoms.

13d. Bond dipole. There is another important effect, however, which appears in the electron pair bond between dissimilar atoms. We have seen that, even in the case of the hydrogen molecule, ionic terms like H^+H^- and H^-H^+ make a small contribution, but that the two ionic states are identical, and hence that their contributions are equal and their electrical dissymmetry cancels out, producing an electrically symmetrical molecule. On the other hand, if the two atoms are not the same, the contributions of A^+B^- and A^-B^+ will in general not be the same, since the ionization potentials and electron affinities are usually different and, moreover, the dimensions of the charge distributions about the two atoms will be different so that an electrically unsymmetrical molecule will result and a dipole will be observed experimentally.

It will be remembered that the Lewis theory obtained dipolar structures on the assumption of a tetrahedrally distributed electron density. The quantum mechanics can obtain a bond dipole by a variation of the relative contribution of the ionic, homopolar, and polarized states of the bonding pair of electrons, irrespective of any assumption concerning the distribution of the other electrons. This, however, is not a denial of the tetrahedral configuration of the carbon valences. In fact, justification has been obtained for the equivalent tetravalence of carbon and for the directed nature of the electron-pair bond in general, a concept which is of such fundamental importance in all of organic structural chemistry.

13e. The tetrahedral carbon atom. The carbon atom in its normal state has a pair of $2s$ electrons and two unpaired $2p$ electrons. This should lead to a divalent carbon atom, since only the unpaired electrons could form bonds with other atoms. If, however, the coupling between the $2s$ pair is broken and one of these electrons promoted into the remaining $2p$ orbital, four unpaired electrons would result, three $2p$ electrons and one $2s$ electron. The energy required for this promotion would be forthcoming in the much larger amount of energy released by the four bonds which would be formed. But, if this were actually the case, it might be expected that three of the bonds ($2p$ electrons) would be different from the fourth ($2s$ electron), since the spatial distributions of the three $2p$ electrons are mutually perpendicular while the $2s$ orbital is spherically symmetrical (see Figure 2, Chapter II). This difference is certainly not observed in carbon.

It can be shown that if two atoms are to combine to form a bond, the exchange integral (and hence the bond energy) will be greatest for that condition in which there is the greatest overlapping (i.e. the largest value of the non-orthogonality integral, Δ^2, equation 13) of the two orbitals concerned. Thus the molecule which has two unpaired $2p$ electrons whose distributions are mutually perpendicular would be expected to form two bonds with the $1s$ (spherically symmetrical) orbitals of two hydrogen atoms with an angle of 90° between them. Actually the angle in the water molecule is 106°, but this can be attributed to the repulsions of the hydrogen atoms and of the bonded orbitals. Following this we would expect the simple promoted carbon atom to have three mutually perpendicular valences and a fourth undirected valence. Pauling[10] resolved this difficulty

[10] Pauling, L., *J. Am. Chem. Soc.*, **53**, 1367 (1931); see also Slater, J. C., *Phys. Rev.*, **37**, 481 (1931); **38**, 1109 (1931).

by a process called hybridization of the orbitals. If the difference in the energy of a $2s$ and a $2p$ orbital is neglected by comparison with the energy of bond formation, the four electrons can be interchanged among the four possible orbitals, ψ_{2s}, ψ_{2p_x}, ψ_{2p_y}, ψ_{2p_z}, and the resulting four orbitals can be represented as four different linear combinations of the original ones. These are

$$\psi_i = a_i\psi_{2s} + b_i\psi_{2p_x} + c_i\psi_{2p_y} + d_i\psi_{2p_z}, \quad i = 1, 2, 3, 4 \qquad (18)$$

together with the conditions of normalization and orthogonality,

$$\int \bar{\psi}_i^2 \, d\tau = 1; \quad \text{i.e., } a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1, \quad i = 1, 2, 3, 4, \qquad (19)$$

and

$$\int \psi_i\psi_j \, d\tau = 0; \quad \text{i.e., } a_ia_j + b_ib_j + c_ic_j + d_id_j = 0,$$

$$i \text{ or } j = 1, 2, 3, 4, \quad i \neq j. \qquad (20)$$

If it is now assumed that the s orbital contributes equally to each of the four hybridized functions, then $a_i^2 = \frac{1}{4}$, and the angle between the directions of maximum extension of any two of the resulting four equivalent orbitals is just the tetrahedral angle 109°28′.

Chapter IV

GROUP INTERACTION

14. GROUP INTERACTIONS WITHOUT CONSIDERING RESONANCE

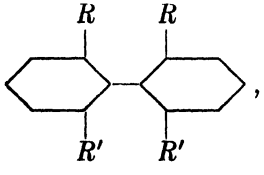
A structural formula of a compound is not only a representation of the space relationships of atoms and electrons; it is also a shorthand description of methods available for its synthesis and of the chemical and physical properties of the compound. As a first approximation, the component parts or groups in the structural formula are associated with definite properties, and a summation of these group properties describes those of the compound. Thus the property of addition of bromine is associated with the carbon-to-carbon double bond. Acidity and ability to be esterified are associated with the carboxyl group. So the formula

$$CH_2{=}CH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}H$$

shows that the compound represented adds bromine, is an acid, and can be esterified.

14a. Steric hindrance. The space relationships represented by a structural formula affect the characteristic properties of a group. Like molecules, groups attract or repel each other at small distances. Also, a molecule reacting with a group may have to come so close to another group that it is subject to forces from this second group. The commonest forces involved are repulsions, and the effects produced are called steric hindrances. Thus the esterifications of ortho substituted benzoic acids are abnormally slow, and this phenomenon has been attributed to the steric hindrance of the ortho substituent.

The existence of optical isomers of tetra- and tri-ortho substituted diphenyls,



,

is an excellent example of steric hindrance. Normally the rotation about a single bond is sufficiently easy to make the isolation of isomers differing only in the degree of rotation about such a bond impossible. But, in compounds of this type, when the two benzene rings are in the same plane, the ortho substituent groups are so close that they strongly repel one another. The rings are therefore not coplanar and can pass through the coplanar configuration only with considerable difficulty. If the sides of neither ring are equivalent, the molecule is asymmetric, and racemization is difficult, as it necessitates a rotation through the coplanar configuration.

14b. Negativity. When chemical properties are expressed quantitatively, by rate and equilibrium constants, by heats of reaction, etc., it is found that a property associated with a group varies from one compound to another even when the variation could not be attributed to steric hindrance. All substituent groups affect the properties of a group and these effects are transmitted through the intervening groups. So it is necessary to include among the properties of a group its ability to influence the reactions of other groups and its ability to transmit the effects of one group upon another. Thus the acidity of the carboxyl group is enhanced by a substituent chlorine atom. This enhancement of acidity is one of the properties that has to be associated with the group —Cl. The enhancement of acidity by a chlorine atom is transmitted across a double bond more readily than across a single bond, and this high conductivity is one of the characteristic properties of unsaturated groups.

Groups that are largely composed of negative elements or are positively charged are often similar in their influence on the properties of other parts of a molecule. They increase the ease of obtaining a negative charge on another group. This property has been called the negativity of the group. It is now generally attributed to a positive charge or to a group dipole with the positive pole directed to the reacting part of the molecule. The groups —Cl, —CCl_3, —NO_2, —COOH, and —$\overset{+}{N}H_3$ are examples of highly negative groups.

14c. Polarity and induction. The distribution of electricity in a molecule is shown in part by a Lewis electron structural formula. When the uneven sharing of bond electrons is read into the picture, the electrical distribution is more completely depicted. We have seen that this uneven sharing of bond electrons can be attributed to the contribution of the ionic form in bond formation. Thus in a Cl—C bond the $\overset{-}{Cl}\ \overset{+}{C}$ component contributes more than the $\overset{+}{Cl}\ \overset{-}{C}$

one, and the carbon atom is positive with respect to the chlorine atom. Should this carbon atom be attached to another, $\overset{1}{C}—\overset{2}{C}—Cl$, the $\overset{1}{C}:\overset{2}{C}$ component of the $\overset{1}{C}—\overset{2}{C}$ bond is more stable than the $C:\overset{2}{C}$ component and $\overset{1}{C}$ as well as $\overset{2}{C}$ acquires a positive potential from the C—Cl bond. This effect is a second-order one and hence $\overset{1}{C}$ is less positive than $\overset{2}{C}$. This effect is carried on ad infinitum through a chain of bonded atoms but with constantly diminishing intensity. If a bond contains a high contribution of both kinds of ionic components, the effect is transmitted readily. Thus in a double bond the semipolar forms (e.g., $\overset{+}{C}—\overset{-}{C}$, $\overset{-}{C}—\overset{+}{C}$, in C=C) have relatively higher contributions to the bond than the ionic components of a single bond, and a double bond conducts the effects of groups more readily than does a single bond. The conductivity of a chain for the chemical effect of a group is due to its electrical polarizability.

From the above discussion it can be seen that if in

$$CH_3—CH_2—COOH$$

the methyl group is replaced by a chlorine atom, a positive charge is imposed on the α carbon atom and that this effect is transmitted through the chain to the oxygen atom, with the result that hydrogen ion is more easily dissociated from $ClCH_2COOH$ than from CH_3CH_2COOH. This is the effect that would be expected from the assumptions that a chlorine atom is a strongly negative group and that a negative group increases the strength of an acid.

A positive formal charge on an atom would also increase the positive charge on an atom bonded to it, and the effect would be transmitted in the same way as that of an electrically neutral but chemically negative group.

The electron theory of bonds therefore gives a mechanism for the effect of a group on the reactions of a distant group. This property of the group we shall call its polarity, and the above method of transmission we shall call induction. Sometimes the property and its transmission are taken as a whole and called the inductive effect of the group. The polarity of a positive charge has the effect of what was called a negative group. The polarities or inductive effects are the same group properties that were previously called their negativities. The idea that the negativities of groups were due to their electrical character preceded the theory of the shared-electron bond.

Since the polarity of a group is due to an electrical charge or dipole, its effect on a distant group is transmitted through the intervening space or solvent as well as by induction through the chain. This effect has been distinguished by calling it the direct effect. The direct effect is dependent on the spatial configuration of the molecule rather than on its structural formula. Since the spatial configuration is largely affected by steric hindrance, the effect of the latter is often an indirect action, through its influence on direct effects. For an example, see the discussion of the dissociation constants of dialkyl malonic acids (page 226, Chapter VI).

We have seen that the nature of the effect of the polarity of a substituent group on the dissociation of an acidic group is a natural consequence of the theory, but this is not true of all its effects. We can say that the polarity of a substituent group must have some influence on the speed of alcoholysis of a benzoyl chloride; but which polarity increases the speed can only be deduced when a complete theory of the reaction is known. Generally it is easier to determine experimentally the type of polarity that increases the speed, and then assume similar effects for similar polarities, together with some quantitative relationship between polarities and their effects.

14d. The Hixon-Johns method. The interesting method used by Hixon and Johns[1] often brings out the similarities of the effects of groups on various general reactions. At the same time it gives a numerical measure of the attribute of the groups whereby they affect the behavior of other groups. This method is not dependent on any theory of the attribute other than that it has a constant value for a given group and is the only cause of the observed effects. The failure of the method to give approximately correct results in any particular case is indicative of some other way in which one group may affect another.

This method may be described as follows: If the equilibrium or velocity constant of a reaction characteristic of a group R is measured for a set of compounds $X'R$, $X''R$, $X'''R$, etc., and the values are located on any simple curve with an undefined abscissa, the projections of the points on the abscissa are values of an attribute of the groups X', X'', X''', etc., whereby they influence the chosen reaction of R. With these values a curve can be obtained for the effects of X', X'', X''', etc., on another property of $X'R$, $X''R$, $X'''R$ or on any property of another set of compounds, $X'R'$, $X''R'$, $X'''R'$.

[1] Hixon, R. M., and Johns, I. B., *J. Am. Chem. Soc.*, **49**, 1786 (1927).

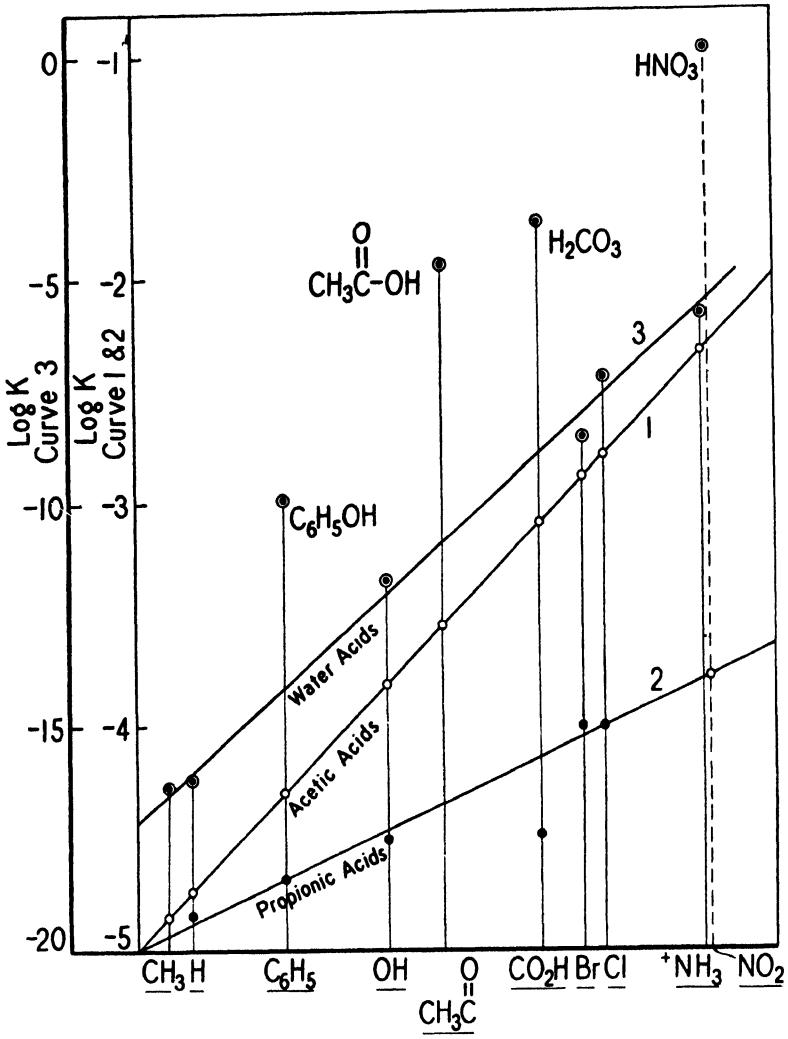


Figure 6. Logarithms of the dissociation constants of XOH and XCH_2CH_2COOH compared with the logarithm of the dissociation constants of XCH_2COOH. The position for NO_2 on the abscissa was fixed by the value of the dissociation constant of $NO_2CH_2CH_2COOH$ and the line for log K of XCH_2CH_2COOH. The abscissa corresponds to a quantity measuring the effect of the group as determined by the 45° line on the acetic acids.

In general, the second curve can be constructed from only a few measurements and approximate values obtained for the missing compounds by extrapolation. The power of this method is increased by

the possibility of obtaining the values of the attributes of complex groups as functions of those of simpler groups.

To exemplify both the success and failure of the method, we have plotted in Figure 6 the logarithms of the dissociation constants of the acid types X—CH_2COOH, X—CH_2CH_2COOH and X—OH against the attribute of X. The logarithm of the dissociation constant of X—CH_2COOH was arbitrarily taken as a linear function of the attribute of X, and the values of the attribute for various groups were obtained from this curve. The curves for

$$X\text{—}CH_2CH_2COOH \text{ and } X\text{—}OH$$

were drawn from the points $X = H$, $X = HO$, and $X = Cl$. It can be seen that the experimental points fit the curve for X—CH_2CH_2COOH very well, but the experimental points for the acids

$$C_6H_5\text{—}OH, \quad CH_3\overset{\overset{O}{\|}}{C}\text{—}OH, \; CO_2H\text{—}OH, \text{ and } NO_2\text{—}OH$$

do not come anywhere near the curve for X—OH. These acids have anomalously high dissociation constants.[2] This anomaly should not be attributed to steric hindrance.

15. CONJUGATION

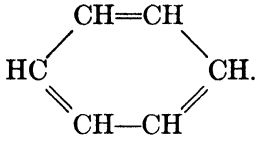
It is necessary to assume that the effects of groups on each other cannot be due entirely to the polarities of the groups. Thus, in the example shown in Figure 6, the C_6H_5, CH_3CO, CO_2H, and NO_2 groups, apart from their polarities, profoundly affect the negatively charged oxygen atoms in the ions $C_6H_5O^-$, CH_3COO^-, CO_3H^-, and NO_3^-. These interactions are shown by other peculiarities of the ions. The formulas

$$CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}O^-, \quad HO\text{—}\overset{\overset{O}{\|}}{C}\text{—}O^-, \quad {}^-O\text{—}\overset{\overset{O}{\|}}{N^+}\text{—}O^-$$

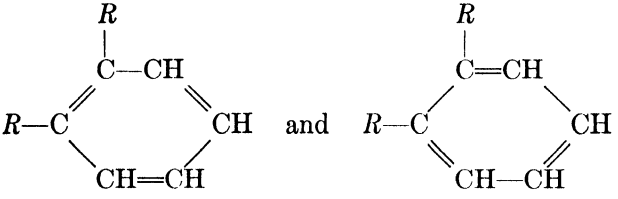
show a lack of equivalence of the oxygen atoms, but X-ray studies of the salts of these ions fail to reveal this lack of equivalence. The interactions of the groups have made the standard formulas inadequate. This phenomenon is not restricted to a few compounds. One of the

[2] It could also be claimed that HOOH and Cl—OH are abnormally weak. There are, however, other reasons for locating the abnormality in the unsaturated acids.

most striking cases is that of benzene. The three ethylenic groups so interact with one another that the heat of combustion fails to show the existence of any of them. Approximately 40 kcal. per mole of energy are missing in benzene. The carbon atoms appear to be evenly spaced instead of separated alternately by the double and single bond distances implied in the standard formula



The isomerism



has not been found. The standard formula for benzene is a quite inadequate description of the compound. In other cases it is found that the formula is inadequate only for special purposes, but gives a fair approximation of many of the properties. Thus in the reaction $Br_2 + CH_2{=}CH{-}CH{=}CH_2 \rightarrow BrCH_2{-}CH{=}CH{-}CH_2Br$, the product is not that which would be obtained in a normal addition of bromine to a double bond; but the heat of combustion of 1,3-butadiene is only a few thousand calories less than would be expected from the formula.

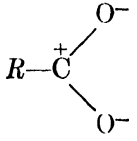
Thiele devised the theory of conjugation for these special interactions between groups. In this theory the idea of a bond as a specific attraction between two atoms is discarded, and A. Werner's[3] theory of an atom radiating affinity with spherical symmetry is adopted. In an ethylene, the double bond represents the neutralization of less than half the affinity of the two carbon atoms. This leaves residual affinity on these atoms. In a system of alternate double and single bonds, the residual affinities of the inner atoms combine across the single bonds, while those of the outer atoms are free to attract the atoms of the addend. As the addition proceeds, more and more free affinity is produced on the inner atoms and they combine more com-

[3] Ref. (9), Chapter I.

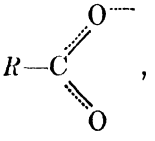
pletely with one another, eventually producing a double bond between them. Thiele's formula for 1,3-butadiene is $CH_2{=}CH{-}CH{=}CH_2$.

It follows from Thiele's theory that if six CH groups are arranged in a hexagon, the affinity from any one carbon atom combines equally with the two adjacent atoms, as there is no necessity to divide the carbon valence into four definite parts. The affinities of the atoms are more completely satisfied in this way than they would be by alternate double and single bonds and the residual affinity is less. The heat of combustion of benzene is therefore less than would be expected from the Kekule formula.

One may consider a carboxylate ion as



in which the positive charge is neutralized by combination of the carbon and oxygen atoms. If a valence is not specifically directed to a particular atom, there is no reason for the carbon atom to combine more with one of the oxygen atoms than with the other. The oxygen atoms are therefore equivalent. The formula may be written



where a sloping dotted line is half a bond and a horizontal dotted line is half a negative charge.

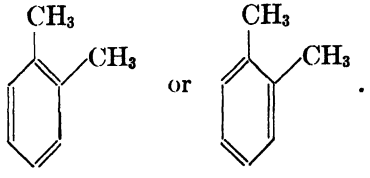
While the theory of conjugation removes many difficulties, the fundamental assumption of undirected and divisible valence presents as many problems as it explains. To mention only one, the affinity of only one side of the fluorine atom in CH_3F is satisfied, but the compound is quite saturated and shows no signs of possessing a large amount of residual affinity. In Lewis' electron formulas the bonds are, of necessity, specific. We shall see that this restriction has been modified in order to explain the same facts that led to Thiele's theory of conjugation. Conjugation, with its assumption of divided bonds, is another though inadequate way of expressing the most modern theories of molecular structure. It appears that classical structural formulas do not adequately describe highly conju-

gated compounds when directed valences are assumed, and do not adequately describe compounds that are not conjugated when directed valences are not assumed.

16. RESONANCE AND MESOMERISM

16a. Mesomerism as a tautomerism. Amongst the phenomena attributed to conjugation is the failure to obtain as many compounds as are predicted from structural theory (e.g., only one *o*-xylene) and the actual equivalence of atoms that are not equivalent according to standard formulas (e.g., the equivalence of the oxygen atoms in a carboxylate ion). Earlier in the history of structural theory keto-enol and similar tautomerisms presented the same problem. A smaller number of compounds was observed. The difficulty was resolved by assuming that the apparent lack of isomers was not real. The right number of isomers existed but, owing to a rapid reversible isomerization, one obtained only one isomer in the solid state, and only the equilibrium mixture in more mobile states of aggregation. This theory was amply confirmed later by the separation of the isomers in many cases.

However, the corresponding phenomena in conjugated compounds is accompanied by a variation in the properties from any weighted mean of the properties expected from the isomers. For instance the heat of formation of *o*-xylene is much greater than what would be expected from either of the formulas

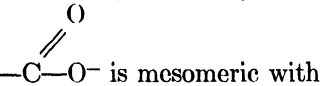


There are, therefore, two kinds of tautomerism; one is due to rapid equilibrium between isomers, and in the other only one substance exists corresponding to two or more structural formulas. The latter type of tautomerism is accompanied by a decrease in the energy of the molecule below the lowest energy that would be expected from any of the structural formulas. It has been called mesomerism by C. K. Ingold.[4] The conjugated compounds are mesomeric substances.

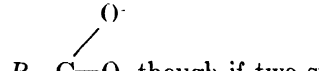
The structural criterion that can be used to distinguish between mesomerism and tautomerism is that, if the tautomeric structures

[4] Ingold, C. K., *Nature*, **141**, 314 (1938).

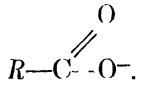
differ in the position of an atom, they correspond to isomers, but if they differ only in the position of electrons, a single mesomeric substance exists. Mesomerism also exists when the structures are equivalent, and differ only with respect to the charge and bonding of atoms of the same element. In this case there are no fewer isomers than are predicted by structural theory, but atoms that are not shown as equivalent by classical structures are so in reality. Thus



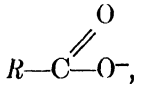
is mesomeric with



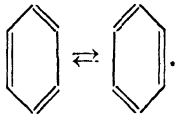
though if two such isomers existed they would be chemically indistinguishable. Since these structures can change from one to the other by a shift of only an electron pair, the actual structure is some blend of these two in which the two oxygen atoms are equivalent and the actual ion is more stable than would be expected from the formula



The change from one structure to another need not be so obviously a shift of electron pairs as in

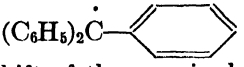


but the electron shifts may result in a change in the bonding arrangement as in

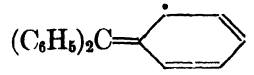


This also leads to a blended structure and a decrease in energy.

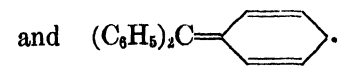
The application of this theory to an otherwise obscure chemical phenomenon can be exemplified by the explanation of the existence of triphenylmethyl and similar free radicals by Professor and Mrs. Ingold.[5] The molecule



might be expected to be tautomeric by a triad shift of the unpaired electron, the tautomers being



and



[5] Ingold, C. K., and Burton, H., *Proc. Leeds Phil. Soc.*, **1**, 421 (1929).

as well as the seven other forms equivalent to these but involving the other ortho position and the other benzene nuclei. As these tautomers are produced by a shift of electrons, they do not exist as isomers in equilibrium, but form a single structure of lower energy. The lowering of the energy is so great that hexaphenylethane readily dissociates into free radicals.

This tautomeric theory pre-dated the application of quantum mechanics to the problem of conjugation.[6] It was soon shown that mesomerism can be deduced from the assumptions of quantum mechanics and could be expressed in quantitative form. It is then called resonance. In fact the principle has already been used in Chapter III in discussing bond formation. In a Lewis formula the electrons are placed on an atom or in a bond, yet, as we have seen, a bond contains ionic components in which both bond electrons are assigned to one or other of the atoms. The extension of assigning electrons to one or other of two bonds leads to mesomerism. One may discuss the phenomenon of mesomerism or resonance either as a quantitative theorem in quantum mechanics or with the aid of the Lewis electron structure theory expanded by postulates. These postulates must be such as to recognize that the limitation of structural formulation that permits electrons to be assigned only to an atom or a bond, is a greater restriction than exists in the molecule. The formula is only an approximate representation of the molecule, the approximation being close in molecules without much conjugation between groups, but being far from the truth in highly conjugated molecules. That we continue to use structural methods instead of quantitative deductions from quantum mechanics is due to the fact that the quantitative character of these deductions when applied to the complex problems of organic chemistry are formal rather than real. We have seen that the energy of only the very simplest diatomic molecule, H_2, can be obtained by direct calculation, and that, only by the use of very complex mathematics. At present more can be obtained by the inductive methods of structural theory. As, however, these methods can be greatly assisted by quantum mechanics, we shall discuss resonance and mesomerism from both points of view.

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[6] Arndt, F., Scholz, E., and Nachtwey, P., *Ber.*, **57**, 1903 (1924); Lowry, *J. Chem. Soc.*, 822, 1866 (1923); Robinson, R., *et al.*, *J. Chem. Soc.*, 401 (1926); Lucas, H. J., and Jameson, A. Y., *J. Am. Chem. Soc.*, **46**, 2475 (1924); Ingold, C. K., and Ingold, E. H., *J. Chem. Soc.*, 1310 (1926).

16b. Molecular resonance as an extension of the Lewis theory. Given any fixed arrangement of atoms, one may ascribe many Lewis electron distributions to it. Each of these show the electrons as either belonging to an atom or shared between two atoms. None of these formulas alone describes the true electron distribution, for all electron distributions having the same multiplicity[7] coalesce to some intermediate arrangement of lower potential energy than that of any single one. This stable arrangement is most like the Lewis electron distribution of lowest energy. The difference between the energy of the most stable Lewis structure and the actual energy minimum is greater the more nearly equal the energy levels of the blended Lewis structures and the greater the number of these arrangements. The change in energy is also great when the distance moved by the electrons in going from one component distribution to another is small or is effectively small because it occurs by a series of transformations between nearly equal energy electron structures.

The coalescence of the electron structures is called resonance. It is sometimes pictured as a vibration of the electrons between the various Lewis formulas. It is perhaps better not to assume any model for resonance, but to consider it as an axiom obtained by induction from the empirical facts of chemistry, or as a deduction from the axioms of quantum mechanics. The component Lewis electron structures may have no existence other than as formulas on paper.

The result of this hypothesis is that if for any given arrangement of atoms there is one Lewis structure whose energy is much lower than any other, this formula is a very close approximation both with respect to energy and electrical distribution to a true description of the system; but if there is no such unique structure, no Lewis formula adequately describes the system.

Further, with a given arrangement of atoms we cannot have isomerism that can be represented by different Lewis formulas that show the same multiplicity, but only by formulas with different numbers of unpaired electrons. For instance, with a fixed distance between two oxygen atoms there cannot be two isomers represented by the formulas $:\dot{O}:\dot{O}:$ and $:\dot{O}:\ddot{O}:$, but an isomer having the formula $:\ddot{O}::\ddot{O}:$ is possible. The two former formulas each show two unpaired elec-

[7] The multiplicity is obtained by adding one to the number of unpaired electrons.

trons and the structures must coalesce, but the last one has no unpaired electrons, and an isomer having this formula would not be forbidden by the postulates.

The energy associated with any electron distribution, whether a true one or a Lewis form, is a function of the relative positions of the atoms. A description of the relative positions of the atoms involves a great many dimensions, but we shall represent them by a single co-ordinate, q, and take it as the abscissa to plot the energy (E)

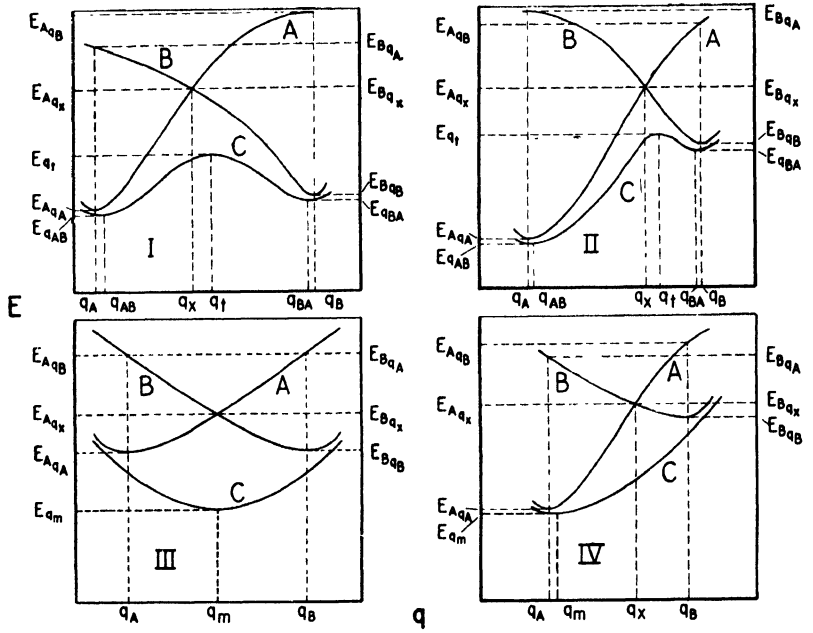


Figure 7. Potential energies of electronic distributions as a function of atomic configurations. In each case curves A and B represent electronic distributions corresponding to two Lewis electronic formulas, and curve C represents the true electronic distribution. I and II show the existence of tautomers. III and IV show the existence of a mesomeric compound.

against the configuration of the atoms. We have plotted in this way in Figure 7 the energy of two Lewis electron distributions, A and B, having the same multiplicity (curves A and B), and the energy of the true electron distribution (curve C). The energy corresponding to any Lewis electron distribution at any configuration is denoted by E with a subscript to indicate the electron distribution and the atomic configuration. Thus the energy minimum on curve A is E_{Aq_A}. For any given atomic configuration, the energy of the true

electron distribution is represented by E with only one subscript, which corresponds to the atomic configuration.

The energy of a Lewis electron distribution is at a minimum at some atomic configuration. The configurations at which electron distributions A and B have energy minima are marked q_A and q_B respectively in the figure. At these minima the energies of the two Lewis electron distributions differ; but as the atomic configuration changes from q_A to q_B, the energies E_A and E_B approach each other and eventually become equal at q_X, which may be called the crossing-point configuration. The energy increase required to obtain this condition depends on the steepness of the energy curves A and B and on the difference between the equilibrium atomic configurations q_A and q_B. This magnitude of the change in the energies of A and B from equilibrium atomic configurations to q_X is an important factor determining the type of the energy curve obtained when resonance is introduced (curve C). Another important factor that determines curve C is the difference in energy for the Lewis electron distributions at their respective equilibrium atomic configurations, i.e. the difference between E_{Aq_A} and E_{Bq_B}. As the two factors are large or small we obtain the four cases shown in the figure.

Cases I and III are alike in that the differences between E_{Aq_A} and E_{Bq_B} are small. They differ in that in case I the Lewis distribution energies greatly increase as we go from equilibrium to crossing-point atomic configurations, while in case III this increase of energy is small. The true energy E is always less than the energy of the more stable Lewis electron distribution, and we can call this energy difference the resonance energy at the atomic configuration under consideration. At equilibrium configurations, the resonance energy is small, for E_A and E_B are very different. As the configurations are shifted from one equilibrium point to another, E_A and E_B approach each other and the resonance energy increases. This increase in resonance energy tends to counterbalance the energy that is expended in changing the atomic configuration from an equilibrium point. If, as in case I, the Lewis electron distribution energy needed to depart markedly from q_A or q_B is large, it is not compensated for by the consequent increase in resonance energy, and between q_A and q_B the true energy, curve C, has a maximum. It will also have two minima. These minima in the true energy, curve C, are minima with respect to both electron distribution and atomic configuration. They correspond to definite isomers.

The two minima in curve C lie at atomic configurations in each of

which E_A and E_B are very different, and the resonance energy is small. The energies of the two isomers are approximately E_A and E_B respectively. Similarly, their electron distributions and atomic configurations are approximately A and q_A for one isomer and B and q_B for the other. There is a slight resonance which increases for small changes from the atomic configuration q_A and q_B more than E_A and E_B increase. The true energies, electron distribution, and atomic configurations are therefore not quite those represented by Lewis formulas. In Figure 7 these small variations are depicted. The true equilibrium atomic configurations are shown as q_{AB} and q_{BA}, and the energies as $E_{q_{AB}}$ and $E_{q_{BA}}$. The conditions given by C, q_{AB}, and $E_{q_{AB}}$ determine properties dependent only on the ground state, and these are approximately the same as the corresponding conditions A, q_A, and E_{Aq_A} of the Lewis theory. Case I is therefore a system for which Lewis electron formulas are adequate.

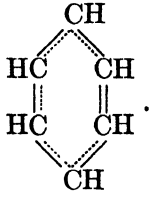
In this system when the atomic configurations are greatly perturbed and brought closer to one another, the energies E_A and E_B are more nearly equal and resonance is large. At the maximum and the crossing points the energies and electron distributions are very different from those to be expected from Lewis electron formulas. At the atomic configuration corresponding to the maximum in curve C, any change decreases the energy. It therefore represents a metastable state through which the formation of one isomer from another must pass. In the diagram the energy and the atomic configuration of this state are represented by E_{q_t} and q_t respectively. The importance of these quantities will become apparent when we discuss reaction rates in Chapters VIII and IX.

Resonance energy is gained when the atomic configuration is changed in such a direction as to tend to equalize the two Lewis electron distributions. In case III this gain always more than compensates for the accompanying increase of the energy of the more stable Lewis electron distribution. In consequence the true energy is at a minimum at some atomic configuration between q_A and q_B, and there are no minima in curve C that correspond to either Lewis formula.

The Lewis method of formulation therefore shows more isomers than actually exist. The minimum in curve C is an energy minimum with respect to both electron distribution and atomic configuration, and hence represents a definite compound; but one that cannot be represented by a single Lewis formula. This compound is a mesomeric one. We have represented its energy and atomic configura-

tion by E_{q_m} and q_m, respectively. We shall attempt to represent the electron distributions of this type by enclosing the formulas of the resonating Lewis electron structures in parentheses. For instance, the electron distribution in this case would be shown as (A, B), but this is only a qualitative method, which can be very complex when many Lewis structures are involved. Thus to represent triphenylmethyl radical in this way we should have to write 44 formulas and then obtain only a first approximation.

It should be noted that the conditions E_{q_m}, q_m, and (A, B), on which the properties of the mesomeric compound shown in case III depend, are very different from either E_{Aq_A}, q_A, and A, or E_{Bq_B}, q_B, and B. Hence this compound is very different from what we might expect from either Lewis formula. It could, however, be more adequately depicted by a structural formula in which bonds were divided and the extent of the bonding between any atom indicated by shading. Benzene, which is a typical mesomeric compound, is fairly well depicted by the structural formula



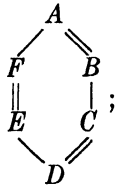
The quantity $E_{Aq_A}-E_{q_m}$ is important. We shall call it the molecular resonance energy. When E_{Bq_B} is less than E_{Aq_A}, the molecular resonance energy is taken as $E_{Bq_B}-E_{q_m}$. There are therefore two resonance energies. The one previously mentioned can be defined as $E_{A_q}-E_q$. The importance of $E_{Aq_A}-E_{q_m}$ lies in the fact that E_{Aq_A} is the energy we would assign the molecule from its most likely Lewis formula while E_{q_m} is its actual energy. By ignoring the theory of resonance, we make an error of $E_{Aq_A}-E_{q_m}$ in any calculation of energy.

Cases II and IV correspond respectively to cases I and III. Cases I and II are examples in which resonance does not prevent isomerism, and cases III and IV are examples in which it produces mesomerism. On the other hand, II and IV are alike in that, in both, the energy level of one of the Lewis electron distributions at its equilibrium atomic configuration is very much lower than that of the other at its equilibrium point. That is, E_{Bq_B} is much greater than E_{Aq_A}. Case II hardly needs much discussion. It is an example of isomerism

in which one isomer is much less stable than the other. The application of resonance theory to it would show that the less stable isomer B is more affected by the possibility of an alternative electron distribution than is the more stable isomer.

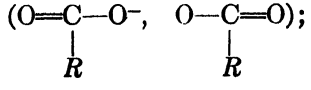
In case IV the mesomeric compound differs in energy, atomic configuration, and electron distribution much less from what would be expected from the Lewis formula A than it does from the Lewis formula B. If the compound is assigned the formula A, the error is not great, whereas the formula B cannot be assigned to any compound. This difference between III and IV shows that resonance effects are large when alternative structural formulas would imply nearly equal energies, but are not great when the implied energies are very different.

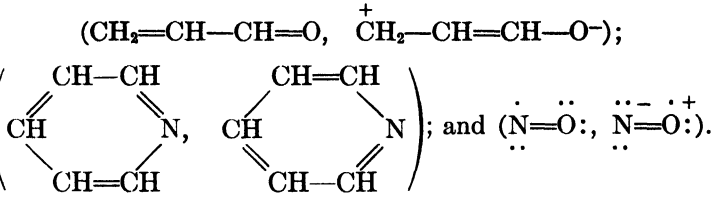
When a Lewis structural formula depicts two atoms bonded together, and another formula shows these atoms as not bonded to each other but to other atoms, the change from the equilibrium atomic configuration of one formula to that of the other requires considerable energy, necessitating as it does a wide separation of bonded atoms. Under these conditions mesomerism is unlikely, and Lewis formulas can be used. When, however, no atom is removed from one to which it is bonded in the change from one equilibrium atomic configuration to the other, but only the type of bonding is altered, mesomerism occurs. Mesomerism therefore occurs in the following structural types: (a) the triad, $A{=}B{-}\overset{*}{C}$ where the asterisk represents an odd electron, an unshared electron pair, or a lack of electrons; (b) the conjugated system of multiple bonds, $A{=}B{-}C{=}D$; (c) the aromatic nucleus



(d) the dyad, $\dot{A}{-}\overset{*}{B}$, where the asterisk represents an unshared pair of electrons or a lack of electrons.

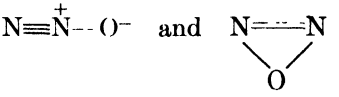
The following pairs of resonating structures are examples of (a), (b), (c), and (d) respectively:





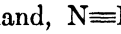
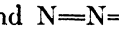
No example of the dyad with *B* lacking electrons is known.

Equilibrium atomic configurations corresponding to Lewis structures require not only certain distances between the atoms but also special shapes for the molecules. The differences in shapes of the atomic configurations corresponding to resonating structures have an effect on the formation of mesomers and the molecular resonance energy. Also, mesomerism tends to impose special shapes on the molecules. Thus it is probable that

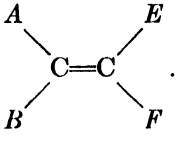


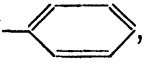
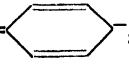
are not mesomeric, as the shapes required by the two structures are quite different. This is not definitely known, as only one isomer has been obtained, but this isomer shows no sign of the triangular shape required by



On the other hand,  and  are mesomeric, as both electron distributions are favored by a linear atomic configuration. Nitrous oxide has the properties of such a mesomer.

There is also a steric factor in resonance, and although this is not generally sufficient to produce isomerism where mesomerism is expected, it frequently greatly reduces resonance effects. These steric factors are generally introduced on account of the planar atomic configuration of the double bond system



When the resonance is with an electron distribution that has the double bond elsewhere, as for instance  ,  ,

the planarity of more atoms is required in order that the atomic configuration will be favorable to both electron distributions. Thus in aniline the resonance tends to bring the amino hydrogen atoms into the plane of the ring. Steric hindrance may interfere with these planar structures and greatly reduce the effects of resonance.

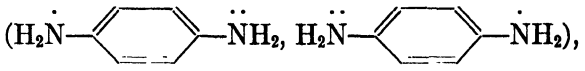
The fundamental postulates on which this theory of molecular resonance is based do not restrict an atomic system to the atoms of a single molecule. However, if one or both electron distributions correspond to more than a single molecule, the energy involved in changing from q_A or q_B to q_X is probably great and true energy curves of the types shown in I and II are more likely than those shown in III and IV. There are, however, some cases in which the true energy curve probably belongs to one of the types shown in III or IV. The system F—H and F^- is probably an example; the resonance would be $(:\ddot{F}:H \quad :\ddot{F}:, \ :\ddot{F}: \quad H:\ddot{F}:)$. The effect of resonance in these cases is to bind the molecules together.

A similar binding together of two separate groups in a molecule can occur. In general when an atom is bonded to one group in one of the Lewis formulas and to another group in the other, the two equilibrium positions of the atom are too widely separated to give mesomerism, but the bond angles and atomic radii of the chain connecting the groups can be such that the two equilibrium positions of the alternatively bonded atom are not far apart. Resonance can then bind the groups together, with the alternatively bonded atom as the link. The resulting structure is cyclic. This process has been called chelation.

There are also cases in which the system is a single molecule according to one Lewis electron distribution but two molecules according to another. On account of the difference in the number of bonds in the two forms, the energy curve would probably be like that in IV. This is sometimes called no-bond resonance. Some examples are mentioned in the discussion of bond distances (Chapter V, page 116).

Among the fundamental postulates of resonance we included the statement that resonance energy was small unless the electron shift was small or effectively small. From the other postulates alone similar resonances might be expected from $(H_2\dot{N}—\ddot{N}H_2, \ H_2\ddot{N}—\dot{N}H_2)$ and $(H_2\dot{N}—CH_2—CH_2—\ddot{N}H_2, \ H_2\ddot{N}—CH_2—CH_2—\dot{N}H_2)$, but this

postulate makes the energy of the latter resonance insignificant. On the other hand a strong resonance is obtained for



although the shift of the electron is large. This shift is effectively small because it can occur through a series of triad and dyad resonances. The failure to obtain resonance effects for electron shifts through a saturated chain is called insulation.

In this discussion of types of resonance we have not included that between the homopolar and ionic components of a bond. This resonance always produces mesomerism, but as we included it in the formation of a bond it is implied by a shared pair of electrons in a Lewis formula, and if we treat it as a necessary consequence of a bond it should not be included as a resonance as well. If we treat it as resonance, not as part of bond formation, polarity and induction are resonance effects.

In Figure 7 there is a marked difference between cases I and III. However, even in case I where mesomerism is absent there are still small resonance effects. Thus the atomic configurations q_{AB} and q_A are not identical, and the energy, $E_{q_{AB}}$, is smaller than the energy E_{Aq_A}. But there is a gradation between cases I and III. Consequently it is possible to have a marked difference between atomic configurations q_{AB} and q_A and the energies $E_{q_{AB}}$ and E_{Aq_A} without actual mesomerism. In such a case the energy of the transition state, E_{q_t}, is also small, and the two isomers are not easily separated. There are therefore compounds that are not actually mesomeric but have many of the properties of mesomeric substances. We shall treat these substances as resonating compounds and not try to decide whether they are truly mesomeric.

16c. Molecular resonance as a theorem in quantum mechanics. We have seen how ordinary structural theory enhanced by the Lewis interpretation of the bond and of the distinction of the ionic link permitted a very good representation of a large group of compounds. We have also seen that for another large group the Lewis theory was inadequate and it was necessary to introduce certain additional assumptions without any apparent theoretical foundation. We shall now see that the quantum mechanical interpretation of the electron-pair bond contains within it the mechanism for understanding and more clearly defining these *ad hoc* assumptions. This, of course, is

not surprising. Indeed it could hardly be otherwise if the Schrödinger equation is the complete description of atomic systems that it is supposed to be.

The precise form which the theory will take depends upon the methods of approximation which are used in the solution of the Schrödinger equation. The procedure here is exactly analogous to the case of the hydrogen molecule, and all of the fundamental ideas concerning the structure of organic molecules which we shall need have already appeared in that discussion. Since we cannot solve the Schrödinger equation directly, our problem is to construct a ψ function which will represent the true state of the molecule as nearly as possible. This is done by selecting a group of simpler ψ functions about which presumably we know something, and any one of which might represent the state of the molecule. These are then combined by means of a perturbation or a variation calculation in the course of which a "secular equation" is obtained for the possible energy states of the system in terms of integrals involving the originally selected ψ functions. From these we can now calculate the coefficients of the original ψ functions in the combinations which are to represent the true state of the system, i.e. the extent to which each of the approximate original states is to contribute to the true state.

The problem is thus again (as in the H_2 molecule) one of selecting the original states from which to make the combinations. The two points of view which were described in connection with the hydrogen molecule have been extended to polyatomic molecules, and are called the method of molecular orbitals (Hund-Mulliken-Hückel) and the method of bond orbitals or the method of electron pairs (Heitler-London-Slater-Pauling).[8]

The method of molecular orbitals considers the molecule in the first instance as an aggregate of nuclei in a fixed configuration. Each electron is then assigned an orbital determined by the electric field of the nuclear system and all the other electrons, and each orbital can be occupied by two electrons having opposite spins. The final wave function of the molecule is then taken as the product of these separate electron molecular orbitals. In the language of the organic chemist, this amounts to the obliteration of any distinctive or characteristic groups in the molecule and would correspond to an attempt to derive the properties of a molecule from a consideration only of the nuclei and the electrons which constitute its structure.

[8] For a comparison of these methods, cf. Van Vleck, J. H., and Sherman, A., "The Quantum Theory of Valence," *Rev. Mod. Phys.*, **7**, 16 (1937).

The method of bond orbitals considers the molecule as made up of atoms with electrons in atomic orbitals on each atom. In its original form, as developed by Slater, a wave function of the molecule, ψ, is the product of all of these atomic orbitals each containing one electron.

$$\psi = u_a(1)u_b(2)u_c(3) \cdots u_q(i)$$

where q is the number of orbitals used and i the number of electrons taking part in the binding.[9] Now an equally good product would be one in which electrons No. 1 and No. 2, or any other pair, were interchanged—

$$\psi = u_a(2)u_b(1)u_c(3) \cdots u_q(i)$$

—and so the actual wave function of the molecule, Ψ, is taken as a sum of these various products obtained by all the "possible" interchanges, with the additional proviso that each orbital might have either of two spins. This "possible" refers to those permutations representing possible states in nature, i.e. conditions which fulfill the Pauli principle when the spin of the electrons is included in the representation. Upon this basis Slater, Pauling, and others simplified the rules by which the proper initial function might be chosen and by which the energy of the system might be calculated. These rules use the electron-pair or valence-bond structures (Lewis structures) as the chemist is accustomed to writing them. A product of a pair of atomic orbitals containing electrons of opposite spin represents a certain bonding state between this pair of atomic orbitals, and then a combination of these bonding states is taken as the wave function of the isolated bond between the pair, i.e. a bond orbital. The wave function of the entire molecule is then a product of the bond orbitals. If more than one such bond arrangement is possible, a further combination of these possible bond arrangements must be taken in order to represent truly the structure of the molecule. Thus if $u_a(1)$ and $u_b(2)$ represent electron No. 1 in an atomic orbital u on atom a, and electron 2 in an atomic orbital u on atom b, then $u_a(1)u_b(2)$ would represent one bonding state. Another would be $u_a(1)u_a(2)$ or $u_b(1)u_b(2)$. Still others could be constructed using other orbitals than u on either or both of the atoms a and b. In this and the following discussion the solution of the H_2 problem

[9] These are usually taken as equal for polyatomic molecules but not necessarily, as may be seen in the case of the hydrogen molecule where p orbitals were used as well as s orbitals in the higher approximations.

should be kept constantly in mind. In general, then, a bonding state ϕ is given by

$$\phi_k = \prod_i^i u_{ki} \tag{1}$$

and the bond orbital is given by

$$\psi_j = \sum_k a_{jk}\phi_k. \tag{2}$$

Then for any given bond structure (bonds between given sets of atom pairs in a molecule) the molecular wave function χ_l will be given by

$$\chi_l = \prod_j^j \psi_j. \tag{3}$$

Now if it is possible to have more than one arrangement of the bonds between the atoms in a molecule, i.e., more than one χ_l, the actual state of the molecule Ψ will be represented by a combination of these χ_l's:

$$\Psi = \sum^l b_l\chi_l. \tag{4}$$

Thus the transition from the single atomic orbitals (u_i) to a complete molecular wave function, Ψ, which was previously described as a single process, has now been accomplished by means of a series of steps, some of the intermediate ones of which represent approximately the older modes of description of molecular systems. Once more in the language of the organic chemist this amounts to constructing a molecule from atoms, bonds, and groups which may retain something of their individuality from molecule to molecule. The old method of the organic chemist of attempting to derive the properties of a molecule from a consideration of the bonds and groups present finds a very convenient translation in the language of quantum mechanics.

The quantitative results obtained by the two methods of approximation for the most part indicate the same tendencies and effects of the structure on the properties of the molecule. In neither case is a completely theoretical result possible. In order to get a verifiable result, at least one other experimentally determined constant must be introduced somewhere in the calculation. So far the really important contributions of the theory have been conceptual ones. It has considerably enhanced and clarified many of the older ideas of molecular structure derived purely on the basis of the electron pair bond and structural theory. Since the method of bonds and

group interactions introduced at the beginning of this chapter is still by far the most useful approach to understanding the properties of molecules, we will restrict ourselves in any quantum mechanical considerations to the method most nearly related to it and which permits of the more direct translation into the familiar language of the chemist.

We have seen how the single electron-pair bond between a pair of atoms, which is represented by a valence line, $A—B$, or a pair of dots, $A:B$, required for its formulation in quantum mechanics (ψ_i) the sum of a group of selected initial approximations for which the proper coefficients could be determined (equation 2). These initial approximations could be represented by the bond formulas:

$$A^{\circ}:B; \quad A:_{\circ}B; \quad A^{\circ -}:B^{+}; \quad A^{+}:^{\circ}B^{-}; \quad \text{etc.}$$

corresponding to the functions ϕ_1, ϕ_2, ϕ_3, ϕ_4, etc. Therefore, when we write a valence line, it will imply the inclusion of all the resonating states of this type. In a polyatomic molecule with several bonds, the wave function of the molecule would be a product of all the bond orbitals present (equation 3). χ_i then is the quantum mechanical representation of a molecule corresponding to a single Lewis structure. When, however, more than one Lewis structure (valence bond formula) can be written for a molecule (the mesomerism of section 15a), the principle of combination must be extended to these as well and the complete description of the molecule, Ψ, is given by equation 4. Thus the idea of resonance or mesomerism is merely a result of the methods of approximation.

There is one rigorous rule which must be satisfied by any set of states which are to be combined, and that is that they must all have the same number of unpaired electron spins, i.e. they must all have the same value of Σm_s where $m_s = \pm\frac{1}{2}$ for each electron. There are other less rigorous rules concerning the relative contributions of the several constituent states and their energies.

The energy of a single valence bond structure χ_I is given by the integral

$$H_{II} = \int \chi_I H \chi_I \, d\tau \tag{5}$$

and the rules have been worked out by which this can be calculated directly in terms of the exchange integrals between single electron pairs, thus:

$$H_{II} = Q + \Sigma J_{ii} - \tfrac{1}{2}\Sigma J_{ij} \tag{6}$$

where Q is the sum of all the coulombic integrals for each pair of electrons, J_{ii} is the single exchange integral between a pair of electrons forming a bond, and J_{ij} is the single exchange integral between a pair of electrons not forming a bond. Since these single exchange integrals are in general negative, we see that J_{ii} actually corresponds to an attraction, i.e. a lowering of the energy, between the pair of atoms which are indicated as bonded in the valence bond formula, and that $-J_{ij}$ corresponds to a repulsion, i.e. an increase in energy, between those atoms which are not bonded together in the valence-bond formula. An analogous set of rules has been evolved for the calculation of the compound exchange integrals

$$H_{\mathrm{I\,II}} = \int \chi_{\mathrm{I}} H \chi_{\mathrm{II}}\, d\tau \tag{7}$$

which are required in the secular equation for W, the true energy of the system, Ψ, made up of a combination of the χ's according to equation 4. The solution of this secular equation for W gives a number of values for W equal to the number of constituent χ's used in the combination. Some of these W's may be identical and the value of the energy is said to be degenerate; i.e., there apparently exist more than one wave function for that value of the energy. The lowest value of W obtained from this secular equation, W_0, is then the energy of the ground state of the system, and the set of coefficients b_l (equation 4) corresponding to this value W_0 will be a measure of the relative contributions of the various valence-states (χ_l's) to the ground state Ψ_0. The value of W_0 must be equal to, or less than, the smallest H_{ii} (H^L_{ii}) appearing in the secular equation.[10] This amounts to saying that the true energy of the system cannot be greater than that of the lowest contributing valence state. In general, W_0 will be less than H^L_{ii} and the difference

$$R = H^L_{ii} - W_0 \tag{8}$$

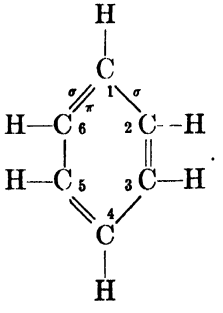
is called the resonance energy, owing to the possibility and contribution of more than one valence-bond formula. We thus have a means of calculating quantitatively, at least in certain cases, the actual degree of additional stability given to a molecule by this possibility of resonance which had been observed by chemists long ago and which was described qualitatively in the earlier part of this chapter.

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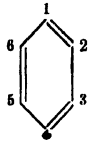
[10] The superscript ^{L} is merely a method of designating the lowest value of H_{ii}.

In those cases for which the calculation has been possible, certain regularities have been observed which can be applied qualitatively to the multitude of cases which cannot yet be calculated. The most important of these generalizations is that R is the greater, the larger is the number of identical H_{ii}'s; and if there is only one H_{ii}^{L}, R is the greater the closer is the next higher value of H_{ii}, and the larger is the number of these, etc. This has as a corollary certain restrictions in the geometry of the constituent states. No particle must be allowed to move very great distances; i.e., R decreases as the distance which the particle must move to change one valence bond state to another increases. Further, the distance which a particle can move and still contribute appreciably falls off very rapidly with the increasing mass of the particle. Electrons can move distances of the order of a bond length comparatively easily, but the next heavier particle, the proton, can move only a small fraction of a bond distance, and for all practical purposes anything heavier cannot move at all, beyond the displacement involved in the ordinary vibrational states of the bonds concerned.

Let us take benzene as an example. A valence bond structure of benzene is



The wave function for this structure would be $\chi_{\mathrm{I}} = \chi^{\sigma}\psi_{23}^{\pi}\psi_{45}^{\pi}\psi_{61}^{\pi}$ where χ^{σ} represents the structure with its six single, σ, bonds between neighboring carbon atoms and its six C—H bonds, and ψ_{23}^{π} represents the second, π, bond between carbon atoms 2 and 3, etc. Now another and exactly equivalent valence bond structure would be



having the wave function $\chi_{II} = \chi^{\sigma}\psi^{\pi}_{12}\psi^{\pi}_{34}\psi^{\pi}_{56}$. Since χ^{σ} and the energy associated with this part of the wave function remain the same in χ_I and χ_{II}, it will not contribute to any effects which the possibility of more than one arrangement of the π bonds might bring about, so we will omit it in the following considerations, remembering that it must multiply the wave function we obtain without it and that its energy must be added to that obtained without it. Now, since more than one bond formula is possible, the true state of the molecule must be some combination of these various bond formulas:

$$\Psi = b_I\chi_I + b_{II}\chi_{II} \tag{9}$$

and the secular equation[11]

$$\begin{vmatrix} H_{I\,I} - \Delta_{I\,I}W & H_{I\,II} - \Delta_{I\,II}W \\ H_{II\,I} - \Delta_{II\,I}W & H_{II\,II} - \Delta_{II\,II}W \end{vmatrix} = 0 \tag{10}$$

in which $H_{I\,I} = H_{II\,II}$, $\Delta_{I\,I} = \Delta_{II\,II}$, $H_{I\,II} = H_{II\,I}$, $\Delta_{I\,II} = \Delta_{II\,I}$, because of the exact equivalence of the two structures. This has as its solutions:

$$W_g = \frac{H_{I\,I} + H_{I\,II}}{\Delta_{I\,I} + \Delta_{I\,II}} \quad \text{and} \quad W_e = \frac{H_{I\,I} - H_{I\,II}}{\Delta_{I\,I} - \Delta_{I\,II}} \tag{11}$$

with $\Psi_g = \frac{1}{\sqrt{2}}(\chi_I + \chi_{II})$ and $\Psi_e = \frac{1}{\sqrt{2}}(\chi_I - \chi_{II})$, where the

[11] The secular equation is obtained by substituting the selected wave function (equation 9) into the Schrodinger equation $(H - W)\Psi = 0$ giving the equation for the coefficients b_I and b_{II}

$$b_I[H\chi_I - W\chi_I] + b_{II}[H\chi_{II} - W\chi_{II}] = 0. \tag{10a}$$

This may be converted into a set of simultaneous equations for b_I and b_{II} by multiplying through by χ_I or χ_{II} and integrating the result, keeping in mind that H is a differential operator (i.e. $H\chi \neq \chi H$), whereas W is simply a multiplier (i.e. $W\chi = \chi W$). Thus multiplying the terms of equation 10a by χ_I and integrating gives

$$b_I\left[\int \chi_I H\chi_I - W\int \chi_I\chi_I\right] + b_{II}\left[\int \chi_I H\chi_{II} - W\int \chi_I\chi_{II}\right] = 0$$

or

$$b_I[H_{I\,I} - W\Delta_{I\,I}] + b_{II}[H_{I\,II} - W\Delta_{I\,II}] = 0 \tag{10b}$$

and similarly multiplying the terms of equation 10a by χ_{II} and integrating gives

$$b_I[H_{II\,I} - W\Delta_{II\,I}] + b_{II}[H_{II\,II} - W\Delta_{II\,II}] = 0. \tag{10c}$$

In order that the pair of simultaneous equations for b_I and b_{II} (10b and 10c) have a finite non-trivial solution, it is necessary that the determinant of the coefficients of b_I and b_{II} be equal to zero. This determinantal equation 10 is known as the secular equation.

subscript g indicates the ground state of the molecule. Whether the values for the excited states (e) found by this method have any physical significance is still a moot question and will be discussed later in connection with the theory of the color of organic compounds.

The evaluation of the elements $H_{\mathrm{I\,I}}$, $H_{\mathrm{I\,II}}$, etc. can now be carried out by means of the rules already set down. They are found to be

$$H_{\mathrm{I\,I}} = Q + \tfrac{3}{2}\alpha = H_{\mathrm{II\,II}}$$

$$H_{\mathrm{I\,II}} = \tfrac{1}{4}Q + \tfrac{3}{2}\alpha = H_{\mathrm{II\,I}}$$

$$\Delta_{\mathrm{I\,I}} = 1 = \Delta_{\mathrm{II\,II}}$$

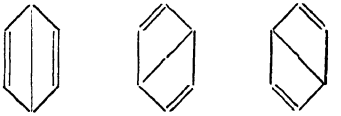
$$\Delta_{\mathrm{I\,II}} = \tfrac{1}{4} = \Delta_{\mathrm{II\,I}}$$

where Q is the coulombic energy and α is a single exchange integral between a pair of adjacent carbon atoms. Exchange integrals between more widely separated atoms are neglected. This gives for the energy $W_g = Q + 2.4\alpha$ and $W_e = Q$. It is upon this basis that we can decide which represents the ground state, since α is generally negative and the largest negative value for the energy represents the most stable state. Thus the resonance energy, by equation 8, is:

$$R = H_{\mathrm{I\,I}} - W_g = (Q + 1.5\alpha) - (Q + 2.4\alpha) = -0.9\alpha.$$

That is, the energy of the actual state of the benzene molecule is 0.9α lower than that represented by a single Kekule structure. It should be noted that each Kekule structure contributes equally to the condition of the molecule; i.e., the coefficients b_{I} and b_{II} are equal.

Now it is possible to write other structures for the benzene molecule in addition to the two Kekule structures. These are the three Dewar structures:



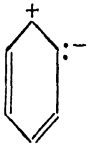
III IV V

Any other structures which must involve crossing of the lines representing the bonds in the planar picture of the molecule can be shown to be representable by combination of the five already drawn. It is to be expected that these Dewar structures will not be as important as the Kekule structures, since they involve bonds between rather widely separated atoms, and this is actually found to be the case when the calculation is carried out including them. W_g is found

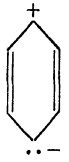
to be $Q + 2.6055\alpha$. The wave function including the three equivalent Dewar structures (χ_{III}, χ_{IV}, and χ_V) is found to be

$$\Psi_0 = 0.624(\chi_I + \chi_{II}) + 0.271(\chi_{III} + \chi_{IV} + \chi_V). \qquad (12)$$

Ionic states such as



involving a separation of charge between a pair of adjacent carbon atoms would be included in the exchange integral α, but those of the type



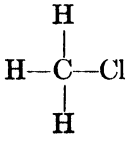
will be completely lacking because of the neglect of interchange integral between non-adjacent carbon atoms. It will be seen from later evidence, both chemical and physical, that such non-adjacent ionic states must be of considerable importance in many cases.

The calculation is not complete, since α must be determined by comparison with experiment. As we shall see, this turns out to be about -1.5 e.volts, giving benzene a resonance energy of about 39 kcal./mole. Similar calculations have been carried out for many compounds containing double bonds, and we will consider the results in more detail in a later chapter.

Chapter V

PHYSICAL PROPERTIES

When we write the structural formula of a compound, that formula is meant to represent not only the elementary composition of the compound but all of its physical and chemical properties as well. Thus the formula



implies a molecule made up of 3 atoms of hydrogen, 1 atom of carbon, and 1 atom of chlorine, the spatial arrangements of these atoms, the electron distribution in the molecule, and the presence of a C—Cl bond with all of its concommitant chemical properties, i.e. behavior toward various reagents such as alkali, sodium, etc. For many years after the introduction of structural formulas they remained pure symbols with which were associated certain properties both chemical and physical. One of the physical properties which was assigned to the carbon atom primarily from a study of the isomerism of its compounds was that the four valences of carbon formed a tetrahedral angle with each other. In the last fifteen years direct physical methods have been devised for determining the spatial configuration of the atoms in a molecule, and the early suggestions of the chemists have been entirely confirmed. In this chapter we shall examine the results of measurements on three of the primary physical properties of molecules: (1) the spatial arrangement of the atoms in a molecule in its ground state; (2) the distribution of electric charge in the molecule in its ground state; (3) the possible excited states of the molecules—electronic, vibrational, and rotational. Other physical properties might be called secondary and can in general be related to these primary ones. Some of these secondary properties are refractive index, magnetic susceptibility, and the large group of properties which depend on the interaction of the molecules (attractive and repulsive forces exerted on each other) and their shapes, such as heats of fusion and vaporization, melting and boiling points, viscosity, density, etc.

17. BOND DISTANCES AND ANGLES

17a. Experimental methods. There are at present three important methods of determining the configurations of atoms in molecules. They are (1) the method of X-ray diffraction, (2) the method of electron diffraction, and (3) the spectroscopic method.

In 1912 *X-ray methods* were first used on crystals by Laue, Friedrich, and Knipping[1] who demonstrated that X-rays were electromagnetic radiations similar to those of visible light but of very much shorter wave length. Just as a monochromatic beam of visible light whose wave length is of the order of 10^{-5} cm. is reflected only at certain specific angles by a system of reflectors whose spacing is of the order of the wave length, i.e. a diffraction grating, so is a monochromatic beam of X-rays diffracted. But the wave length of the X-rays is of the order of 10^{-7} to 10^{-9} cm., and no grating so fine can be ruled. A crystal lattice, however, is a periodic system of reflectors (or scattering centers) whose spacing is of just this order of magnitude. These periodically arranged scattering centers are the atoms themselves; and the relation connecting the distance d between the periodically recurring planes of atoms, the wave length λ of the diffracted X-rays, and the angle of scattering θ, is the well-known Bragg law, $n\lambda = 2d \sin \theta$, where n is the integral order of reflection. Thus, if a beam of X-rays of known wave length λ is passed through or reflected from a crystal and the angle of reflection θ measured, it is possible to determine the interplanar distance d from one or more of the series of reflections obtained corresponding to the integral values of n. If this be done for all three directions of the crystal axis, it is possible to determine the geometrical elements of symmetry belonging to the crystals.

This knowledge, together with the fact that the number of possible periodic arrangements in space is limited, permits the localization of atoms in planes or along axes of symmetry. But this information alone is insufficient to tell us which atoms correspond to any given plane. For this purpose an analysis of the intensities of the various reflections must be made. Since the X-rays are scattered mainly by the electrons of the atom, the scattering power of an atom increases with the atomic number. The function of the atomic number which measures this scattering power is called the atomic form factor, and this has been established for all the atoms both experimentally and theoretically. It thus becomes possible to identify the atoms in each plane.

[1] Laue, M., Friedrich, W., and Knipping, P., *Ann. Physik*, **41**, 971 (1913).

within the molecule and r_{ij} the distance between them. K is a constant involving the initial intensity of the beam and the geometry of the system. ϕ_i is a function measuring the scattering power for

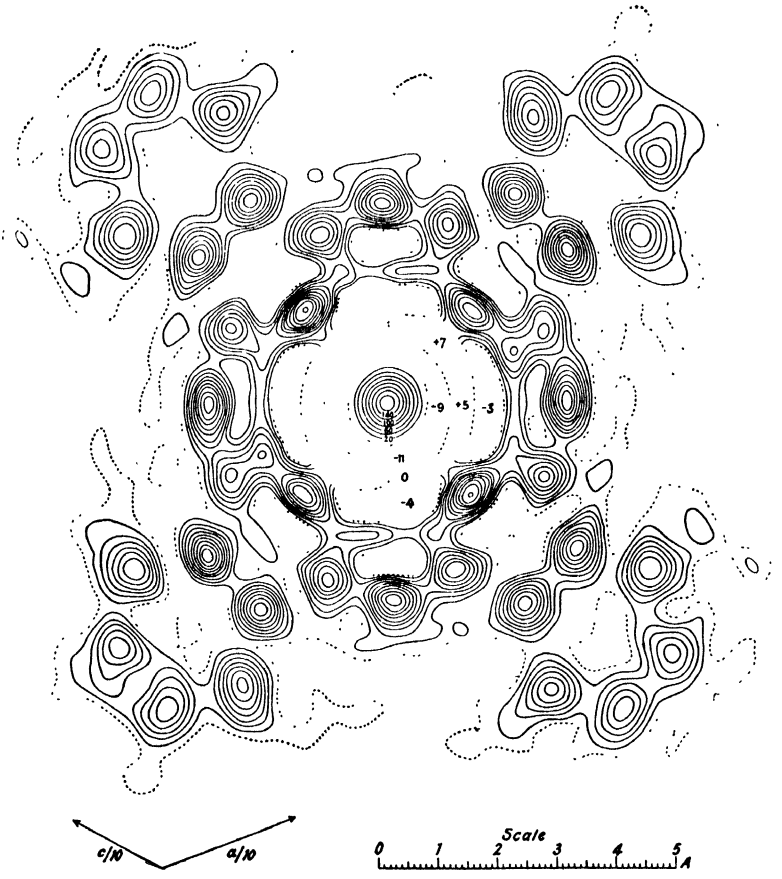


Figure 8a. The structure of platinum phthalocyanine. Electron density map of the molecule projected on a plane inclined at angle of 26.5° to the plane of the molecule.

X-rays of atom i and is given, in the limiting case of all the electrons of atom i concentrated at the hypothetical center of the atom, by

$$\phi_i = Z_i \frac{e^2}{mc^2} \left(\frac{1 + \cos^2 \theta}{2} \right)^{\frac{1}{2}} \tag{2}$$

where e is the electronic charge, m is the electronic mass, c is the velocity of light, and Z_i the atomic number of atom i. The correction for the fact that the electrons are not actually concentrated at

the center of the atom is introduced by reducing Z by means of an atom form factor (as in the diffraction of X-rays by crystals) which is known for each atom.

The *electron diffraction* method is based on the same principles as the X-ray method but, because of the charge on the electrons, their penetrating power is very much less than X-rays and they can be

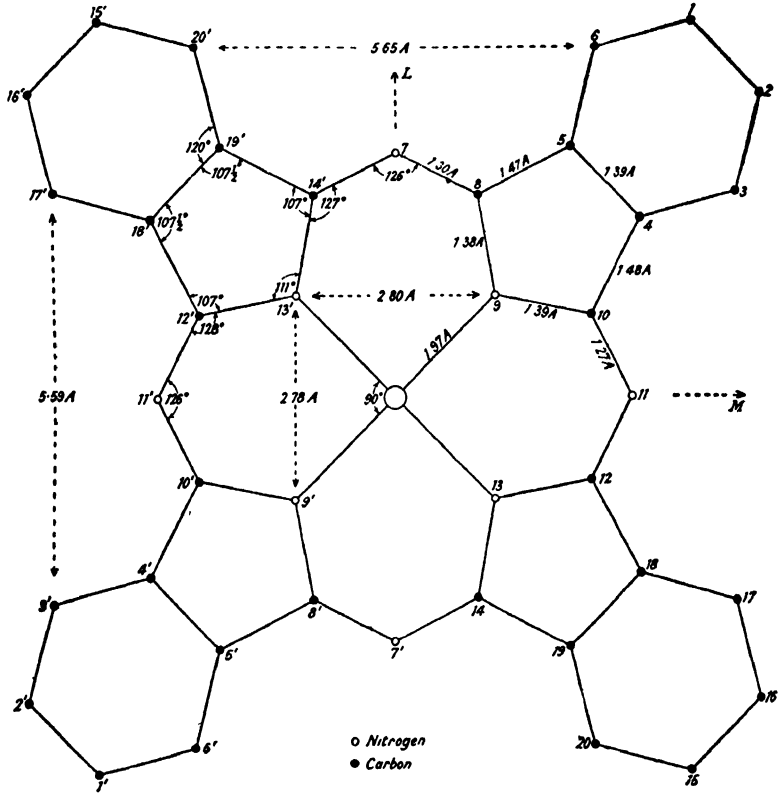


Figure 8b. Interatomic distances and bond angles derived from (a).

used only for the study of solid surfaces and molecules in the vapor phase. It is the latter application in which we are most interested here. The electrons are assigned a wave length according to the de Broglie relation $\lambda = \frac{h}{mv}$, where λ is the wave length, h is the quantum constant, m the mass and v the velocity of the electron. In practical units this is given by $\lambda = \frac{10^{-7}}{V}$ cm., where V is the ac-

celerating potential, in volts, which has been applied to the electron. Thus a 1-volt electron has a wave length of 10^{-7} cm. and a 40 kilovolt electron, which is the usual velocity used, has a wave length of 2.5×10^{-12} cm. The general form of the equation giving the dependence of the intensity I_θ of the coherently (elastically) scattered beam of electrons on the angle of scattering θ is identical with that for X-rays (equation 1). Since, however, the electron beam is scattered mainly from the nuclei of the atoms, the scattering power, ϕ, for electrons is different from that for X-rays and is given by

$$\phi_i = Z_i \frac{e^2}{2mv^2} \frac{1}{\sin^2 \theta/2} \tag{3}$$

where v is the velocity of the scattered electron. Here again Z_i must be reduced by the same atom form factor as was used in the case of X-rays, to correct for the fact that the atoms are not points but have a finite size.

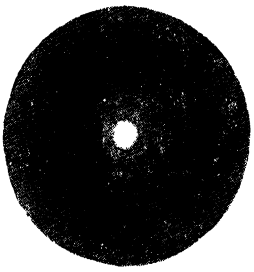


Figure 9. Electron diffraction picture of carbon tetrachloride vapor. (From a negative by Pauling.)

Carbon tetrachloride has been most completely studied by means of the diffraction of both X-rays and electrons by the vapor. With increasing experience and the progress of technique, the results of the two methods are in complete agreement. Since the methods are so nearly alike, we will follow through the interpretation of the electron diffraction data on CCl_4, to illustrate just what information concerning the atomic configuration in a molecule may be obtained by these methods.

The experimental result of passing a beam of electrons through the CCl_4 vapor is usually obtained in the form of a photograph (Figure 9), in which the central spot is the undiffracted beam and each concentric ring corresponds to an angle θ of maximum scattering. There is no rigorous, direct way of deriving from this picture a unique structure of the molecule producing it. An attempt must now be made to reproduce this picture by use of the theoretical equation (1) and an assumed model for the molecule. On the basis of all the chemical information existing concerning the arrangement of four equivalent atoms about a carbon atom, it would seem most reasonable to see if a tetrahedral model could be used to fit these data. We would then have only two distances to consider, namely the C—Cl distance,

r_{C-Cl}, and the Cl—Cl distance r_{Cl-Cl}. With this assumption, the theoretical elastic scattering curve becomes

$$I_\theta = K\left[\phi_C^2 + 4\phi_{Cl}^2 + 12\phi_{Cl}^2 \frac{\sin sr_{Cl-Cl}}{sr_{Cl-Cl}} + 8\phi_C\phi_{Cl} \frac{\sin sr_{C-Cl}}{sr_{C-Cl}}\right] \quad (4)$$

since when $i = j$, $r_{ij} = 0$, and $\frac{\sin sr_{ij}}{sr_{ij}} = 1$.

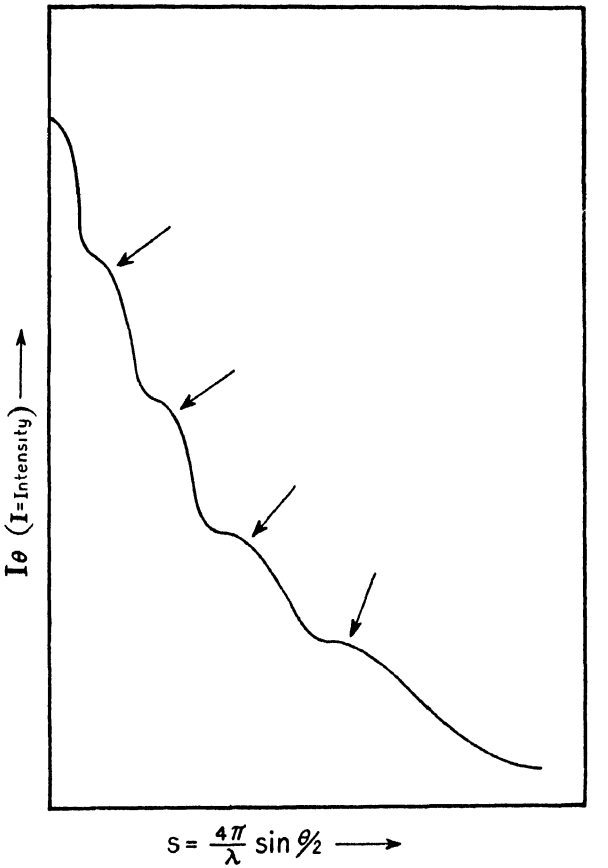


Figure 10. Intensity of scattering of electrons by carbon tetrachloride vapor as a function of the angle of scattering (diagrammatic).

To this must now be added the inelastic (incoherent) scattering which is independent of the configuration of the molecule, depending only on the number and kinds of atoms present. This inelastic

scattering, plus the terms in equation 4 not involving the interatomic distances (elastic scattering from the atoms), are aperiodic functions of the scattering angle (for angles used in this type of experiment) and give the continuous background upon which is superimposed the periodic scattering represented by the terms in equation 4 involving the interatomic distances. Such a curve for some selected values of r_{C-Cl} and r_{Cl-Cl} is represented diagrammatically in Figure 10. The points marked with the arrows should correspond to the rings found in the photograph. Now the model may be changed or the distances may be adjusted until a correspondence is obtained between the theoretically calculated maxima and the experimentally observed ones. There are a number of methods of making the comparison which attempt to minimize the sharp falling off of intensity due to the incoherent scattering, but the principle remains the same. It is found that for CCl_4 the tetrahedron with $r_{C-Cl} = 1.755$ Å gives almost exactly the experimentally observed distribution of intensities.

Although the scattering of electrons is mainly done by the atomic nuclei, this method is still incapable of placing hydrogen atoms with any degree of accuracy, although a number of C—H distances have been so determined. The only method which can accurately place H atoms is the spectroscopic one, but this method, as we shall see, is useful only for the very simplest molecules.

The *spectroscopic method*[3] depends upon the interaction of molecules with electromagnetic radiation whose wave length is many times greater than the average size of a molecule and hence is not a diffraction method as are the previous ones. It depends upon the ability of electromagnetic radiation to be absorbed or emitted by the molecule and thus change the energy content of the molecule.

In Chapter II we saw how it is possible for the electrons in an isolated atom to exist in any of a number of energy states and that, if an electron changes its energy state, radiation of frequency ν is emitted or absorbed according to the law $h\nu = E_2 - E_1$ where E_2 and E_1 are the energy levels of the two states between which the electron has moved. In the case of the hydrogen atom with only a

[3] An excellent account of the detail of the following discussion may be found in *Molecular Spectra and Molecular Structure*: *I. Diatomic Molecules*, by G. Herzberg (Prentice-Hall, Inc., New York, 1939). See also *The Optical Basis of the Theory of Valency*, by R. de L. Kronig (Cambridge University Press, 1935); *Report on Band-Spectra of Diatomic Molecules*, by W. Jevons (The Physical Society, London, 1932).

single electron, the electronic energy levels could be calculated from first principles and were found to be

$$E_n = -\frac{Rhc}{n^2}; \qquad R = \frac{2\pi^2 me^4}{h^3 c}$$

where n could have the integral values 1, 2, ... ∞, all of the other factors being fundamental physical constants. If a hydrogen atom absorbs radiation so that the electron is raised from a level in which $n = 1$ to a level in which $n = 2$, the frequency of the absorbed radiation will be

$$\nu = Rc\left[\frac{1}{1^2} - \frac{1}{2^2}\right].$$

The same frequency would be emitted in the return process. If by some means, such as electron bombardment, a group of hydrogen atoms could be raised into any of the series of levels $n = 2, 3, 4$, etc. and then permitted to fall back to the level $n = 1$, a series of lines would be emitted whose frequencies would be given by

$$\nu_{n,1} = Rc\left[\frac{1}{1^2} - \frac{1}{n^2}\right]$$

with n corresponding to the level from which the electron dropped. This series is known as the Lyman series. If the state to which the electron drops is $n = 2$, the resulting series of lines is the Balmer series. For more complex atoms a line spectrum is observed, but a complete analysis as in the case of the hydrogen atom has not yet been possible. It is, however, possible to assign various excited electronic states to these more complex atoms, even if they cannot be calculated. In some cases the chemical properties of atoms in these excited states have been observed and measured.

An exactly similar process of electronic excitation is possible in molecules. But, as may well be imagined, even the assignment or identification of these excited electronic states has so far proved impossible in any but the simplest molecules, namely the diatomic molecules. We have reason to believe that some understanding of the electronic spectra of large unsaturated organic molecules can be obtained with the aid of resonance theory. They will be considered in some detail in section 20.

In addition to electronic energy, a molecule can take up energy to bring its constituent atoms into vibration against one another, and further, to bring the entire molecule into rotation about some

axis of the molecule, both of which processes are absent for single atoms. Now, just as the electronic motion and energy is quantized (the electron can exist only in certain discretely separated states of energy), so are these vibrational and rotational motions of the molecule quantized. Here again the vibrational state of the molecule may be characterized by a vibrational quantum number v, and the rotational state by a rotational quantum number J. Thus the total energy of a molecule in some specified electronic state of quantum number n, vibrational state of quantum number v, and rotational state of quantum number J, is given by

$$E_{(n,\,v,\,J)} = E_n(\text{electronic}) + E_v(\text{vibrational}) + E_J(\text{rotational}) \qquad (5)$$

The actual calculation of the vibrational and rotational energies is possible only in the very simplest of molecules, primarily the diatomic molecule, but the concepts once obtained may be applied in principle to the more complex molecules. Let us consider then the case of a diatomic molecule in some detail.

As we have seen in the case of the hydrogen molecule, the mutual potential energy of a pair of atoms capable of forming a bond decreases as the atoms approach each other, reaching a minimum and then rising very sharply as the atoms are brought still closer together. The initial decrease is due to the increasing contribution of the electronic resonance as the atoms are brought closer together, and the rise is due to the repulsion of the nuclear charges, which becomes the most important factor at small distances. For an ionic bond, the resonance or homopolar decrease would be replaced by a coulombic decrease due to the initial attraction of the oppositely charged ion components of the molecule. This sort of curve may be used to represent any bond, the differences being in the depth and in the position of the minimum and small changes in the shape. Such a curve is represented by curve A in Figure 11. In general, these curves must be obtained empirically from experiment, but in order to understand them we will examine the simplified theory which may be considered as a limiting case.

Because of the very small mass of the electron, its motion is of very high frequency compared to that of the much heavier nuclei. We may assume, therefore, that, for any instantaneous position of the nuclei in the course of their motion, the electrons have always assumed their best position corresponding to their quantum condition. Thus it may be assumed that the nuclei are moving in an averaged field, owing to the electrons, for any given electronic state

of the molecule, and we may consider the energy associated with the atomic motion as characteristic for each electronic state of the molecule and independent of the other electronic states. We can now consider a diatomic molecule in its ground electronic state made up of atoms of mass M_1 and M_2, and having an equilibrium separation of r_e. Let us suppose that for small displacements from the equilibrium distance the force tending to restore the atoms to their equilibrium position is proportional to their displacement from it, $F = k(r - r_e)$, so that the potential energy becomes $V = \frac{k}{2}(r - r_e)^2$, setting the zero of potential for the atoms at their equilibrium separation. This potential function represents a linear harmonic oscillator. If now we permit no other type of motion, e.g., rotation, and use this potential in the Schrödinger equation, the resulting energy levels are found to be

$$E_v = (v + \tfrac{1}{2})h\nu_0 \quad \text{with} \quad \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{M}} \quad \text{and} \quad M = \frac{M_1 M_2}{M_1 + M_2} \tag{6}$$

The vibrational quantum number v can have any integral value from zero up—0, 1, 2, 3 . . . . This represents the possibility of an infinite amount of energy being absorbed into the vibration in units of $h\nu_0$, and we know that this is not true since the molecules do dissociate eventually into atoms. Hence this equation is valid only for small vibrations. For higher vibrations we must introduce higher terms in the potential to take into account their anharmonic character. This could be done by setting up V as a series in terms of the displacement

$$V = \frac{k}{2}(r - r_e)^2 + \frac{k'}{3}(r - r_e)^3 + \frac{k''}{4}(r - r_e)^4 \cdots \tag{7}$$

or, in terms of an exponential as Morse has done,

$$V = D[1 + e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}]. \tag{8}$$

In either case the energy becomes

$$E_v = (v + \tfrac{1}{2})h\nu_0 - X_e(v + \tfrac{1}{2})^2 h\nu_0 + \ldots \tag{9}$$

If equation 7 is used, ν_0 has the same value as in equation 6 and X_e is a function of the other constants k', k'', etc. If equation 8 is used, the following relationships hold:

$$\nu_0 = \frac{a}{2\pi}\sqrt{\frac{2D}{M}}; \qquad X_e = \frac{h\nu_0}{4D}.$$

D is here the difference in energy between the minimum and the asymptote approached at large separations. It is not the actual thermal dissociation energy of the molecule, since even in its lowest vibrational state, $v = 0$, the molecule still has the vibrational energy $\frac{1}{2}h\nu_0$. This is called the zero-point energy and would exist in the molecule even at the absolute zero of temperature. The actual dissociation energy would then be $D_0 = D - \frac{1}{2}h\nu_0$. These vibrational states of the ground electronic state can be represented by the lines v_0^A, v_1^A, v_2^A in Figure 12.

Now, keeping the molecule in some vibrational state, it may rotate about an axis normal to the line joining the two atoms. This motion is quantized, so that the molecule may rotate only in a series of discrete energy states given by

$$E_J = hB_eJ(J + 1), \text{ with } J = 0, 1, 2, \ldots \qquad (10)$$

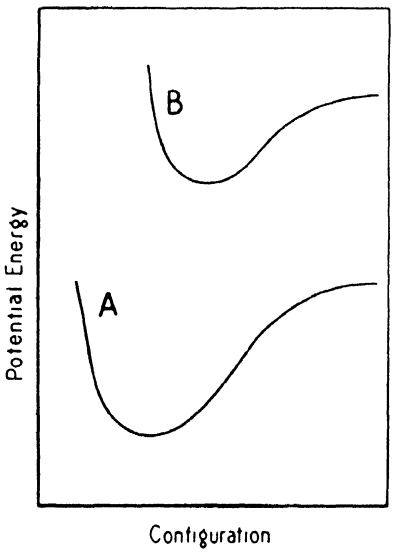


Figure 11. Potential energy curves for two electronic states.

and $B_e = \dfrac{h}{8\pi^2 I}$, where I is the moment of inertia of the molecule about the axis of rotation. The moment of inertia is given by $I = Mr_e^2$, where M is again the reduced mass as in equation 6.

These rotational states for each vibrational level of the ground electronic states (A) are represented in Figure 12 by the dotted lines marked $J(v_1^A)$, $J(v_2^A)$, etc., the numbers corresponding to the value of J.

A similar set of vibrational and rotational states will exist for the molecule in another (excited) electronic state. This is represented by curve B, Figure 11. The one factor in equation 10 which depends on the molecule is I, the moment of inertia. This depends on the masses of the atoms and their equilibrium distance of separation. The masses, of course, remain unchanged throughout any changes in state which the molecule may undergo, but their equilibrium separation does not. Thus,

in general, each vibrational state will have its own equilibrium separation and, hence, moment of inertia. Even the higher rotational

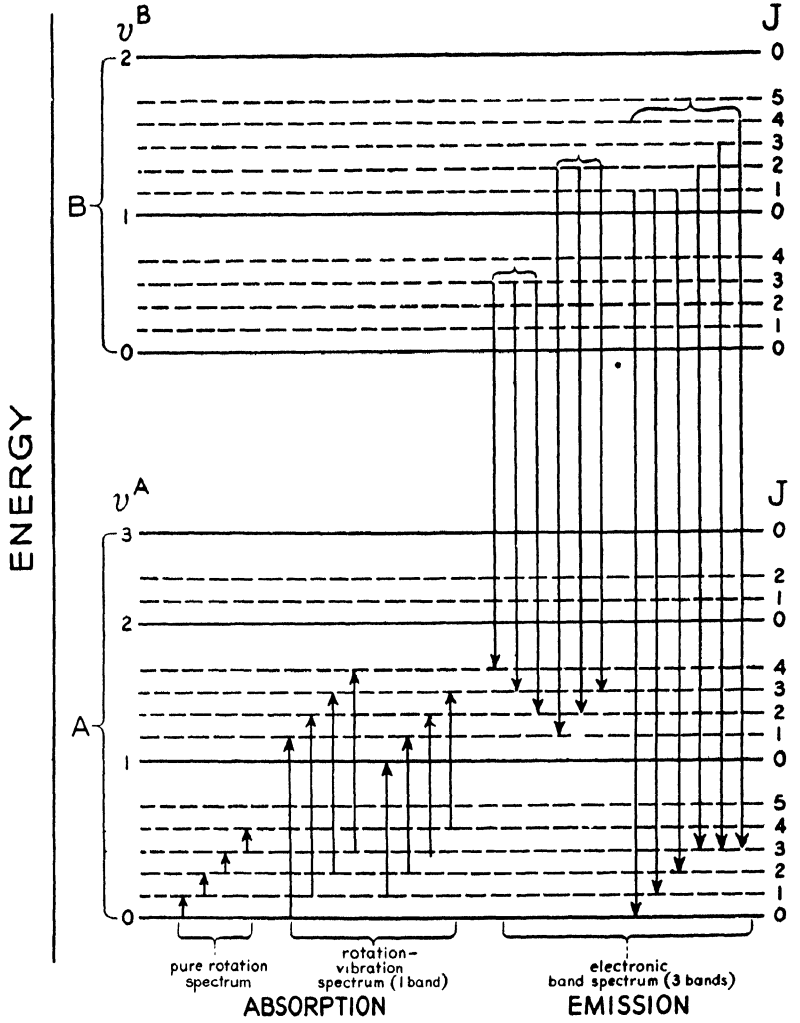


Figure 12. Energy level diagram showing electronic, vibrational, and rotational states.

states in a single vibrational state will have a slightly larger moment of inertia due to the increased atomic separation resulting from the centrifugal force. Therefore, when we write the total energy of the

molecule in some specified quantum state as the sum of the energies of the various types of motion, as in

$$E_{(n,v,J)} = E_n(\text{electronic}) + \overbrace{(v + \tfrac{1}{2})h\nu_0 - X_e(v + \tfrac{1}{2})^2 h\nu_0}^{\text{(vibrational)}} + \underbrace{hB_e(v, J)J(J + 1)}_{\text{(rotational)}}, \tag{11}$$

it must be remembered that B_e is dependent on the values of n, v, and J and corrections must be appropriately applied.

Now it becomes possible, from a study of the frequencies and intensities of the light absorbed or emitted by a molecule in going from one state to another, to gain some information concerning the interatomic distances and atomic configurations in the molecule.

The arrangement of energy levels in a diatomic molecule can be represented by a diagram, as in Figure 12. The horizontal lines each represent a quantum state of the molecule. Two electronic states A and B are shown. The vertical lines show transitions between states, and the length of these vertical lines is a measure of the frequency of the light associated with the transition. The important quantity for the present purpose is B_e, which gives the moment of inertia. This makes itself apparent only in the separation of the rotation lines as given by the formula

$$E_{J+1} - E_J = 2hB_e(J + 1), \text{ for } J = 0, 1, 2, 3, \ldots$$

We need only consider changes in J of ± 1, since there is a selection rule which forbids any other transitions within a single electronic state. This would result in a series of lines whose frequencies are given to a first approximation for small values of J by

$$\frac{E_{J+1} - E_J}{h} = \nu_{J,J+1} = 2B_e(J + 1), \quad J = 0, 1, 2, \cdots \tag{12}$$

If no change other than rotational takes place, i.e. if a molecule in a specific vibrational state of a given electronic state changes from one rotational state to another, the resulting spectrum, known as a pure rotation spectrum, would be a series of lines of frequency $2B_e$; $4B_e$; $6B_e$, etc. This type of spectrum is not important to us for two reasons. First, only molecules possessing a permanent dipole moment would show it, and second, it is in the far infra-red ($\lambda = 0.1$ cm.), a region of the spectrum very difficult to work in. Pure rotation frequencies

are of the order of $\nu = 30 \times 10^{10}$ sec.$^{-1}$ or, expressed in wave numbers (vibrations per cm.), $\tilde{\nu} = \frac{\nu}{c} = 10$ cm.$^{-1}$. This would correspond to approximately 30 cals./mole[4] and, since $RT = 600$ cals./mole at room temperatures, the molecules would normally be thermally excited to a distribution among most of the rotational states of the ground vibrational state. A transition between two vibrational states of the same electronic state is accompanied by a change in the rotational state. The resulting spectrum is known as a vibration-rotation spectrum. Since these are generally observed in absorption, and since their wave numbers are of the order of 1000 cm.$^{-1}$ (3000 cals./mole), the vibration band is generally the one from the ground vibrational state ($v = 0$) to the first excited vibrational ($v = 1$) state. The frequencies in a vibration-rotation band will thus be (since $\Delta J = \pm 1$)

$$\nu_{J,J+1}^{v_0 v_1} = \nu_0 + 2B_e(J+1) \qquad J = 0, 1, 2, \cdots$$

and **(13)**

$$\nu_{J,J-1}^{v_0 v_1} = \nu_0 - 2B_e J \qquad J = 1, 2, 3, \cdots$$

and we again have the rotation structure consisting of a series of approximately equidistant lines grouped around the vibration frequency ν_0 and separated by the frequency $2B_e$. These appear in the region 10,000 to 100,000 Å and can be observed much more readily than the pure rotation bands. Here again, however, vibration bands are absent for homonuclear molecules such as H_2, N_2, O_2, etc.

Finally, the transitions may occur between the various vibrational and rotational states of two different electronic levels such as A and B in Figures 11 and 12. In that case, because of the relatively large difference in energy between electronic levels, the light emitted or absorbed is in general in the near infra-red, visible, or ultra-violet (1000 – 10,000 Å). All of the transitions between any pair of electronic levels give rise to an electronic band system, each band consisting of the rotational structure in only those transitions involving a given pair of vibrational states. It is from this rotational structure that we are able to determine values of B_e and hence the moment of inertia of the molecule in both of its electronic states involved in the particular band system. This is the type of spectrum

[4] The relations among the units are $\lambda\nu = c$ where c is the velocity of light $(3 \times 10^{10}$ cm./sec.), $\tilde{\nu} = \frac{\nu}{c}$, and E (cals./mole) $= 2.84\,\tilde{\nu}$.

TABLE 5

BOND DISTANCES IN SOME ORGANIC COMPOUNDS

Compound	Distance, Å	Bond Character	Method of Determination*	Ref.
C—C Bond				
Diamond	1.542±0.001		X-ray	(45)
Dibenzyl	1.58	C_{al}—C_{al}	X-ray	(28)
$C_{29}H_{60}$ (Nonacosane)	1.55		X-ray	(20)
Ethane	1.55±0.03		E.D.	(10)
Propane, Isobutane, Neopentane	1.54±0.02		E.D.	(10)
$CH_3(CH_2)_{16}COOH$	1.54		X-ray	(19)
Hexamethylbenzene	1.54±0.12	C_{ar}—C_{al}	X-ray	(22)
Isobutene, Tetramethylethylene	1.54±0.02	=C—C	E.D.	(10)
Diacetyl	1.54±0.02	H_3C—C=O	E.D.	(54)
Mesitylene, Hexamethylbenzene	1.54±0.01	C_{ar}—C_{al}	E.D.	(10)
Cyclopropane, Cyclohexane	1.53±0.03		E.D.	(10)
Cyclopentane	1.52±0.03		E.D.	(10)
Pentaerythrityl tetracetate	1.52±0.03	C C_1 C_2—C_3	X-ray	(21)
Succinic acid	1.51 and 1.52		X-ray	(35)
Acetaldehyde	1.51±0.05	O=C—CH_3	Sp.	(50)
Acetaldehyde	1.50±0.02	O=C—CH_3	E.D.	(56)
Benzoquinone	1.50	O=C—C=	X-ray	(27)
Hexamethylbenzene, *p*-Xylene	1.50±0.01	C_{ar}—C_{al}	E.D.	(13)
Methyl cyanide	1.49±0.03	≡C—C	E.D.	(52)
Diphenyl	1.48	C_1—$C_{1'}$	X-ray	(15)
Glyoxal, Diacetyl	1.47±0.02	O=C—C=O	E.D.	(54)
Durene	1.47±0.02	C_{ar}—C_{al}	X-ray	(25)
Diketopiperazine	1.47±0.03	O=C—C	X-ray	(18)
Glycine	1.47	O=C—C	X-ray	(48)
Dimethylacetylene, Dimethyldiacetylene	1.47±0.02	≡C—C	X-ray	(52)
Dibenzyl	1.47	C_{ar}—C_{al}	X-ray	(28)
Butadiene	1 46±.03	=C—C=	E.D.	(53)
Cyclopentadiene	1 46±.04		E.D.	(53)
Methylacetylene	1.463	≡C—C	Sp.	(41)
Furan	1.46	=C—C=	E.D.	(53)
Methylacetylene	1.462±0.005	≡C—C	Sp.	(43)
Pyrrole	1.44	=C—C=	E.D.	(53)
Stilbene	1 44±0.02	=C—C_{ar}	X-ray	(31)
Thiophene	1.44	=C—C=	E.D.	(53)
Oxalic acid dihydrate	1.44±0.01	O=C - C=O	X-ray	(30)
Graphite	1.420±0.002		X-ray	(44)
Benzene, Hexachlorobenzene	1.42±0.03	C_{ar}—C_{ar}	X-ray	(22, 23)

* E.D. = electron diffraction; Sp. = spectroscopic; X-ray = X-ray crystal analysis.

TABLE 5 (*Continued*)

Compound	Distance, Å	Bond Character	Method of Determination*	Ref.
C—C Bond				
Durene, Anthracene, Naphthalene	1.41±0.01	C_{ar}—C_{ar}	X-ray	(24, 25, 26)
Tolan	1.40±0.02	≡C—C_{ar}	X-ray	(32)
Benzene, *p*-Xylene, Hexamethylbenzene	1.40±0.01	C_{ar}—C_{ar}	E.D.	(13)
Benzene	1.390±0.005	C_{ar}—C_{ar}	E.D.	(1)
Hexamethylbenzene	1.39	C_{ar}—C_{ar}	E.D.	(10)
Dibenzyl	1.41	C_{ar}—C_{ar}	X-ray	(28)
Stilbene	1.39±0.02	C_{ar}—C_{ar}	X-ray	(31)
Tolan	1.39±0.02	C_{ar}—C_{ar}	X-ray	(32)
Pyridine, Pyrazine	1.39±0.02		E.D.	(53)
Azobenzene	1.39±0.03	C_{ar}—C_{ar}	X-ray	(34)
β-Resorcinol	1.39	C_{ar}—C_{ar}	X-ray	(33)
Dimethyl-diacetylene	1 38±0.03	≡C—C≡	E.D.	(52)
Cyanogen	1.37±0.02	≡C—C≡	E.D.	(52)
Diacetylene	1 36±0.03	≡C C≡	E.D.	(52)
C—F Bond				
Methyl fluoride	1.42±0.02		E.D.	(4)
Monofluoro-dichloromethane	1 41±0.03		E.D.	(4)
Monofluoro-monochloromethane.	1.40±0.03		E.D.	(4)
Monofluoro-trichloromethane	1 40±0.04		E.D.	(4)
Carbon tetrafluoride	1.36±0.02		E.D.	(5)
Difluoromethane	1.36±0.02		E.D.	(4)
Difluoromonochloro-methane	1.36±0 03		E.D.	(4)
Difluoro-dichloromethane	1.35±0.03		E.D.	(4)
C—Cl Bond				
Carbon tetrachloride	1 755±0.005		E.D.	(9)
Trichloroethylene, Tetrachloroethylene	1.82±0.08	=C - Cl	E.D.	(12)
Chloroform, Dichloromethane, Monochloromethane	1.77±0.02		E.D.	(9)
Fluorochloromethane	1.76±0.02		E.D.	(4)
Dichloro-dibromomethane	1.75		E.D.	(46)
Difluoro-dichloromethane	1.74±0.03		E.D.	(4)
Tetrachloroethylene.	1.73±0.02	=C--Cl	E.D.	(6)
Difluoro-monochloromethane.	1.73±0.03		E.D.	(4)

TABLE 5 (*Continued*)

Compound	Distance, Å	Bond Character	Method of Determination*	Ref.
C—Cl Bond				
Monofluoro-dichloromethane	1.73±0.04		E.D.	(4)
Thiophosgene	1.70±0.02	S=C—Cl	E.D.	(6)
Trichloroethylene	1.71±0.03	=C—Cl	E.D.	(6)
Vinyl chloride *uns*-Dichloroethylene *trans-sym*-Dichloro-ethylene	1.69±0.02	=C—Cl	E.D.	(6)
Phosgene	1.68±0.02	O=C—Cl	E.D.	(6)
cis-sym-Dichloroethylene	1.67±0.03	=C—Cl	E.D.	(6)
Hexachlorobenzene	1.665		X-ray	(23)
C—Br Bond				
Carbon tetrabromide	1.92±0.02		E.D.	(11, 47)
Methyl bromide	1.91±0.02		E.D.	(11)
Dichloro-dibromomethane	1.91±0.06		E.D.	(46)
Vinyl bromide Tribromoethylene *sym*-Dibromoethylene (*cis-trans* mix.)	2.05±0.08		E.D.	(12)
C—I Bond				
Carbon tetraiodide	2.12±0.02		E.D.	(47)
1,2-, 1,3-, and 1,4-Diiodobenzene	2.00±0.10		X-ray E.D.	(14)
C=C Bond				
Vinyl chloride *uns*-Dichloroethylene *sym*-Dichloroethylene (*cis-trans* mix.) Trichloroethylene Tetrachloroethylene	1.38	*X*—C=C	E.D.	(6)
Allene Ethylene	1.34±0.02	=C=C— —C=C—	E.D.	(10)
Butadiene Cyclobutadiene Furan Pyrrole Thiophene	1.35±0.02	*X*—C=C—	E.D.	(53)
Stilbene	1.33±0.04	ϕ—C=C—ϕ	X-ray	(31)
Benzoquinone	1.32		X-ray	(27)
Vinyl bromide *sym*-Dibromoethylene (*cis-trans* mix.) Tribromoethylene Trichloroethylene Tetrachloroethylene	1.32±0.08	*X*—C=C	E.D.	(12)

TABLE 5 (*Continued*)

Compound	Distance, Å	Bond Character	Method of Determination*	Ref.
C≡C Bond				
Acetylene	1.204±0.002		Sp.	(42)
Methyl acetylene Dimethyl diacetylene	1.20±0.03		E.D.	(52)
Tolan	1.19±0.02		X-ray	(32)
Diacetylene	1.19±0.03		E.D.	(52)
C—H Bond				
Methane	1.093		Sp.	(49)
Pyridine Pyrazine Butadiene Cyclopentadiene Furan Pyrrole Thiophene	1.09±0.04		E.D.	(53)
Ethane	1.09±0.03		E.D.	(10)
Formaldehyde	1.09±0.01	O=C—H	E.D.	(55)
Ethylene	1.06±0 03	=C—H	E.D.	(10)
Ethylene	1.04	=C—H	Sp.	(40)
Acetylene	1.057±0.002	≡C—H	Sp.	(42)
Benzene	1.08±0.04		E.D.	(53)
Benzene	1.14±0.01		E.D.	(13)
C—O Bond				
α-Methylhydroxylamine.	1.44±0.02		E.D.	(6)
Dimethyl ether	1.44±0.03		E.D.	(3)
Paraldehyde	1.43±0.02	C—O(ring)	E.D.	(7)
Metaldehyde	1.43±0.03	C—O(ring)	E.D.	(8)
Trioxymethylene	1.42±0.03	C—O(ring)	X-ray	(37)
Furan	1.41±0.02	C—O(ring)	E.D.	(53)
Pentaerythrityl tetracetate	1.41±0 03	C_1—O_1 C_2—O_1	X-ray	(21)
Glycine	1.39		X-ray	(48)
β-Resorcinol	1.36 and 1.37		X-ray	(33)
C=O Bond				
Pentaerythrityl-tetracetate	1.33	C_2—O_2	X-ray	(21)
Formic acid	1.29±0.02		E.D.	(2)
Basic beryllium acetate.	1.29±0.05		E.D.	(2)
Phosgene	1.28±0.03		E.D.	(6)
Cyanuric acid (keto form)	1.28±0.04		X-ray	(39)
Succinic acid	1.28 and 1.31		X-ray	(35)
Diketopiperazine	1.25±0.03		X-ray	(18)
Urea	1.25		X-ray	(17)
Oxalic acid dihydrate	1.24 and 1.30	O=C—O	X-ray	(30)
Acetaldehyde	1.22±0.02		E.D.	(56)
Formaldehyde	1.21±0.01		E.D.	(55)
Glyoxal Diacetyl	1.20±0.02		E.D.	(54)

TABLE 5 (*Continued*)

Compound	Distance, Å	Bond Character	Method of Determination*	Ref.
C=O Bond				
Benzoquinone	1.14		X-ray	(27)
C—S Bond				
Tri-thioformaldehyde	1.81±0.06	C—S(ring)	X-ray	(38)
Thiophene	1.74±0.03	C—S(ring)	E.D.	(53)
C=S Bond				
Thiophosgene	1.63		E.D.	(6)
Thiourea	1.64		X-ray	(16)
C—N Bond				
Nitromethane	1.46±0.02	$C—NO_2$	E.D.	(6)
Azobenzene (*cis*)	1.45±0.04	$C_{ar}—N=$	X-ray	(34)
Pyrrole	1.42±0.02	C—N(ring)	E.D.	(53)
Hexamethylenetetramine	1.42		X-ray	(17)
Azobenzene (*trans*)	1.41±0.03	$C_{ar}—N=$	X-ray	(34)
Diketopiperazine	1.41±0.03	$CH_2—N$	X-ray	(18)
Glycine	1.40		X-ray	(48)
Cyanuric triazide	1.38	=C—N	X-ray	(51)
Pyridine	1.37±0.03	C—N(ring)	E.D.	(53)
Cyanuric acid (keto form)	1.37±0 02	O=C—N—C=O	X-ray	(39)
Urea	1.37		X-ray	(17)
Thiourea	1.35		X-ray	(16)
Pyrazine	1.35±0.02	(ring)	E.D.	(53)
Phthalocyanines	1.34±0.03	N—C=N	X-ray	(29)
Diketopiperazine	1.33±0.03	O=C N	X-ray	(18)
C=N Bond				
Cyanuric triazide	1.31	C=N	X-ray	(51)

REFERENCES

[1] Brockway, L. O., and Pauling, L., *J. Chem. Phys.*, **2**, 867 (1934).
[2] Brockway, L. O., and Pauling, L., *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).
[3] Brockway, L. O., and Sutton, L. E., *J. Am. Chem. Soc.*, **57**, 473 (1935).
[4] Brockway, L. O., *J. Phys. Chem.*, **41**, 747 (1937).
[5] Brockway, L. O., and Pauling, L., *J. Am. Chem. Soc.*, **57**, 2684 (1935).
[6] Brockway, L. O., Pauling, L., and Beach, J. V., *J. Am. Chem. Soc.*, **57**, 2693 (1935).
[7] Brockway, L. O., and Carpenter, D. C., *J. Am. Chem. Soc.*, **58**, 1270 (1936).
[8] Pauling, L., and Carpenter, D. C., *J. Am. Chem. Soc.*, **58**, 1274 (1936).
[9] Brockway, L. O., and Jenkins, H. O., *J. Am. Chem. Soc.*, **58**, 2036 (1936).
[10] Brockway, L. O., and Pauling, L., *J. Am. Chem. Soc.*, **59**, 1223 (1937).
[11] Brockway, L. O., and Levy, H. A., *J. Am. Chem. Soc.*, **59**, 1662 (1937).
[12] Dornte, R. W., *J. Chem. Phys.*, **1**, 566 (1933).
[13] Jones, P. L. F., *Trans. Faraday Soc.*, **31**, 1036 (1935).
[14] Hendricks, S. B., Maxwell, L. R., Moseley, V. L., and Jefferson, M. E., *J. Chem. Phys.*, **1**, 549 (1933).
[15] Dhar, J., *Indian J. Phys.*, **16**, 43 (1932).
[16] Corey, R. B., and Wyckoff, R. W. G., *Z. Krist.*, **81**, 386 (1932).
[17] Corey, R. B., and Wyckoff, R. W. G., *Z. Krist.*, **89**, 462 (1934).
[18] Corey, R. B., *J. Am. Chem. Soc.*, **60**, 1598 (1938).
[19] Müller, A., *Proc. Roy. Soc.*, **114A**, 542 (1927).
[20] Müller, A., *Proc. Roy. Soc.*, **120A**, 437 (1928).
[21] Goodwin, T. H., and Hardy, R., *Proc. Roy. Soc.*, **164A**, 369 (1938).
[22] Lonsdale, K., *Proc. Roy. Soc.*, **123A**, 494 (1929).

result which is obtained, we have collected in Table 5 a number of bond distances more or less arbitrarily chosen from some of the more recent measurements.

An examination of the table shows that, to a first approximation, the internuclear distance for each kind of bond remains fairly constant throughout a wide variety of molecules in which the secondary effects which we will mention later are absent. By "kind of bond" we mean a bond of definite multiplicity, i.e. single, double, or triple, between a given pair of atoms. Thus the C—C distance undisturbed by these secondary influences can be taken as that found in diamond, which has been most accurately determined to be 1.542 Å. Similarly, for the C=C distance we take that found for ethylene as 1.34 Å. From these experimental values it is possible to assign covalent radii to atoms so that addition of the two radii

Table 6

ATOMIC COVALENT RADII*

	H	C	N	O	F
Single	0.30	0.77	0.70	0.66	0.64
Double		.67	.61	.55	
Triple		.60	.55		
		Si	P	S	Cl
Single		1.17	1.10	1.04	0.99
		Ge	As	Se	Br
Single		1.22	1.21	1.17	1.14
		Sn	Sb	Te	I
Single		1.40	1.41	1.37	1.33

* The values are the purely experimental ones to be found in *The Nature of the Chemical Bond*, by L. Pauling (Cornell University Press, 1939). See also the review by Pauling, "Recent Work on the Configuration and Electronic Structure of Molecules; with some Applications to Natural Products," in *Fortschritte der Chemie Organischer Naturstoffe*, 3 (1939).

involved in a bond will give a good approximation to the bond length. For example, the radius taken for singly covalent carbon is 0.77 Å. and for doubly covalent carbon is 0.67 Å. In Table 6 are given a number of such covalent radii which have been obtained from experimental values of internuclear distances.

A number of regularities are clearly evident in this table. The radius decreases in each row of the periodic system with increasing atomic number, and in each column it increases with increasing atomic number. This is no doubt connected with the increasing nuclear charge for the same electronic shell as one proceeds through a row, and with the increasing number of shells as one proceeds down

a single column. Furthermore, the ratio of double to single bond radii, and triple to single, seems to be constant through a row. For the first row these ratios are $\frac{\text{double}}{\text{single}} = 0.87$ and $\frac{\text{triple}}{\text{single}} = 0.78$. Using these trends, Pauling[5] made estimates that are undoubtedly fairly accurate for covalent bond radii other than those that have been measured.

In many organic compounds the chemical properties are represented by neither a single bond nor a double bond. The same is of course true of the physical properties, and here, in the bond distance, we have an empirical way of estimating the amount of contribution

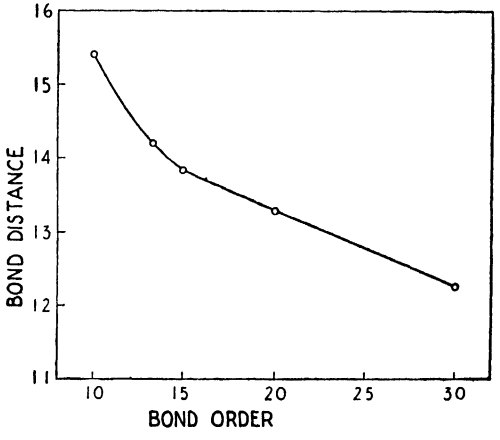


Figure 13. Carbon-carbon distances for single, double, triple, and intermediate bonds.

of each kind of bond to the actual state of the molecule. If we plot as ordinate internuclear distance and as abscissa a function called bond order, which has the value 1 for a pure single bond, 2 for a pure double bond, and 3 for a pure triple bond, we get the points shown in Figure 13 representing the carbon-carbon distance in ethane, ethylene, and acetylene.[6]

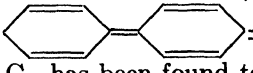
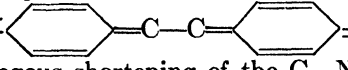
We have seen in the last chapter that the two most important resonance contributors to the benzene molecule are the two Kekule structures. If these are taken as the only contributors, both con-

[5] Ref. of Table 6.

[6] Pauling, L., Brockway, L. O., and Beach, J. Y., *J. Am. Chem. Soc.*, **57**, 2705 (1935); Pauling, L., and Brockway, L. O., *J. Am. Chem. Soc.*, **59**, 1223 (1937).

tributing equally, the resulting molecule would contain only one kind of bond, which would be midway between single and double. Thus the carbon-carbon distance in benzene, 1.39 Å, gives a point on the bond-order scale at 1.5. Another point on this curve can be obtained from graphite, in which each carbon atom is bonded by four bonds to three other carbon atoms. In a single valence-bond structure, one of the bonds must be double and the other two single, but there is no specification as to which one must be double; i.e., this double bond may resonate between three positions, and hence each bond can be said to have an order of $1\frac{1}{3}$. We now have five points through which to draw a smooth curve. This curve can actually be represented analytically, as shown by Pauling; and Penney and others[7] have derived similar curves on a theoretical basis.

Now, when an internuclear distance is measured and its contributing forms are only single, double, or triple covalent bonds, the relative amounts of each contribution can be estimated by use of such a curve. It can be used for internuclear distances other than carbon—carbon by suitable changes of the ordinate scale.

In diphenyl, the length of the bond joining the two benzene rings has been found to be 1.48 Å, which is between that of a single and that of a double bond. It corresponds to a bond having about 14 per cent double bond character, which can be attributed to the resonance $\mp$  $\pm$. Similarly in stilbene, the distance $C_{al} - C_{ar}$ has been found to be 1.44 Å, which corresponds to about 40 per cent double bond character attributable to the resonance $\mp$  $\pm$. *trans*-Azobenzene exhibits an analogous shortening of the C—N bond from 1.47 Å to 1.41 Å. In the *cis*-azobenzene, however, the distance is 1.45 Å. This can be taken as an example of the general principle that a single-double bond resonance can occur only in a planar system. The crystal structure analysis has shown that, while the *trans*-azobenzene is indeed planar, the *cis* compound is not. Apparently in the *cis* compound the interference of ortho hydrogen atoms is sufficient to force the two benzene rings into a position in which their planes make an angle of about 40° with each other, thus reducing the type of resonance structure drawn above for stilbene.[8]

Another example involving an atom other than carbon is to be found in the chloroethylenes, where the C=C distance is given as

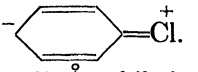
[7] Penney, W. G., *Proc. Roy. Soc.*, **A158**, 306 (1937); Coulson, C. A., *Proc. Roy. Soc.*, **A169**, 413 (1939).

[8] See section 34 on the *cis-trans* equilibrium.

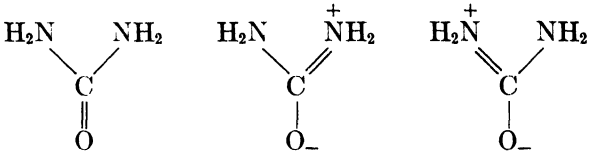
1.38 Å and the C—Cl distance (in chloroethylene) as 1.69 Å. The normal C—Cl distance is taken as 1.76 Å from the chlorinated methanes, so that structure II must contribute something to the state of the molecule, which contribution is estimated to be about 14 per cent.



I II

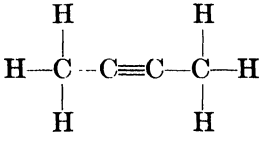
A similar resonance can be used to account for the C—Cl distance 1.69 Å in the chlorinated benzenes,  .

The C—N distance in urea is given as 1.37 Å, while in the aliphatic amines it is around 1.47 Å. This difference may be due to the contributions of II and III to the actual state of urea.

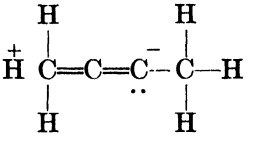


I II III

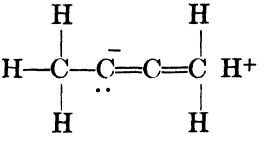
There are, however, many cases of anomalous bond distances for which none of these readily acceptable resonances can be written. The ≡C—C distance in the methyl acetylenes is given as 1.46 Å with a high degree of accuracy. It may be possible that some sort of resonance involving structures (II and III) having unbonded atoms are important, i.e.:



I

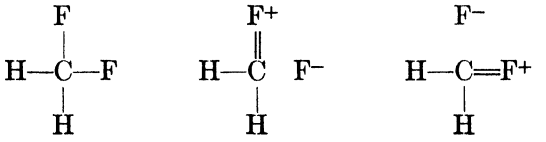


II



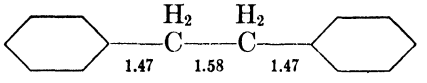
III

Another case is that of the difluorinated methanes, where the C—F distance is given as 1.36 Å as compared with 1.42 Å for methyl fluoride. The forms which we may write in this case are:

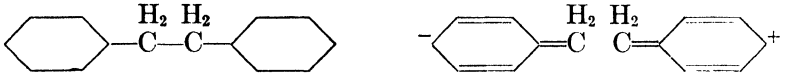


I II III

While it is true that in II and III the carbon-fluorine bond is double, it is also true that it is less than single. The effect of charge is not yet definitely known. There is a case, however, in which the lengthening of a bond to something greater than would be expected for a single bond has been observed. In dibenzyl, the bond distances have been found to be $C_{al}—C_{al}$ = 1.58 Å and $C_{al}—C_{ar}$ = 1.47 Å.



This could very nicely be accounted for by the inclusion of the following forms:



I II

in which formula II actually represents nine different forms when the ortho-quinoidal structures are included. In this connection it would be interesting to examine the tetra- and hexaphenylethanes.

In view of these and other similar anomalies, some doubt is cast upon the quantitative estimation by the above methods of the amount of the contribution of the several contributing states. If one does not accept these "no-bond" resonances, one cannot attribute a bond shortening solely to a degree of double bondedness resulting from a resonance. If one accepts such "no-bond" resonances, one cannot calculate, from bond lengths, the contribution of a single type of resonance without knowing how the "no-bond" resonance is also affecting the bond length.

17c. The hydrogen bond. Two atoms may be held together by the electron-pair bond, by coulombic forces (ionic binding) or in still another way: namely, by the hydrogen bond. The hydrogen bond occurs between elcctronegative atoms having completed octets of

which at least one electron-pair is unshared, such as O, N, F, and to a smaller degree Cl and S. These atoms may be in the same molecule, or they may be in different molecules. If they are on the same molecule, a ring formation is involved and usually a conjugation resonance within the ring. These are usually the chelate rings in which the hydrogen is very readily replaced by a metal such as Cu, Ni, Fe, Mg, etc. If they are in different molecules the result is an unusually high melting point for the crystal or low volatility for the liquid (association); or in general, properties that would result from an attraction between the molecules. Irrespective of whether this bond is purely coulombic attraction of the positive proton for two

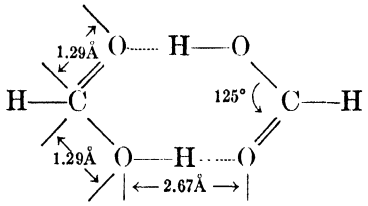
TABLE 7
HYDROGEN-BOND DISTANCES

Bond	Distance, Å	Substance
O..H O	2.76	H_2O(Ice)
	2.70	$C(CH_2OH)_4$
	2.70	o-$C_6H_4(OH)_2$
	2.55±.15	α-$(CO_2H)_2$
	2.71±.15	β-$(CO_2H)_2$
	2.67	$(HCO_2H)_2$
	2.55	$NaHCO_3$
F .H F	2.25±.2	KHF_2
	2.51±.2	$NaHF_2$
N..H N	2.96	NH_4N_3
	2.65	Phthalocyanine
N .H O ..	2.98, 3.03	$(NH_2)_2CO$
	2 85	Diketopiperazine
	2 76, 2.88	$NH_2CH_2CO_2H$
N. H .F	2.63	NH_4F
	2.76	NH_4HF_2

negative atoms, or is affected by a covalent resonance of the unshared pairs on each of the two bonded atoms, or is the result of a combination of both these mechanisms, its length and some of its steric relationships have been determined, in many cases, by the same methods that have been used for the other types of bonds. By the bond length we mean the distance between the two atoms which are supposed to be bonded by the proton between them. The precise location of the proton has not yet been directly determined, although some indirect methods have been used to estimate its position. In Table 7 are given some of the observed values of the interatomic distances involved in hydrogen bonds.

The case of formic acid is especially interesting because it is the only case to date for which the measurement of a hydrogen bond

distance has been made in the vapor phase. The reason for this is that the bond energy is sufficiently great to produce an appreciable concentration of the dimer in the vapor. The structure is the following:

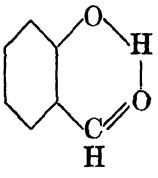


It should be noted that the position of the binding proton cannot be specified. It has been estimated for the acetic acid dimer, from the frequencies of the infra-red bands of the proton and deuteron bonded dimer, to be 1.07 Å from the nearest oxygen atom. This places the proton nearer to one of the bonded oxygen atoms than to the other. The evidence in this case is not very decisive; but there is little doubt that in ice, in which each oxygen atom is bonded by protons to four other oxygen atoms at the corners of a tetrahedron, two of the four bonding protons are nearer to the central oxygen atom than are the other two. Although the variation for each type of hydrogen bond is much greater than for the covalent bonds, the distances are considerably greater, as would be expected for such a comparatively weak bond.

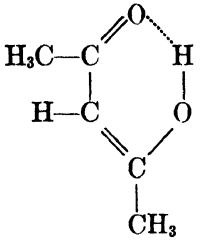
That we are indeed dealing here with something of a bond and not merely an association, either polar or van der Waal's, has been very well demonstrated by the work of Hilbert, Wulf, Hendricks, and Liddel[9] on the infra-red absorption of compounds containing OH and NH groups. The OH group has an absorption band in the region of 7000 cm.$^{-1}$ which has been correlated with the first harmonic of the fundamental O—H stretching vibration at 3500 cm.$^{-1}$. The NH group shows a similar band in the region of 6800 cm.$^{-1}$. These appear in compounds in which no hydrogen bonds are to be expected, such as ethanol and phenol for the OH group, and carbazole and pyrrole for the NH group, the absorption for which, in CCl_4 solution, is given in Figure 14. When, however, we have reason to expect an intramolecular hydrogen bond from other evidence, these bands are

[9] Wulf, O. R., and Liddel, U., *J. Am. Chem. Soc.*, **57**, 1464 (1935).

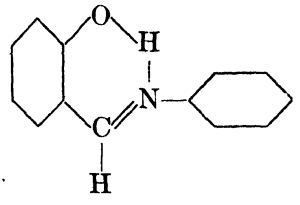
completely absent; e.g., salicylaldehyde and acetylacetone having O . . H . . O bonds, and salicylaldehyde anil and β-naphthol-α-azobenzene having O . . H . . N bonds. The structural formulas for these substances showing the ring formation of the hydrogen bonds are as follows:



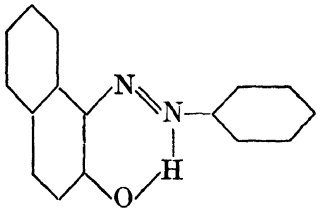
Salicylaldehyde



Acetylacetone

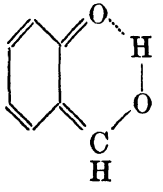


Salicylanil
(Salicylaldehyde anil)



β-Naphthol-α-azobenzene

It should be noted that in all of these compounds it is possible to write stabilizing resonance structures of the type



which would necessitate a coplanar configuration for the chelate ring involving the hydrogen atom.

There are also many compounds which, although they do show absorption in the 7000 cm.$^{-1}$ region, have it shifted both in frequency and intensity. In some cases these shifts have proved amenable to interpretation in terms of a sort of *cis-trans* isomerism, depending on the position of the hydrogen atom. Thus the two bands shown

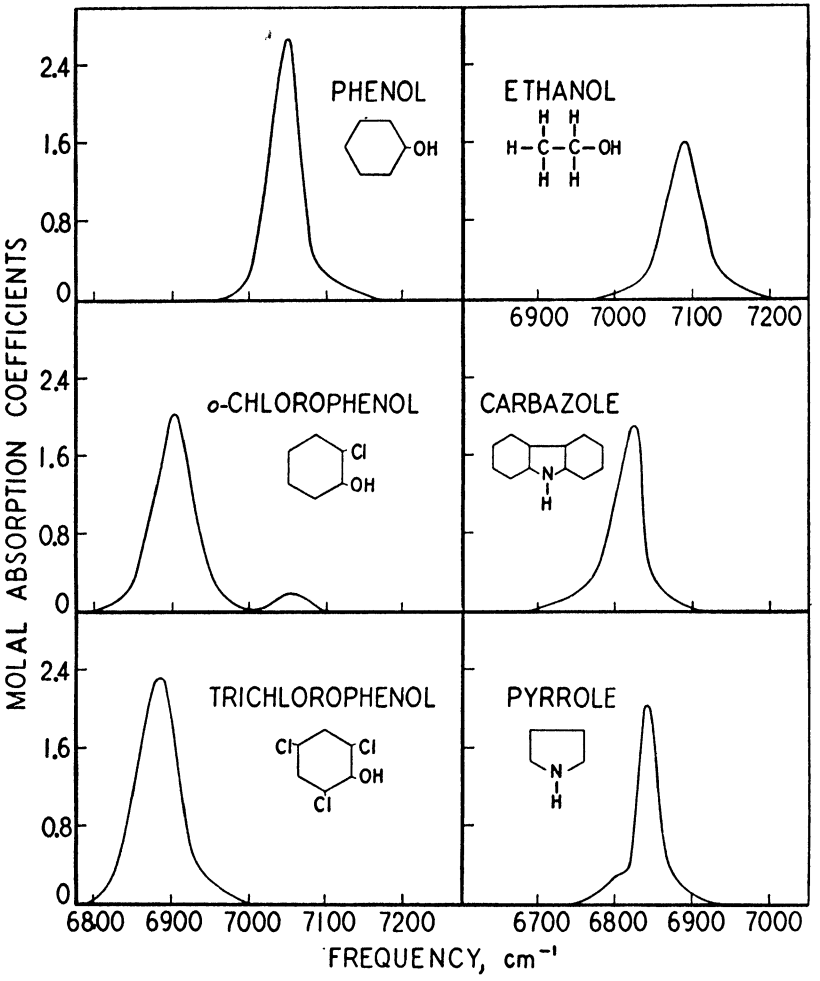
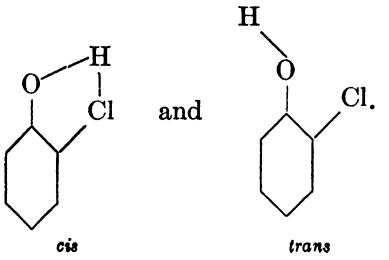


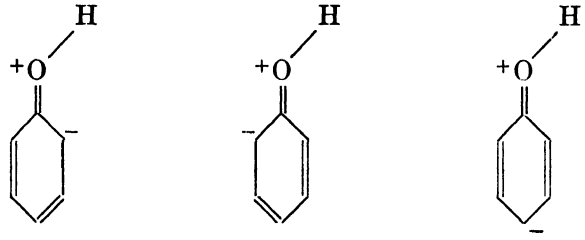
Figure 14. Infra-red absorption for certain O—H and N—H bonds.

by *o*-chlorophenol (Figure 14) can be attributed to the presence of the two isomers represented by



The band at 6900 cm.$^{-1}$ can be assigned to the *cis* form and that at 7050 cm.$^{-1}$ to the *trans* form, since in 2,4,6-trichlorophenol, which has a single band at 6900 cm.$^{-1}$, only a form analogous to the *cis* form is possible, and in phenol (7050 cm.$^{-1}$) only a form analogous to the *trans* form may obtain. Furthermore, such a shift due to the interaction with the chlorine atom, with a consequent reduction of bond force constant, is to be expected. Whether this interaction is to be attributed to a hydrogen bond or not, it is sufficient to make the *cis* form more stable than the *trans*. From the relative areas of the two peaks, the *cis* form is found to be more stable by 1.4 kcals./mole (free energy difference).

The presence of a *trans* band in the *o*-chlorophenol and similar compounds necessitates a stabilization of the position of the hydrogen atom by some force other than the chlorine interaction. This can be found in the phenol resonances,

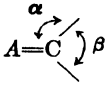
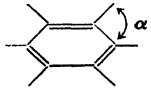
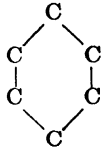
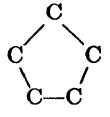
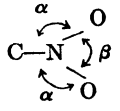


which require the hydrogen atom to lie in the same plane as the benzene ring.

17d. Bond angles. The direct determination of atomic configurations has afforded an excellent confirmation of the conclusions reached by the old inductive methods and which were described in Chapter I. They can be summarized for the carbon atom by the statement that a carbon atom has its four valence directions toward the corners of a tetrahedron of which it is the center; a single bond involves the sharing of a corner between the two tetrahedra representing the pair of bonded atoms; a double bond involves the sharing of an edge, i.e. two corners; and a triple bond involves the sharing of a face, i.e. three corners. The modern theoretical foundations for these angular relationships were given in Chapter III for a very important case, the tetrahedral arrangement of the four-covalent carbon atom. There is little more that can be said unequivocally about the theoretical work on the angles in organic molecules. The idea of bond orbital hybridization (*s*, *p*, and sometimes *d* orbitals) has been extended in a qualitative way to many atoms with considerable success.

TABLE 8

MOLECULAR CONFIGURATION—BOND ANGLES

Type	Angle	Compound	Method*
	tetrahedral $\alpha = 109°28'$ (110°)	Many organic compounds.	All methods.
	planar $\alpha = 122° \pm 2°, 124° \pm 2°$ $\beta = 116° \pm 2°$	Ethylene, butadiene, haloethylenes	E.D.
—C≡C—	linear	Acetylene, diacetylene, methylacetylene, dimethylacetylene	E.D., Sp.
	planar $\beta = 116° \pm 2°$ $\alpha = 120° \pm 1°$	$COCl_2$ $CSCl_2$ H_2CO	E.D.
C=C=C	linear	Allene	E.D.
	planar $\alpha = 120°$	$C_6(CH_3)_6$ Benzene deriv.	E.D., X-ray
	puckered ring with tetrahedral angles	Cyclohexane	E.D.
	planar	Cyclopentane	E.D.
	planar $\beta = 127° \pm 3°$ $\alpha = 116° \pm 3°$	CH_3NO_2	E.D.
C—C≡N	linear	$(CN)_2$, CH_3CN	E.D.
	105°–110° 110°±5° 107°±4°	H_2O, R_2O Dioxane Furan	E.D., Sp., X-ray E.D. E.D.
	92° 91°±4°	H_2S Thiophene	Sp. E.D.
	pyramidal 108°	NH_3	Sp.

* E.D. = electron diffraction; Sp. = spectroscopic; X-ray = X-ray crystal analysis.

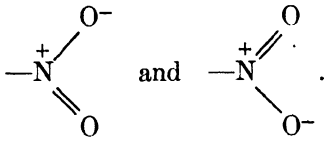
Just as using one s and three p orbitals equally around a carbon atom results in four equal tetrahedral bond orbitals, so it is possible to use other orbitals in the hybridization process and get other configurations. For example if one s, two p, and one d orbital are used, the result is four equivalent orbitals in a plane and directed toward the corners of a square (sp^2d hybridization). Ions and molecules of the type XY_4, where X may be Pd^{++}, Pt^{++}, Cu^{++}, or Ni^{++}, are examples of such a structure. Some other structures are sp^3d^2, octahedral ($PtCl_6^=$); sp^2, planar with 120° bond angles (BCl_3); sp, linear ($HgCl_2$); sp^3d, trigonal bipyramid (PBr_5); sd^3 and spd^2, tetrahedral. It should be borne in mind that these considerations apply only to bonds which are predominantly covalent. When the ionic contribution becomes very appreciable, wide departures from the above predictions may result.

In Table 8 are given the angles which have been observed directly for a number of the common organic groups.

In addition to the results to be expected from the tetrahedral carbon atom and the concomitant rules, including the linearity of triple bonds and adjacent double bonds, we see a number of other things which were not so directly deducible. The planar configuration is maintained about a double bond to other atoms as well as to carbon, as in $Cl_2C{=}O$, $Cl_2C{=}S$, and $CH_3N{=}NCH_3$.

The benzene ring is a completely planar and symmetrical hexagon while the six-membered saturated ring is puckered so as to maintain the tetrahedral single-bond angles.

In nitromethane the nitro group is symmetrical, indicating the resonance



Similar considerations apply for CO_3^{--}, NO_3^-, RCO_2^- and the like.

The valency angle for oxygen—105° in H_2O, 110° in $(CH_3)_2O$—is considerably larger than what would be expected if two mutually perpendicular p orbitals were involved in the binding, while that for sulfur (92°) is much closer to the expected value. Pauling has attributed the spreading in the case of oxygen to mutual repulsion of the attached groups due to the highly polar character of the bond. In the case of sulfur the attached groups need not be so close together (larger radius of S) and, furthermore, the bonds to sulfur are not

so polar. Similar effects are used to account for the spreading of the three bonds from nitrogen to 108° in the case of trimethyl amine. This spreading becomes smaller as one goes down the column in the periodic system, coming to 96° in $(CH_3)_3As$.

17e. Free rotation. One aspect of the old concepts of molecular structure has been modified as a result of such measurements as these. We have been accustomed to the ideas that the parts of a molecule connected by a single bond are free to rotate with respect to each other about the axis of the bond, and that any multiple bond fixes in position the parts connected by it. We have now to revise our ideas and realize that these are not differences in kind but rather of degree, and that under certain conditions a restriction of the rotation about a single bond may be observed.

TABLE 9

CHLORINE-CHLORINE DISTANCES IN CHLOROETHANES AND CHLOROETHYLENES

	Cl—Cl Distance
1,1-Dichloroethane.	2.9 ±.3
1,2-Dichloroethane.	4.53±.1
cis-Dichloroethylene.	3.30±.1
trans-Dichloroethylene.	4.33±.1
1,1-Dichloroethylene.	2.9 ±.3

One of the most clear-cut cases is that of the symmetrical dichloroethane. The Cl—Cl distance in a group of chlorinated ethanes and ethylenes is given in Table 9. These distances, which are averages of the temperature variations of vibration or any internal rotation there may be, show quite clearly that the equilibrium position of the chlorine atoms in the symmetrical dichloroethane must be near the *trans* configuration; i.e., that the two CH_2Cl groups do not rotate freely with respect to each other. We may formulate this in terms of a potential energy diagram in which the azimuth or angle of rotation of one part of the molecule with respect to the other is plotted as abscissa and the potential energy of the system is plotted as ordinate. As yet there is no direct experimental way of determining the exact shape of this potential curve, but on the basis of certain assumptions a curve has been calculated[10] which is not in disagreement with the experimentally observed Cl—Cl separation. The assumptions regarding the sources of interaction within the

[10] Beach, J. Y., and Palmer, K. J., *J. Chem. Phys.*, **6**, 639 (1938). Beach, J. Y., and Turkevitch, A., *J. Am. Chem. Soc.*, **61**, 303 (1939).

molecule which lead to the curve shown in Figure 15 are, in the order of their importance, (1) exchange steric repulsions between all atoms not bonded together, (2) electrostatic interaction of dipoles,

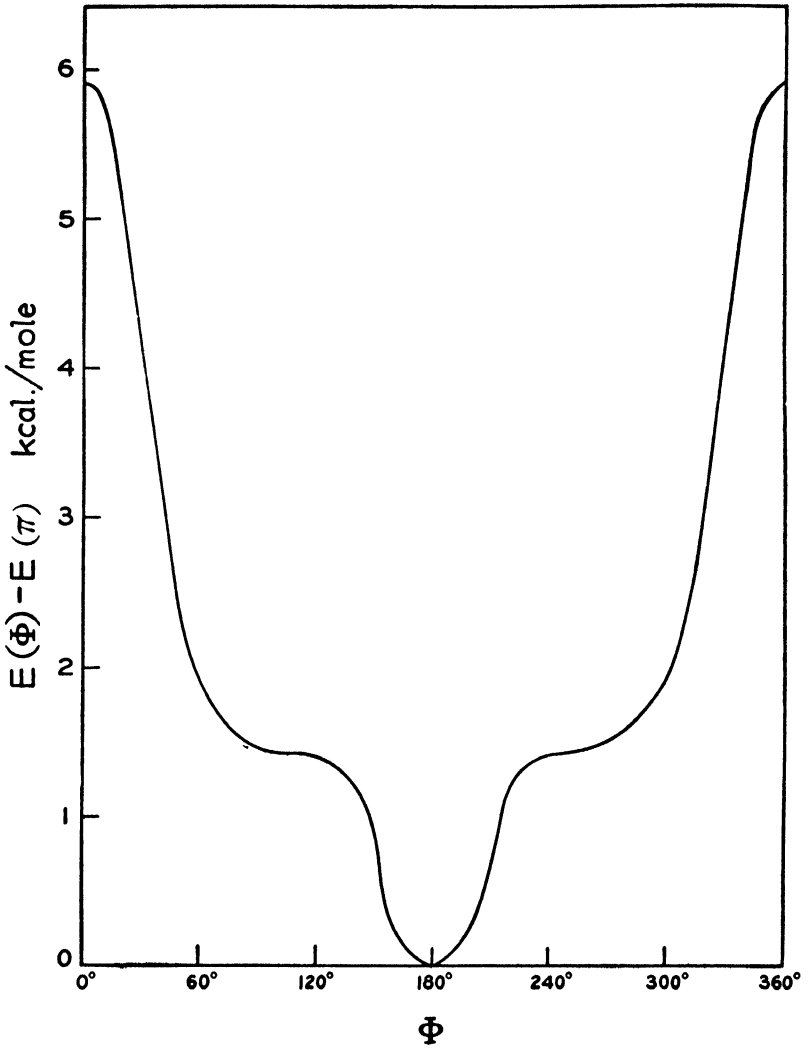


Figure 15. Potential energy curve for rotation about a single bond.

and (3) interaction between orbitals on the carbon atoms. In Figure 15, Φ is the angle between the planes determined by the axis of rotation and the C—Cl bonds, and $E(\pi)$ is the energy of the system in the *trans* position; i.e., $\pi = \Phi = 180°$. This gives a dif-

In an inorganic crystal where the atomic numbers may vary widely, this process is comparatively easy. An organic crystal, however, is made up largely of carbon, nitrogen, oxygen, and hydrogen. The hydrogen has no scattering power at all; the other three have atomic numbers of 6, 7, and 8, and hence differ very little in scattering power. This makes their separate identification extremely difficult. Relatively few organic crystals have been analyzed completely. Each crystal presents an entirely new set of problems, and many other properties of the crystal such as compressibility, piezo-electricity, optical properties, and the like, are called upon to assist the solution. Often the presence in the crystal of a heavy atom whose reflections are easily identified greatly facilitates the complete analysis of the structure. This was the case for the first organic crystal (phthalocyanine and its heavy metal salts) to be completely mapped without the use of any information other than that obtained from the X-ray diffraction pictures. It is an excellent example of the type of information we may expect in increasing amounts by the use of this method. The structure of platinum phthalocyanine as obtained by Robertson[2] is shown in Figure 8.

The use of X-rays is not limited to substances in the crystalline state. They may also give us information concerning the arrangements of molecules in a liquid and the arrangements of atoms in molecules in the vapor state. Although the molecules in the vapor are randomly oriented with respect to each other, the atoms in each molecule maintain a definite relationship to each other. Then the part of the X-ray beam scattered without change of wave length (coherent scattering) by one of the atoms of the molecule will interfere with another part similarly scattered from another atom of the same molecule. For this reason the intensity of a coherently scattered beam of X-rays may show systematic variations which depend upon the spatial relationships of the atoms in each molecule. This coherent scattering will be superimposed on a background of incoherent scattering, i.e. scattering with a change in wave length due to Compton effect and hence unable to interfere.

The dependence of the intensity, I, of the coherently scattered beam on the angle of scattering θ has been given by Debye as

$$I_\theta = K \sum_i \sum_j \phi_i \phi_j \frac{\sin sr_{ij}}{sr_{ij}} \qquad (1)$$

where $s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$ and the subscripts i and j refer to any two atoms

[2] Robertson, J. M., and Woodward, I., *J. Chem. Soc.*, 36 (1940).

TABLE 5 (*Concluded*)

REFERENCES

[23] Lonsdale, K., *Proc. Roy. Soc.*, **133A**, 536 (1931).
[24] Robertson, J. M., *Proc. Roy. Soc.*, **140A**, 79 (1933).
[25] Robertson, J. M., *Proc. Roy. Soc.*, **142A**, 659 (1933).
[26] Robertson, J. M., *Proc. Roy. Soc.*, **142A**, 674 (1933).
[27] Robertson, J. M., *Proc. Roy. Soc.*, **150A**, 106 (1935).
[28] Robertson, J. M., *Proc. Roy Soc.*, **150A**, 348 (1935).
[29] Robertson, J. M., *J. Chem. Soc.*, 1195 (1936).
[30] Robertson, J. M., and Woodward, I., *J. Chem. Soc.*, 1817 (1936).
[31] Robertson, J. M., and Woodward, I., *Proc. Roy. Soc.*, **162A**, 568 (1937).
[32] Robertson, J. M., and Woodward, I., *Proc. Roy. Soc.*, **164A**, 436 (1938).
[33] Robertson, J. M., and Ubbelohde, A. R., *Proc. Roy. Soc.*, **167A**, 122 (1938).
[34] Robertson, J. M., *J. Chem. Soc.*, 233 (1939).
[35] Verweel, H. J., and MacGillavry, C. H., *Nature*, **142**, 161 (1938).
[36] James, R. W., King, G., and Horrocks, H., *Proc. Roy. Soc.*, **153A**, 225 (1936)
[37] Moerman, N. F., *Rec. trav. chim.*, **56**, 661 (1937).
[38] Moerman, N. F., *Z. Krist.*, **97**, 323 (1937).
[39] Moerman, N. F., and Wiebenga, E. H., *Z. Krist.*, **99**, 217 (1938).
[40] Badger, R. M., *Phys. Rev.*, **45**, 648 (1934).
[41] Badger, R. M., and Bauer, S. H., *J. Chem. Phys.*, **5**, 599 (1937).
[42] Herzberg, G., Patat, F., and Spinks, J. W. T., *Z. Physik*, **92**, 87 (1934).
[43] Herzberg, G., Patat, F., and Verleger, H., *J. Phys. Chem.*, **41**, 123 (1937).
[44] Bernal, J. D., *Proc. Roy. Soc.*, **106A**, 749 (1924).
[45] Bragg, W. H., and Bragg, W. L., *Proc. Roy. Soc.*, **89A**, 277 (1913).
[46] Capron, P., and Perlinghi, S. L. T., *Bull. soc. chim.* (Belg.), **45**, 730 (1936).
[47] Finbak, C., and Hassel, O., *Z. physik. Chem.*, **36B**, 301 (1937).
[48] Kitaygorodsky, A., *Acta Physicochim.* (U.S.S.R.), **5**, 749 (1936).
[49] Ginsberg, N., and Barker, E. F., *J. Chem. Phys.*, **3**, 668 (1935).
[50] Ackermann, P. G., and Mayer, J. E., *J. Chem. Phys.*, **4**, 377 (1936).
[51] Knaggs, I. E., *Proc. Roy. Soc.*, **150A**, 576 (1935).
[52] Pauling, L., Springall, H. D., and Palmer, K. J., *J. Am. Chem. Soc.*, **61**, 927 (1939).
[53] Schomaker, V., and Pauling, L., *J. Am. Chem. Soc.*, **61**, 1769 (1939).
[54] Lu Valle, J. E., and Schomaker, V., *J. Am. Chem. Soc.*, **61**, 3520 (1939).
[55] Stevenson, D. P., Lu Valle, J. E., and Schomaker, V., *J. Am. Chem. Soc.*, **61**, 2508 (1939).
[56] Stevenson, D. P., Burnham, H. D., and Schomaker, V., *J. Am. Chem. Soc.*, **61**, 2922 (1939).

which has been most thoroughly investigated, especially for diatomic molecules.

The problem for triatomic and polyatomic molecules is much more complex, but in a number of cases it has been possible to arrive at conclusions concerning the moments of inertia and symmetry in such molecules which permit a definite statement as to the atomic arrangements and interatomic distances. One very important advantage of the spectroscopic method of determining molecular configurations is the fact that here it is possible to place hydrogen atoms, something which the other methods cannot do very well.

17b. Bond distances. Many hundreds of organic compounds have been examined by these methods in the past few years and new measurements are appearing almost daily. It is beyond the scope of this book even to attempt a complete collection of the results. But, in order that the reader may gain some impression of the kind of

ference in energy between *cis* and *trans* forms of about 6 kcals./mole. Since this is about ten times the value of RT at room temperature ($\sim$0.6 kcal.), it is to be expected that most of the molecules will be in the trough, i.e. in the *trans* position, and executing only small oscillations about it.

Similar conclusions regarding the restriction of rotation about a single bond have been reached even in the simple case of ethane on the basis of measurements of the entropy.[11] In this case, however, because of the symmetry of the molecule, there are three equivalent minima in the potential curve representing the rotation of the two CH_3 groups through 360° with respect to each other.

We shall see other evidences of restriction of rotation, as well as confirmation of the above conclusions, among the measurements of dipole moments.

18. DIPOLE MOMENTS

So far we have been discussing the methods of measuring, and the significance of, the configuration of the atomic nuclei within the molecule. These methods give no direct information concerning the distribution of the electrons with respect to the nuclear structure of the molecule. Since the electrons and nuclei are of opposite electric charge, they will suffer oppositely directed forces when placed in an electrical field, and it is this principle upon which measurements of the distribution of electricity within the molecule, and the stability of that distribution, are based.

The molecule can be considered as a system of positive and of negative electric charge. If the center of negative charge is at one point in the molecule and the center of positive charge at another point, as in Figure 16, the molecule is said to have a permanent dipole moment and it is quantitatively defined as equal to the product of the charge e (+ or −, since they must be equal if the molecule has no net charge) and the distance between the positive and negative centers:

$$\mu = ed \tag{14}$$

If, however, d is zero, i.e. if the positive and negative centers coincide, the molecule has no resultant permanent dipole moment. It should be emphasized that a statement of the value of μ does not alone give any information concerning how much charge is separated or how far apart these charge centers are; all that we have is the value of the product of the two.

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[11] Kemp, J. D., and Pitzer, K. S., *J. Am. Chem. Soc.*, **59**, 276 (1937).

Now if a molecule, polar or non-polar (i.e., having a permanent dipole moment or not) is placed in an electric field, the forces exerted by the electric field on the aggregate of positive and negative charges which constitute the molecule displace them in opposite directions, according to their sign, and so induce a dipole moment in the molecule, which lasts only as long as the applied field remains. The magnitude of the dipole moment induced in a molecule by unit field is called the polarizability, α, of the molecule:

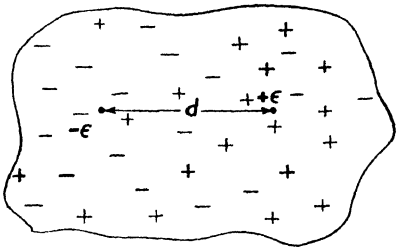


Figure 16. Unsymmetrical electric distribution resulting in a dipole moment.

$$\mu_{\text{ind.}} = \alpha F \qquad (15)$$

where $\mu_{\text{ind.}}$ is the induced dipole moment and F is the applied electric field. The polarizability, α, is thus a measure of the ease with which the electrons in a molecule may be displaced from their normal positions.[12]

If, now, molecules having a permanent dipole moment, μ, and a polarizability, α, are introduced between the plates of a condenser to which unit field has been applied, the total polarization per gm. mole will be

$$P = P_\alpha + P_\mu = \frac{4\pi}{3} N\alpha + \frac{4\pi}{3} N \frac{\mu^2}{3kT} \qquad (16)$$

where $P_\alpha = \frac{4\pi}{3} N\alpha$ is the induced molar polarization; $P_\mu = \frac{4\pi}{3} N \frac{\mu^2}{3kT}$ is the permanent molar polarization; N is the Avogadro number; k is the Boltzmann constant; and T is the absolute temperature. An essential difference between the two polarizations is apparent. When the electric field is applied, the electrons are immediately displaced independently of the orientation of the molecule as a whole.[13] The contribution of the permanent dipole to the polarization, however,

[12] Actually, the polarizability as here defined includes the opposite displacement of the atoms (positive centers); but, since their masses are generally so very much greater than that of the electrons, the atomic polarization can be neglected for our purposes.

[13] The molecule may not be isotropic with respect to polarization—i.e., it may have three different polarizabilities in the three directions—but these will average out when all orientations are possible in the medium with equal probabilities. The small differences which appear when the field is applied are negligible compared to the effect of the presence of a permanent dipole.

must await the rotation of the whole molecule into the proper position and its maintainence in that position. This leads to two important experimental ways by which the induced polarization may be distinguished from the permanent polarization.

At ordinary temperatures the molecules are in continual motion: translational, rotational, and sometimes vibrational. This heat motion tends to resist the alignment of the molecules in the electric field with a resistance which increases with the temperature. Thus the contribution of P_μ will decrease with increasing temperature, according to equation 16.

The polarization is measured by the dielectric constant, ϵ, according to the well-known relation of Clausius-Mosotti,[14]

$$\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho} = P \tag{17}$$

where M is the molecular weight and ρ the density. Combining this with equation 16, we have:

$$P = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho} = \frac{4\pi}{3}N(\alpha + \mu^2/3kT) \tag{18}$$

Thus, if we measure the dielectric constant as a function of temperature and then plot P against $1/T$, the result should be a straight line whose slope is given by $\frac{4\pi N}{9k}\mu^2$, from which the value of μ may be obtained. With this the value of α may be obtained by difference or from the intercept on the P axis at $1/T = 0$.

This method is strictly applicable only to molecules in the vapor phase, but it may be used on dilute solutions in non-polar solvents. In more concentrated solutions and pure liquids, interaction of the dipoles is so great as to introduce associations and specific resistances to orientation which are not accounted for above. In a dilute solution, the total polarization can be calculated on the assumption that each substance contributes in proportion to its mole fraction

$$P = N_1P_1 + N_2P_2$$

$$\text{and } N_1 + N_2 = 1 \tag{19}$$

where N_1 and N_2 are the mole fractions of components 1 and 2, respectively, and P_1 and P_2 are the corresponding molar polariza-

[14] A more detailed account of the principles involved here may be found in *Polar Molecules*, by P. Debye. Chemical Catalog Co., New York, 1929.

tions. Actually, this relation should be extrapolated to infinite dilution.

The other method of distinguishing between the dipole moment and the polarizability arises from the fact that the molecules require a comparatively long time to orient themselves in the electric field whereas the electrons are displaced practically instantaneously. Thus, if the applied field is an alternating one and the frequency is sufficiently high, the dipoles will have insufficient time to orient and the resulting polarization will be primarily the result of the polarizability of the molecule. Now, light is a wave consisting of mutually perpendicular electric and magnetic fields oscillating at a comparatively high frequency. The electric vector of the light beam can thus be used as the rapidly alternating electric field, and the relation between the refractive index, n, and the dielectric constant is given by the Maxwell equations as $\epsilon = n^2$. Thus from the refractive index we can get a fairly good approximation to the electronic polarization according to

$$P_\alpha = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} = \frac{4\pi}{3} N\alpha \qquad (20)$$

With this equation the dipole moment can be obtained from a single measurement of the static dielectric constant. Here again the value of the electronic polarization obtained in this manner should be extrapolated to infinite frequency.

The electronic charge is 4.77×10^{-10} e.s.u., so that the dipole moment of one electronic charge separated by 1Å (10^{-8} cm.) would be 4.77×10^{-18} e.s.u. Most dipole moments are of this order of magnitude, and the unit of the dipole moment 1×10^{-18} e.s.u. has been called the "debye." All the moment values hereafter given will be in debyes. The polarizability, α, has the dimensions of volume, and the order of magnitude is 10^{-25} cm.^{3}.

18a. Bond moments.[15] A number of single atoms have been examined, including the rare gases, phosphorus, and sulfur, and have been found to have no dipole moment. Further, all elementary diatomic molecules—H_2, Cl_2, O_2, N_2, etc.– are found to be without

[15] Unless otherwise specified, all the numerical values of dipole moments used in this and the following sections were taken from the following compilations: (a) Fuchs, O., and Wolf, K. L., in *Hand- und Jahrbuch der Chemischen Physik*, Vol. 6, part 1 (Akad. Verlag., Leipzig, 1935); (b) *Trans. Faraday Soc.*, **30,** Appendix (1934); (c) "Sterischer Bau und elektrische Eigenschaften," by K. L. Wolf and O. Fuchs, in Freudenberg's *Stereochemie* (Franz Deuticke, Leipzig u. Wien, 1932).

dipoles. If, however, two unlike atoms are bonded together, the resulting diatomic molecule is always electrically unsymmetrical and will have a dipole moment; i.e., HCl(μ = 1.04), ICl(μ = 0.5), CO(μ = 0.11), NO(μ = 0.1). In polyatomic molecules, even though containing bonds between unlike atoms, it is possible to have no dipole for the molecule as a whole. This is the case for molecules in which, from other types of data, we have reason to believe the atoms are symmetrically arranged, such as CCl_4, $SnCl_4$, BCl_3, SF_6, PCl_5, *p*-$C_6H_4Cl_2$, *trans*-$C_2H_2Cl_2$. For other simple polyatomic molecules whose atomic arrangement we know to be unsymmetrical, we find a dipole moment: NH_3(μ = 1.46), H_2O(μ = 1.84), PCl_3(μ = 1.1), etc. These facts, together with the knowledge that a dipole moment must be a vector leads us to the association of a dipole moment with each bond (between unlike atoms, or atomic groups in more complex cases) and to the idea that the dipole moment of a molecule is the vector resultant of all the constituent bond or group moments to be found in the molecule. The question of the vector addition we will consider later. Our next consideration is the source of the individual bond moments.

It will be recalled that, in our consideration of the formation of the hydrogen molecule from a pair of hydrogen atoms, it was necessary to introduce into the calculation terms which corresponded to the ionic forms $\overset{-}{H}:\overset{+}{H}$ and $\overset{+}{H}:\overset{-}{H}$ in addition to the exchange of the single electrons between the two nuclei. Each ionic form has a high dipole moment, but in a homonuclear molecule the two opposite forms must of necessity contribute equally, with the result that the molecule would have no permanent moment. If, however, the two nuclei between which an electron pair is to form a bond are not identical, the contribution of the two ionic forms need not, and in general will not, be the same, and the molecule may have a resultant moment. It is to this unequal sharing of the electron pair that we are going to attribute the appearance of a bond moment. Thus, for example, in HCl the electron pair is certainly not shared equally between the H and the Cl atoms. The electron affinity of chlorine, which is a measure of the tendency of the chlorine atom to pick up an electron to form chloride ion, is about 4 e.v.[16] while that of hydrogen is about 0.7 e.v. The ionization potential of the hydrogen atom, which is a measure of the tendency of the hydrogen atom to

[16] An electron-volt (e.v.) is the energy of an electron which has been accelerated through a potential of 1 volt. It is equal to 23,055 cal./mole.

lose an electron, is not very different from the first ionization potential of the chlorine atom (13.5 and 13.0 e.v., respectively), and the difference in the relative contributions of the two structures $\overset{+}{\mathrm{H}}:\overset{-}{\mathrm{Cl}}$ and $\overset{-}{\mathrm{H}}:\overset{+}{\mathrm{Cl}}$ will be determined primarily by the difference in the electron affinities. Thus we see that the structure $\overset{+}{\mathrm{H}}:\overset{-}{\mathrm{Cl}}$ must certainly contribute considerably more to the ground state of the molecule than the opposite ionic structure, with the result that HCl has a considerable dipole moment.

There are other sources of electrical dissymmetry in a bond, some of which have at some time been blamed for the entire bond moment. For example, the mutual polarization of the atoms as they approach

TABLE 10

DIPOLE MOMENTS OF ALIPHATIC HOMOLOGUES *RX*

R \ X	OH	$CH_3C(=O)$	Cl
CH_3	1.66	2.73	1.86
C_2H_5	1.70	2.76	2.03
n-C_3H_7	1.66	2.71	2.05
n-C_4H_9	1.66	2.70	1.9
n-C_5H_{11}	—	—	—
n-C_6H_{13}	1.64	2.70	—
n-C_7H_{15}	—	—	1.9
n-C_8H_{17}	1.67	—	—
n-C_9H_{19}	1.60	2.69	—
n-$C_{10}H_{21}$	1.63	—	—

each other to form a bond may contribute quite an important part, especially when one of the atoms is as small as a proton. It should be recalled that such a term was also introduced in some of the refinements of the Heitler-London calculation of the hydrogen molecule. But we believe that, for most of the molecules that interest organic chemists, this phenomenon is not important.

A strong bit of evidence indicating that the dipole moment may actually be localized in a given bond or group in a molecule is the constancy of the dipole moment in a homologous series of compounds. In Table 10 are given the dipole moments of a number of the members of three different series. It should be noted that the degree of constancy is greatest when the moment need not be attributed solely to the bond between the group and the carbon atom, but that more or less of it may reside in the group itself. It is from such measurements as these that it is possible to assign either bond

or group moments; but, until we have examined the validity of the principle of vector addition and the sign of the dipole moment, the value of such a general assignment cannot be judged.

18b. Sign of dipole moment. In order to test the additivity of bond or group moments, it is necessary to be able to attach two or more polar groups to a rigid structure so that certain geometrical relationships between them will be maintained. The most convenient structure for this purpose is the benzene ring, which we already know to be a comparatively rigid planar structure. Thus, if we substitute the atom *A* for one of the hydrogens of the ring, the bond moments may be represented by the arrows in Figure 17.

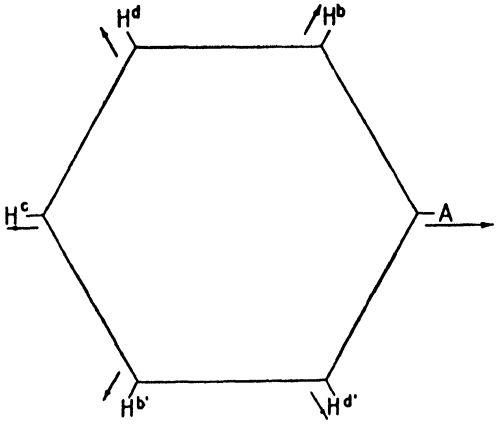
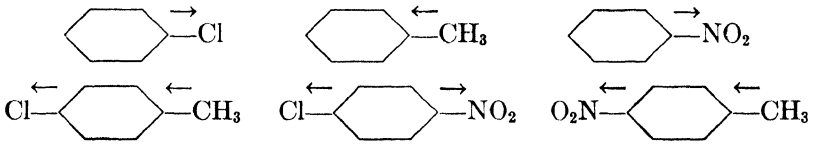


Figure 17. Component dipoles of a monosubstituted benzene.

Benzene itself has no dipole moment, since each of the C—H dipoles is balanced by an equal and oppositely directed moment, just as the H atoms *d*, *d'*, *b*, and *b'* balance each other in this substituted benzene. Here, however, the moment of the C—*A* bond and the C—H^c bond, although they are along the same line, do not balance. They may have the same or the opposite direction and will, in general, be of different magnitudes. The resulting molecular dipole moment will then be the sum or the difference of the C—H^c and C—*A* moments.

If now H atom *c* is also replaced by another *A* atom, the resultant moment will be zero. If, however, it is replaced by another atom (or group) *B*, a dipole moment will result whose magnitude and sign will depend on the relative direction and size of the individual

C_6H_5A and C_6H_5B moments. Let us take, for example, the molecules toluene, chlorobenzene, nitrobenzene, and the several *p*-disubstituted compounds which can be made with these groups. The observed moments are given in Table 11 together with those calculated for the disubstituted compounds as suggested above. From this we can see that, in whichever direction the displacement of charge is between the phenyl and the methyl group in toluene, it must be in the opposite direction between phenyl and chlorine in chlorobenzene, and between phenyl and nitro in nitrobenzene.



The question as to what sign of charge the head of the arrow is to represent is not answered by these data alone. It is fairly certain, however, that the direction of the dipole in C_6H_5Cl is the same as it is in HCl and that the arrows as drawn represent the direction of

Table 11

COMBINATION OF MOMENTS IN PARA-DISUBSTITUTED BENZENES

	Obs.	Calc.
$C_6H_5CH_3$	0.4	—
C_6H_5Cl	1.55	—
$C_6H_5NO_2$	3.95	—
p-$ClC_6H_4CH_3$	1.90	1.95
p-$NO_2C_6H_4CH_3$	4.4	4.35
p-$ClC_6H_5NO_2$	2.5	2.40

displacement of electrons; i.e., that the head of the arrow is negative. From such data as these it is possible to place a large number of elements and groups in a series according to their tendency to draw electrons to them; i.e., according to their electronegativity. (A similar series is obtained in Chapter VI from the effects of atoms and groups on acid strengths.) But in general these are directions relative to hydrogen, the direction of the C—H bond dipole being still a moot question. All that can be said is that hydrogen attached to an aromatic carbon atom is more negative than hydrogen attached to an aliphatic carbon atom, since toluene has a small but finite positive moment, i.e. a moment whose positive end is toward the methyl group.

18c. Vector addition of dipole moments. The vector combination of group moments, when these groups are in positions other

than para, works fairly well too. Recalling that benzene is a regular plane hexagon, the angle between a pair of ortho substituents is 60°, a pair of meta substituents is 120°, and a pair of para substituents is 180°, and the relationships between the constituent and resultant moments are shown in Figure 18. If the two substituents are identical, the values become $\mu = \sqrt{3}\mu_1$ (ortho); $\mu = \mu_1$ (meta); and $\mu = 0$ (para). The validity of these rules for the para position we have already seen. In Table 12 are some values for other disubstituted benzenes. The meta and para derivatives in general

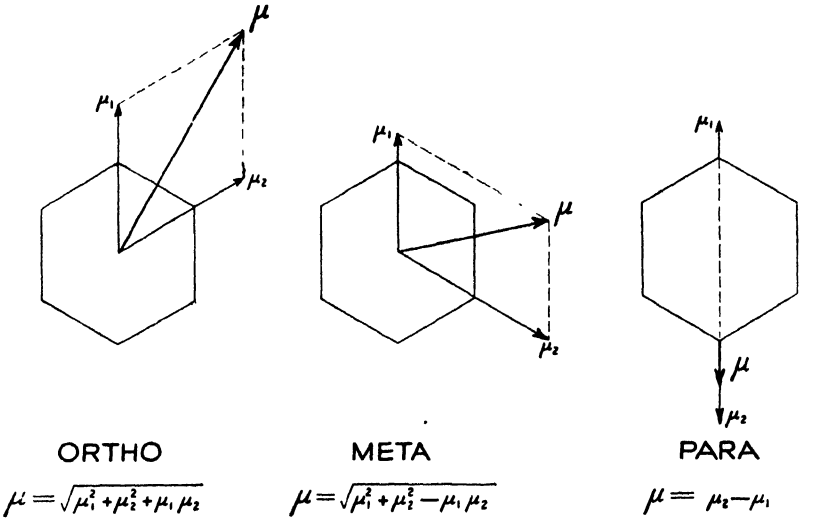


Figure 18. Vector addition for disubstituted benzenes.

give the best agreement between the observed values and those to be expected on the basis of simple vector addition. The ortho compounds fail for large groups and are not so bad for smaller groups, e.g., F. This can be attributed to a steric repulsion of the large groups in the ortho position which spreads them apart, making the actual angle between their moments somewhat greater than 60°, with a net decrease in the resultant moment. The discrepancy is especially bad in the cases of the very large groups such as I and NO_2. A similar effect may be made to account for certain discrepancies in another case of a rigid structure where vector addition would be expected to be valid, i.e. the case of several polar groups attached to the same carbon atom.

Upon the basis of simple vector addition, it is to be expected that

compounds of the type CH_3X and CHX_3 would have identical moments. This arises from the fact that the vector resultant of three identical moments at tetrahedral angles is in a direction through the face of the tetrahedron formed by these three directions, i.e. along the line of the fourth bond of the tetrahedron, and has the magnitude equal to that of a single one of the components. Actually the moment of CH_3X is always larger than that of CHX_3 and the discrepancy is greater the larger the atom X (Table 13). This

Table 12

VECTOR ADDITION OF DIPOLE MOMENTS IN SOME DISUBSTITUTED BENZENES

C_6H_4XY				Ortho		Meta		Para	
X	(C_6H_5X)	Y	(C_6H_5Y)	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
CH_3	0.4	CH_3	0.4	0.5	0.70	0.4	0.40	0	0
F	1.43	F	1.43	2.4	2.48				
Cl	1.55	Cl	1.55	2.3	2.67	1.48	1.55	0	0
Br	1.52	Br	1.52	2.0	2.63	1.5	1 52	0	0
I	1.3	I	1 3	1.7	2.25	1.3	1 30	0	0
NO_2	3.95	NO_2	3 95	6.0	6.83	3.79	3.95	0	0
CH_3	0.4	Cl	1.55	1.3	1 39	1.78	1.79	1.90	1.95
CH_3	0.4	NO_2	3 95	3.66	3.76	4.17	4 16	4.4	4 35
Cl	1.55	NO_2	3 95	4 3	4.91	3.4	3.44	2.5	2.40
Cl	1.55	Br	1.52	2.2	2.67	1.5	1.54	0	0.03

Table 13

DIPOLE MOMENTS OF SOME HALOGENATED METHANES

CH_3Cl	1.86	CH_3Br	1.79	CH_3I	1.60
CH_2Cl_2	1.57	CH_2Br_2	1.39	CH_2I_2	1.10
$CHCl_3$	1.15	$CHBr_3$	0.99	CHI_3	0.91

could very nicely be accounted for by the spreading apart of the larger atoms as compared to hydrogen. Such a spreading has actually been observed by electron diffraction pictures of the vapors of CHX_3 when X is Cl, Br, or I. In the case of Cl, the angle has been estimated at 112°. This is just about sufficient to account for the observed decrease in moment.

When the polar groups are attached to an atom other than carbon the moment will again be determined by the individual group moments and the angles at which they extend from the central atom. In the first instance, the existence or non-existence of a moment gives a direct clue as to the general shape of the molecule, as we have

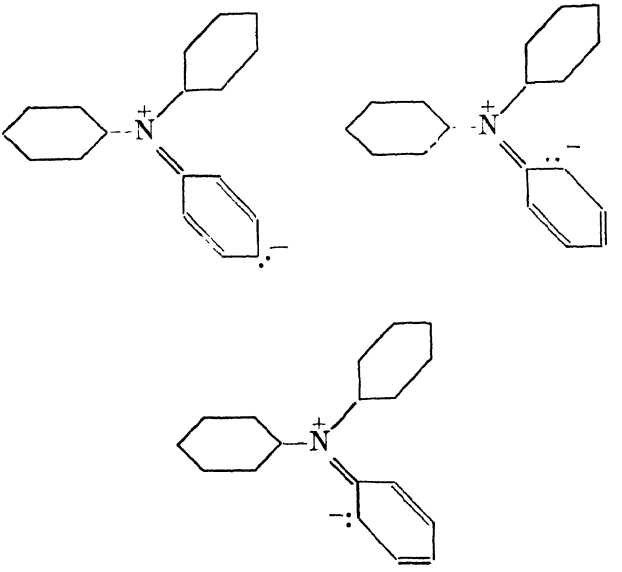
already seen in some simple inorganic molecules and as we see further in Table 14.

TABLE 14

DIPOLE MOMENTS ABOUT SOME ATOMS OTHER THAN CARBON

$(C_6H_5)_2O$	1.14	$(C_6H_5)_3N$	0
$(C_6H_5)_2S$	1.51	$(C_6H_5)_3P$	1.45
$(C_6H_5)_2Se$	1.38	$(C_6H_5)_3As$	1.07
$(C_6H_5)_2Te$	1.13	$(C_6H_5)_3Sb$	0.57
$(C_6H_5)_2Hg$	0	$(C_6H_5)_3Bi$	0

The diphenyl derivatives of O, S, Se, and Te are all angled, while that of Hg must be linear. The triphenyl derivatives of P, As, and Sb are pyramidal, while those of N and Bi must be planar. The case of triphenylamine is an excellent example of the effect of resonance on a bond angle. Ammonia and the aliphatic amines all have a dipole moment—$(CH_3)_3N$, $\mu = 0.7$—and from other evidence, such as band spectra or electron diffraction, they are known to be pyramidal. The planar structure of triphenylamine can be attributed to the important contribution of the resonance forms involving the unshared electron pair of the nitrogen atom in the rings:



Exactly similar structures are to be written for each of the other two rings, and the double bond contribution between nitrogen and the three phenyls requires that they all lie in a plane.

In some cases it is possible to calculate quantitatively the angle about a central atom from the proper dipole moment measurements. Thus diphenyl ether has a dipole moment ($\mu = 1.14$) which, because of the symmetry of the molecule, must be a vector bisecting the ϕ–O–ϕ angle β. If we assume that the angle β in Figure 19 remains the same in p, p'-dibromodiphenyl ether and the various constituent group moments remain the same as they are in the unsubstituted diphenyl ether and bromobenzene, it becomes possible to calculate the angle β. The dipole moment of the p,p'-dibromodiphenyl ether

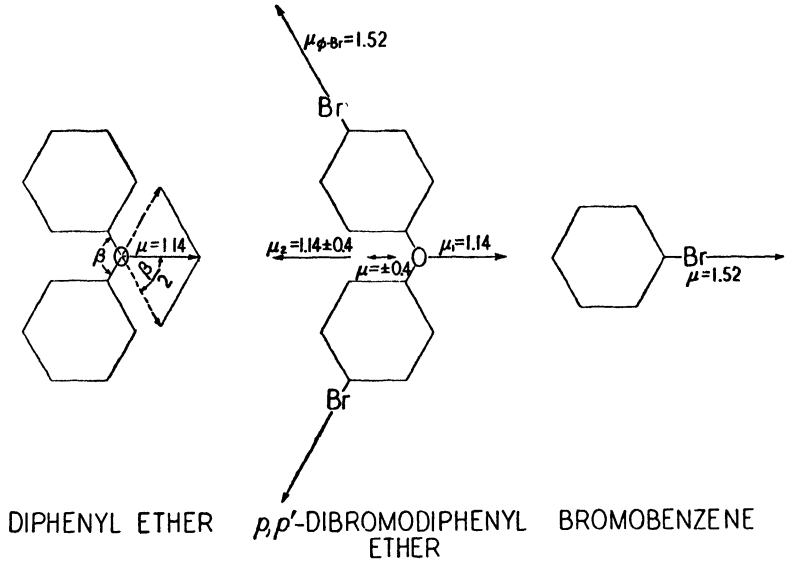


Figure 19. Dipole moments of diphenyl ether, p,p'-dibromodiphenyl ether, and bromobenzene.

($\mu = 0.4$) must be the sum of μ_2, the resultant of the phenyl-Br group moments, and μ_1, the resultant of the phenyl-O group moments. An examination of Figure 19 will show that μ_2 must be equal to either $1.14 + 0.4 = 1.54$ or $1.14 - 0.4 = 0.74$, depending on whether μ for the dibromo compound is in the opposite or the same direction as μ_1, the moment of the unsubstituted ether. Since $\mu_2 = 2 \times 1.52 \times \cos \beta/2$, we have two possible values of β corresponding to the two possible orientations of the resultant $\mu = 0.4$: 119° and 152°. The angle for p,p'-di-iododiphenyl ether has been found from X-ray diffraction work to be 118° ± 3°.

If it is assumed that the bond angles and dipoles of the unsym-

metrical *p*-bromodiphenyl ether are the same as those of the symmetrical dibromo compound, the 152° angle would be chosen. The evidence from the X-ray diffraction is more direct and conclusive than that from the dipole of the monobromo compound.

The *double bond* is another comparatively rigid structure where it is particularly useful to apply at least qualitatively the idea of vector addition. The isomers of the symmetrical dichloroethylenes present an excellent example of the determination of structure by the several physical methods we have so far discussed. We would expect the *cis* compound to have a rather large dipole moment and

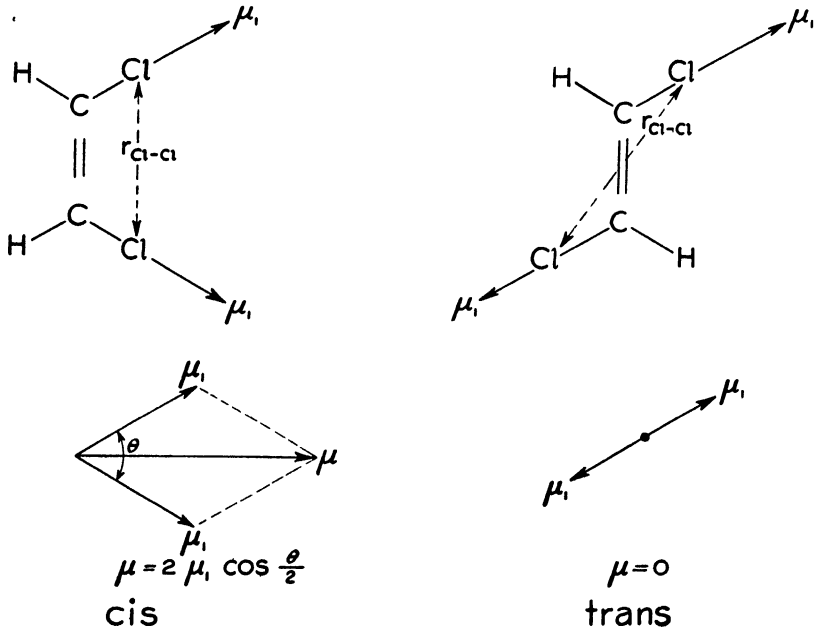


Figure 20. Dipole moments of *cis*- and *trans*-dichloroethylene.

the Cl—Cl distance to be small, while the *trans* should have no dipole moment and the Cl—Cl distance should be large (Figure 20). The experimentally observed quantities for the two isomers are: *cis* $u = 1.8$, $r_{Cl-Cl} = 3.30$ Å; *trans*, $\mu = 0$, $r_{Cl-Cl} = 4.33$ Å. The observed value for the dipole moment of the *cis* compound is actually considerably smaller than would be expected on simple vector addition. This may be due in part to the presence of a twisting oscillation about the axis of the double bond with the consequent presence of considerable numbers of molecules in configurations having smaller

dipoles than that of the rigidly *cis* form, or to a spreading of the bond angles as in the *o*-dichlorobenzene. However, a large part of this discrepancy is probably due to the form of resonance which was called upon to account for the small C—Cl distance in this and similar compounds.

Considerations such as these have been used in aiding the determination of the structure of a wide variety of positional and geometric isomers, but it should be borne in mind that the quantitative aspects of vector addition are not at all unequivocal. Some of the causes for discrepancy have already been mentioned. Another and very universal though generally small effect is the polarization of the rest of the molecule by the dipolar part, with resulting changes in the magnitude of the molecular dipole.

18d. Dipole moment and rotation about a single bond. In case two or more polar groups are attached to a molecule in such a way as to make possible many orientations with respect to each other, i.e. with at least one single bond between the polar groups, the principle of vector addition may frequently lead to definite conclusions concerning the freedom, or lack of freedom, of rotation about the single bond.

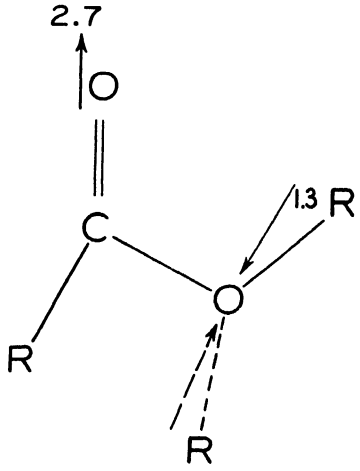


Figure 21. Component dipole moments of an ester.

The carboxylic acids and their esters are probably cases of restricted rotation with a single minimum in the planar position shown by the solid lines in Figure 21. The dotted lines represent the alternative position. The moments of aliphatic esters lie in the range of 1 to 1.3, and this, as may be seen from the figure, corresponds very nearly to the difference between the ketone and ether moments. For the acids, it is necessary to take into account the possibility of dimerization. The dipole moment of the monomer of formic acid has been assigned the value of 1.51, which corresponds pretty closely to the vector addition result for the configuration shown.

We have already encountered evidence for a restricted rotation in the electron diffraction data on the symmetrical dichloroethane.

The same result appears from the dipole moment measurements on this and similar molecules. At 32°C. the dipole moment of the dichloroethane is 1.12. The calculated moments for the *cis* and *trans* positions, and for the free rotation of the two CH_2Cl groups about the bond between them, are 3.6, 0.0, and 2.5, respectively. These are obtained in the following way: The carbon-chlorine bond moment, μ_1, is taken from CH_3Cl as 1.86. Assuming tetrahedral angles, θ is 71°; and we see that, whatever the azimuth of the C—Cl groups may be, the components, $\mu_1 \cos\theta$ always balance each other. The components $\mu_1 \sin\theta$, however, add in the *cis* position and cancel, in the *trans* position, so that $\mu_{cis} = 2\mu_1 \sin\theta$ and $\mu_{trans} = 0$. The integration carried out for equal probabilities of all positions, i.e. for

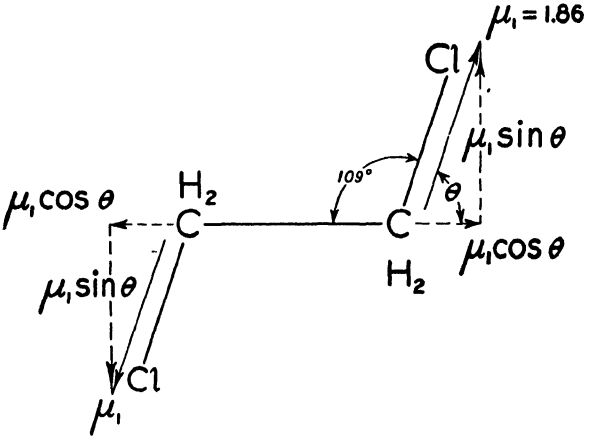


Figure 22. Component dipole moments of 1,2-dichloroethane.

free rotation, gives $\mu_{f.r.} = \sqrt{2}\mu_1 \sin\theta$. At this point another important condition should be noted. If the substance consists of only *cis* and *trans* forms in equal amounts, the measured moment would be the square root of the average of the squares of the moments of the two forms, i.e.

$$\mu_{mix} = \sqrt{\frac{\mu_{cis}^2 + \mu_{trans}^2}{2}};$$

and, since in these cases of symmetrically substituted molecules $\mu_{trans} = 0$ and $\mu_{cis} = 2\mu_1 \sin\theta$, $\mu_{mix} = \sqrt{2}\mu_1 \sin\theta$, which is the same result as for free rotation.

Now, the value 1.12 lies between that of the *trans* and that for

free rotation. This can be understood in the light of the potential curve of Figure 15. Since the barrier is only about 10 *RT* at its maximum, some of the molecules will be oscillating about the *trans* position into configurations which have an appreciable moment and thus give a measurable moment to the molecule. Furthermore, with a potential of this order of magnitude, an increase of temperature in the range which can be obtained should increase the number of oscillating molecules and the amplitude of the oscillations. This temperature dependence of the permanent moment has indeed been observed for a number of molecules as shown in Table 15 taken from the work of Zahn.[17] It is important to note that, when comparing

TABLE 15
TEMPERATURE DEPENDENCE OF DIPOLE MOMENT

	Temp. Range, $T°K$	μ(observed)	μ(for free rot.)
$ClH_2C—CH_2Cl$	305–554	1.12–1.54	2.54
$BrH_2C—CH_2Br$	339–436	0.94–1.10	2.54
$BrH_2C—CH_2Cl$	339–436	1.09–1.28	2.54
$CH_3C(=O)—C(=O)CH_3$	329–504	1.25–1.48	3.20
$ClH_2C—C(=O)CH_3$	336–454	2.17–2 24	3.0

dipole moments of molecules with rotatable polar groups, the vapor phase measurements are to be preferred, since the presence of a solvent, no matter how inert or nonpolar, may very easily disturb the configurational relationship or affect the rotation.

It is interesting to observe that no temperature variation of the moment of monocarboxylic esters or acids has yet been observed in the temperature range attainable. This leads to the conclusion that the restricting potential must be considerably greater than 10 *RT*.

Similar considerations may be applied to substituted benzenes in which the substituents are not atoms or symmetrical groups, so that the group dipole is not along the axis of the bond to the benzene ring. One such case is the hydroquinone dimethyl ether (as is also hydroquinone). Because of the valency angle of the oxygen (110°), the dipole of the group is at some large angle to the axis of the benzene ring. In anisole itself and such compounds as *p*-chloranisole,

[17] Zahn, C. T., *Phys. Rev.*, **40**, 291 (1932).

in which the second substituent is a symmetrical group, the presence or absence of free rotation about the C—O bond cannot be determined from dipole measurements. This is strictly true for *p*-disubstituted compounds only. In principle, free rotation should be detectable in meta and ortho compounds of this type; but in ortho derivatives the disturbing steric effects are large, and in meta derivatives the difference between free and hindered rotation is small. These para derivatives can, however, be used to determine the angle θ which the rotatable group dipole makes with the axis of rotation. Assuming the group moments $\mu_{\phi Cl} = 1.55$ and $\mu_{\phi OCH_3} = 1.23$, we can calculate the angle $\theta \backsim 73°$. This of course will be slightly larger than that ($\sim 70°$) which would correspond to the oxygen valence angle (110°) if the anisole moment were all along the OCH_3 bond.

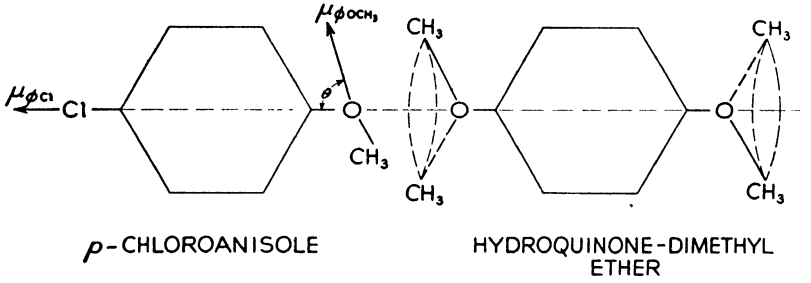
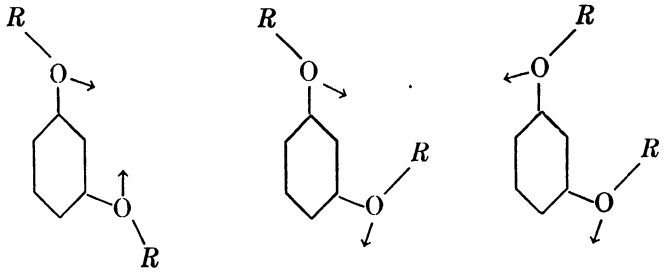


Figure 23. Component dipole moments of *p*-chloroanisole and of hydroquinone-dimethyl ether.

We can now use this angle, assuming it to be unchanged, on the hydroquinone dimethyl ether, and we find, according to the formulas already mentioned in the case of dichloroethane, that $\mu_{trans} = 0$, $\mu_{cis} = 2.34$, $\mu_{f.r.} = 1.67$. The observed value is about 1.73. This certainly seems to indicate the presence of a free rotation about the phenyl-oxygen bond.

Any hindrance of the rotation would be expected to arise from a resonance between the oxygen of the O*R* group and the benzene ring. This would give a double bond character to the phenyl-oxygen bond which would tend to hold the alkyl group in the plane of the benzene ring, producing *cis* and *trans* isomers. If these were present in equal quantities, the moment obtained would be the same as for free rotation. The measured moment, therefore, does not distinguish between free rotation and the existence of equal quantities of the *cis* and the *trans* configurations. An exactly analogous set of arguments is to be applied to the meta compound, resorcinol dimethyl

ether, for which, in the case of restricted rotation, there are three possible isomers:



I II III

The dipole moments calculated for these three forms, using 1.23 as the methoxyl moment and 73° as the angle between the moment and the axis of rotation, are $\mu_I = 1.67$, $\mu_{II} = 1.23$, and $\mu_{III} = 2.38$. The moment calculated for free rotation is $\mu_{f.r.} = 1.69$. If we assume that the three forms have equal energies, and giving form II double weight (because there are two ways in which it may occur), the mean moment is 1.63. The observed moment is 1.59. It is thus still not possible to decide the question of free or restricted rotation[18] in these and similar cases such as the phenylene diamines, xylylene dihalides, phthalic acids and esters, etc. In case of two different substituents, e.g., *p*-aminoacetophenone $\mu_{obs.} = 4.29$, $\mu_{(calc.\ for\ free\ rotation)} = 3.89$, the calculated values for free rotation are often very far from the observed values. But in these cases the part played by resonance is somewhat clearer and will be interpreted in a succeeding section.

We have seen the evidence for the existence of restricted rotation in the symmetrical dihalogen-ethanes. As the distance between the polar groups is increased, i.e. increasing number of CH_2 groups between the halogen atoms, the two dipoles act more and more independently of each other, the resulting dipole approaching the value $\mu = \sqrt{\mu_1^2 + \mu_2^2}$, which becomes $\mu = \sqrt{2}\,\mu_1$ if the two groups are identical. The dipole moments, μ_n, for the compound

$$BrCH_2(CH_2)_nCH_2Br$$

are $\mu_0 = 1.03$, $\mu_1 = 1.97$, $\mu_2 = 2.00$, $\mu_3 = 2.25$, $\mu_4 = 2.39$, $\mu_7 = 2.55$, $\mu_8 = 2.54$, and $\mu_{f.r.} = 2.63$.

[18] It is interesting to note that a change of angle from 73° to 70° will leave all but one of the calculated moments practically unchanged, that one being μ_I which becomes 1.57.

18e. Dipole moment and resonance. Since many of the resonance structures which are written for molecules are electrically unsymmetrical, we have reason to expect this phenomenon to make itself apparent in the dipole moments of such molecules. In fact, we have already attributed the dipole moment which appears associated with a single electron pair bond to the presence in the resonance system (I) $A : B$, (II) $\bar{A} : \overset{+}{B}$, (III) $\overset{+}{A} : \bar{B}$, of ionic forms of the type (II) or (III), the resulting moment being the weighted average of the moments of each contributing form.[19] We shall concern ourselves here only with the resonance which appears in systems containing multiple bonds.

For an isolated double bond, we might expect such resonance contributions as (I) $A::B$, (II) $\overset{\cdot\cdot-}{A} : \overset{+}{B}$, (III) $\overset{+}{A} : \overset{\cdot\cdot-}{B}$. When the atoms A and B are the same we should expect II and III to contribute equally if at all with a resulting dipole of zero, e.g., ethylene. If the atoms are unlike, the contributions of the forms II and III may be very different. In acetone, for example, as in other carbonyl compounds with a moment around 2.8, a considerable contribution from $R_2\overset{+}{C}:\overset{\cdot\cdot-}{\underset{\cdot\cdot}{O}}:$ probably obtains, with little from the opposite form $R_2C:\overset{\cdot\cdot-\cdot\cdot+}{\underset{\cdot\cdot}{O}}:$. Actually, if we assume that the purely homopolar form $R_2C::\underset{\cdot\cdot}{O}:$ has zero moment and calculate a moment for the form $R_2\overset{+}{C}:\overset{\cdot\cdot-}{\underset{\cdot\cdot}{O}}:$ of about 5.9 (using the double-bond radius sum 1.24 as

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[19] If two forms having the wave functions ψ_1 and ψ_2 contribute, the resulting wave function will be given by $\psi = \alpha_1\psi_1 + \alpha_2\psi_2$ with $\alpha_1^2 + \alpha_2^2 = 1$. The resulting dipole moment will be

$$\mu = e\int \psi x \psi d\tau = e\int (\alpha_1\psi_1 + \alpha_2\psi_2)x(\alpha_1\psi_1 + \alpha_2\psi_2)\, d\tau$$

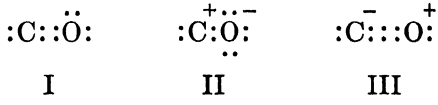
where x represents the positional co-ordinate of the electrons. Since α_1 and α_2 are constants whose squares represent the fractional contribution of each form, ψ_1 and ψ_2, we have

$$\mu = e\left\{\alpha_1^2 \int \psi_1 x \psi_1\, d\tau + \alpha_2^2 \int \psi_2 x \psi_2\, d\tau + 2\alpha_1\alpha_2 \int \psi_1 x \psi_2\, d\tau\right\}.$$

But $e\int \psi_1 x \psi_1\, d\tau$ is just the dipole moment of the form ψ_1 and similarly for ψ_2.

If we neglect the cross-term, we have as a first approximation to the resulting moment just the weighted mean of the contributing moments, $\mu = \alpha_1^2\mu_1 + \alpha_2^2\mu_2$. This is assuming the two resonating moments to be along the same line, which is usually the case.

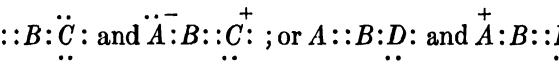
the carbon-oxygen distance), we find that the ionic form should contribute about 47 per cent to the structure of acetone. On the other hand, carbon monoxide has a moment of the order of 0.1. This might be taken to indicate no resonance at all, but the small C—O distance (1.15 Å), and energy considerations which we shall review in another chapter, indicate a considerable deviation which must be attributed to resonance among the forms



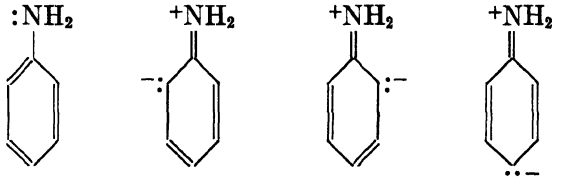
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of which II and III have about equal and opposite dipole moments and must contribute about equally to the state of the molecule.

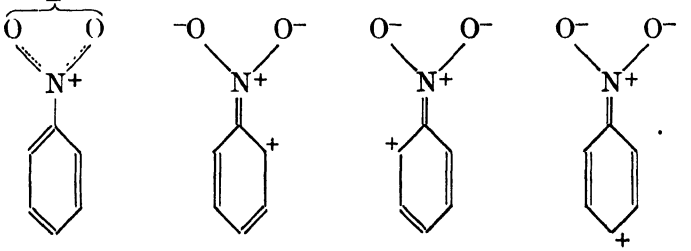
Another and very general case which we have already observed in the interatomic distance discussion occurs when an atom capable of donating or accepting a pair of electrons is attached adjacent to a double bond or system capable of analogous resonance, the phenyl group. In this case we have the possibilities



which correspond to the following resonance systems in aniline



and nitrobenzene



Although no case of bond shortening due to the movement of electrons from the double bond system to an acceptor atom or group has yet been measured, a number of the opposite type have already been considered, namely the vinyl and phenyl halides. In their effects on

the dipole moments, both effects are immediately apparent, as we can see in Table 16, which gives the moments associated with a number of groups in both aliphatic and aromatic combination. With the possible exception of amino groups, all the groups listed there are negative with respect to aliphatic carbon, and so we should expect the phenyl compounds of those groups capable of accepting an electron pair from the ring, i.e. NO_2, CO_2H, NO, CN, etc., to have greater dipole moments than their corresponding alkyl compounds,

TABLE 16

DIPOLE MOMENTS OF ALIPHATIC AND AROMATIC COMPOUNDS*

X \ R	CH_3		$CH(CH_3)_2$ or $C(CH_3)_3$	$H_2C{=}CH$	C_6H_5	
	Soln.	Vapor	Soln.	Vapor	Soln.	Vapor
H	0	0			0	0
CH_3		0			0.41	0.37
OH	1.68	1.69	1.66		1 61	
OCH_3		1.31	1.29		1.16	
F		1.81			1.45	1.57
Cl		1.87	2.14	1.44	1.56	1.73
Br		1.80	2.15	1.41	1.53	1.71
I	1.60	1.64	2.13	1.26	1.30	1.50
CHO		2.70	2.46		2.75	
$COCH_3$	2.76	2.85			2.93	3.00
$COOC_2H_5$	1.85	1.76			1.92	1.95
CN	3.44	3.94			3.90	4.37
NO_2	3.02	3.54	3.29		3 97	4 24
NO			2.51		3.14	
NH_2		1.23	1.23		1.52	
$N(CH_3)_2$	0.7	0.67			1.58	

* *Trans. Faraday Soc.*, Sept. 1934; Eucken-Wolf, *Hand u. Jahrbuch der Chemischen Physik*, 6, 1 (1935); Cowley, E. G., and Partington, J. R., *J. Chem. Soc.*, 1252 (1933); 604 (1935); Groves, L. G., and Sugden, S., *J. Chem. Soc.*, 971 (1935); 158 (1937); Hugill, J. A. C., Coop, I. E., and Sutton, L. E., *Trans. Faraday Soc.*, **34**, 1518 (1938).

while the phenyl compounds of those groups capable of donating an electron pair to the ring, i.e. halogen, NH_2, OH, etc., to have smaller dipole moments than their corresponding alkyl compounds. It should be remembered, however, that these resonances affect the moment only along the axis of the ring and the bond joining the group to the ring, so that when there exists a major contribution to the moment along some other direction the relationships may not be so simple as they have just been stated. Those groups whose major component, at least, is along the axis of the bond to the carbon atom are the halogens (electron donating groups) and NO_2 and CN (electron accepting groups). Here the relationships are very

definitely as expected, as they are in the case of the CO and NO groups as well.

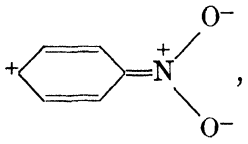
A number of attempts have been made to estimate quantitatively the amount of contribution of the various resonating forms from a comparison of the dipole moments of alkyl and phenyl compounds and the assignment of a value to the moment resulting from this contribution, called the mesomeric moment. But even in the simplest cases of the halogens, difficulties are encountered. In the first place, the introduction of the large and polarizable phenyl group in the place of an alkyl group permits the possibility of a comparatively large induced moment (induced by the intrinsic bond dipole) which would be in such a direction as to increase the resulting moment of the molecule. This means that, aside from any resonance effects, the dipole moment of, say, chlorobenzene should be considerably larger than that of methyl chloride. Actually an increase in moment is observed upon simply increasing the size of the alkyl group. Grove and Sugden[20] have attempted to calculate this polarization term for all the atoms except those concerned directly in the polar bond and have given the following values for the mesomeric moment, μ_e: C_6H_5F, -1.00; C_6H_5Cl, -0.97; C_6H_5I, -0.87; $(C_6H_5)_2O$, -0.47 (in each phenyl); anisole, -0.40; phenol, -1.12; acetophenone, 0.17; benzonitrile, 0.05; nitrobenzene, 0.29. While this same arrangement appears in other compilations, the magnitude may vary considerably. One thing they all have in common is the comparatively large mesomeric moment for the halogens, phenol, etc., and the smaller one of opposite sign for NO_2, CN, CO, etc. It hardly seems reasonable from other considerations that the halogens should partake of double bonded resonance to the same extent as OH, or that NO_2 or CO should have so much less resonance than OH or halogen (in the opposite direction).

This difficulty can be eliminated, at least partially, by remembering that the phenyl group is negative with respect to the alkyl group to such an extent as to give toluene a dipole moment of about 0.4. It is interesting to note that styrene has been reported to have zero dipole moment, indicating a similarity in the character of the vinyl and phenyl groups. If this negativity of the phenyl group is used to correct the mesomeric moments of Groves and Sugden by the subtraction of 0.4 from the negative mesomeric moments and the addition of 0.4 to the positive ones, the values appear a little more

[20] Ref. of Table 16.

reasonable, the value for phenol becoming −0.72 and for nitrobenzene 0.69. These considerations receive some confirmation in the next paragraph.

In the resonance form of nitrobenzene in which the bond between carbon and nitrogen is double



it is necessary that the oxygen be in the same plane as the benzene ring. Thus we can suppose that, in order that this form contribute appreciably to the state of nitrobenzene, it must be possible for the

TABLE 17

DIPOLE MOMENTS OF SOME SUBSTITUTED AROMATIC COMPOUNDS*

ILLUSTRATING THE RESONANCE INTERACTION OF GROUPS AND THE STERIC REQUIREMENTS FOR SUCH INTERACTION (ALL IN BENZENE SOLUTION)

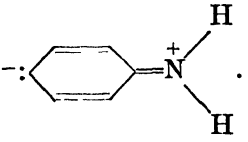
Nitrobenzene	3.95	Nitrodurene	3.39		
Aniline	1.53	Aminodurene	1.39	Mesidine	1.40
Bromobenzene	1.52	Bromodurene	1.55		
Toluene	0.41				
Dimethylaniline	1.58			Dimethylmesidine	1.03
Phenol	1.61	Durenol	1.68		
Anisole	1.16				
p-Nitroaniline	6.10	Nitroaminodurene	4.98	4-Nitro-*sym*-*m*-xylidine	5.04
p-Nitrodimethylaniline	6.87	Nitrodimethylaminodurene	4.11		
p-Nitrophenol	5.04	Nitrodurenol	4.08		
p-Nitroanisole	4.76	Nitroethoxydurene	3.69		
p-Bromonitrobenzene	2.65	Bromonitrodurene	2.36		
p-Toluidine	1.36	Pentamethylaniline	1.10		
p-Bromoaniline	2.93	Bromoaminodurene	2.75		

* Birtles, R. H., and Hampson, G. C., *J. Chem. Soc.*, 10 (1937); Ingham, C. E., and Hampson, G. C., *J. Chem. Soc.*, 981 (1939).

nitro group to be coplanar with the ring, and that if for some reason this coplanarity is prevented, the contribution of this form will be eliminated. This is apparently what happens when a pair of methyl groups are placed ortho to the nitro group as in nitrodurene or the

mesitylene compound. In Table 17 are given the dipole moments of some substituted benzenes, durenes, and mesitylenes. The fact that the bromo-compounds, for which there can be no question of coplanarity or steric prevention, have practically the same moment with and without the methyl groups while the nitro and dimethyl amino compounds show a marked reduction in dipole moment upon the introduction of the methyl groups, is good indication that we are indeed dealing with a prohibition of the mesomeric moment by steric influences. Furthermore, if we assume that the mesomeric moment is entirely eliminated in nitrodurene, we get as a lower limit to its value 0.56. Similarly we have 0.55 for the dimethylamino group. This is not too bad an agreement with the value of 0.69, which was obtained by correcting the value of Sugden and Groves for the difference in the negativity of the phenyl and methyl groups (0.4).

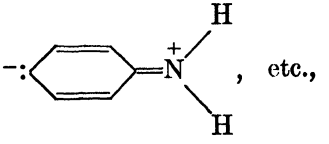
The decrease in moment of 0.14 of the aminodurene with respect to aniline indicates that even the hydrogen atoms are sufficiently large to interfere with the methyl groups, and further gives us some clue to the apparent anomaly that aniline ($\mu = 1.52$) has a larger moment than alkyl amine ($\mu = 1.23$). This might be interpreted as meaning that the nitrogen in the aliphatic compound is positive with respect to carbon and that the difference (0.29) is the increase due to the resonance



However, there would then be no way of accounting for the negativity difference between alkyl and phenyl, or the fact that the N—H bond angles must be considerably changed by the resonance in aniline so as to increase the moment.

Much of this difficulty can be resolved if one considers all the components of the amino dipole in both the aliphatic and aromatic compounds shown in Figure 24, and if one assumes that, in the aliphatic compound, the component along the N—C bond is such as to make the nitrogen negative with respect to the carbon. If the resonance decreases this component through zero and then increases it in the opposite direction, the result may be a greater moment in the aniline than in the amine and with its largest component such as to make the phenyl group appear negative with respect to the amino group. This is evidenced by the moment of

p-chloroaniline (2.92), in which the moments of the chlorine and the amino group are neafly additive. Furthermore, if the resonance



, etc.,

is to play an important part in the structure of aniline, the hydrogens must tend to lie in the plane of the ring. The resultant of the two N—H moments would then be in the same direction as the nitrogen-phenyl moment. This would further increase the aniline moment over that of the amine.

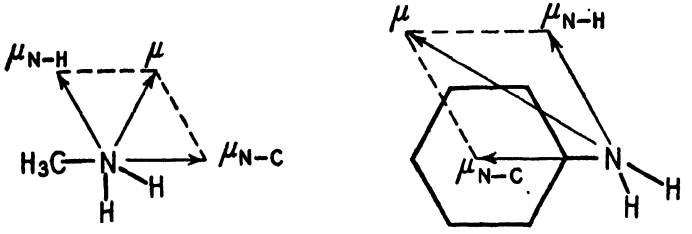
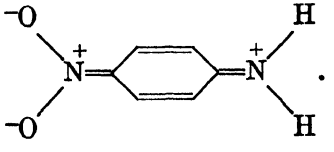


Figure 24. The direction of the nitrogen-carbon dipole moment.

When two oppositely resonating groups, such as nitro and amino, are attached para to each other in a benzene ring, they interact so as to enhance the total resonance over the simple sum of the two independent group-phenyl interactions. This is immediately apparent when we compare the dipole moment of *p*-nitroaniline (6.10) with the sum of the moments of nitrobenzene and aniline (5.48). This enhancement is to be attributed to the presence of the form



.

Here again, and to an even more marked degree, the steric inhibition of the completely coplanar configuration by the presence of methyl groups will have its effect on the resonance, as is evidenced by the reduction of the dipole moment to 4.98 in nitroaminodurene. This is not very much greater than the sum of the moments of nitrodurene and aminodurene.

19. RAMAN SPECTRA AND FORCE CONSTANTS

In our discussion so far we have considered only the equilibrium configuration of molecules in their lowest electronic state. Another important characteristic of these electronically unexcited molecules is the force resisting any change in these equilibrium atomic configurations. These forces were introduced in the discussion of spectra, and it is apparent how they can be determined for some of the simpler molecules at the same time that the internuclear distances are determined from an examination of their infra-red spectra. Here again we are limited to relatively simple molecules and to relatively high vibrational frequencies, since the lower ones would appear in the more difficultly accessible region in the far infra-red. In 1928 Sir C. V. Raman[21] discovered an effect that makes it possible to observe these vibrational frequencies in the visible region. If light of frequency, ν_e, impinges on a molecule, it is possible for that light to be scattered without any change of frequency (Rayleigh scattering), or it may be scattered with a degraded (lowered) or enhanced (increased) frequency (Raman scattering). The lowered frequency corresponds to the absorption from the exciting light, ν_e, of a quantum of energy resulting in the excitation of a vibrational state of the molecule, while the increased frequency corresponds to the absorption by the exciting light, ν_e, of a quantum of energy resulting in the dropping of the molecule from an excited vibrational state to some lower one. These processes are illustrated in Figure 25 in which ν_R is the frequency of the scattered Raman line. In terms of the shift of frequency of the exciting line, $\Delta\tilde{\nu}$,

$$h\nu = h\nu_e \mp h\nu_R \quad \text{or} \quad \Delta\tilde{\nu} = \frac{\nu_e \mp \nu_R}{c} \tag{21}$$

This $\Delta\tilde{\nu}$ corresponds to some vibrational frequency of the molecule as a whole. Now for any given molecular model it is possible to a first approximation to analyze all the various modes of vibration in terms of a set of principal modes each involving its own set of restoring force constants. If one of these principal modes involves primarily the vibration of a small mass against a much larger one, the frequency associated with it depends mainly on the force constant

[21] For a complete account of the methods and results of Raman spectra, see *The Raman Effect and Its Chemical Applications*, by James H. Hibben (Reinhold Publishing Corp., New York, 1939), and *Der Smekal-Raman Effekt*, by K. W. Kohlrausch (Julius Springer, Berlin, 1931 and 1938).

of the bond and the mass of the smaller part of the vibrating system, and is relatively independent of the nature or structure of the rest of the molecule. Such a frequency is called a valence vibration frequency and is associated with the particular bond most concerned in the vibration. This system can be treated as a two-mass problem

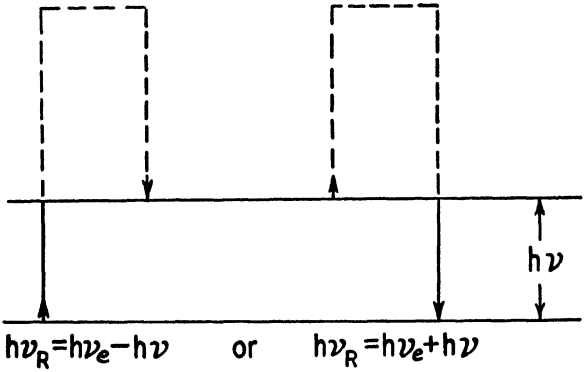


Figure 25. Energy levels involved in Raman scattering.

(m_1 = smaller mass, m_2 = larger mass) with the force constant f between them; and, if the force is strictly harmonic, the frequency will be

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{M}},$$

where M, the reduced mass, is given by

$$\frac{1}{M} = \frac{1}{m_1} + \frac{1}{m_2}.$$

It is thus apparent why the larger mass m_2 has very little effect on the frequency if $m_2 >>> m_1$.

In general, for a molecule consisting of n atoms there are $3n - 6$ normal modes of vibration, each having its own characteristic frequency. The number of different frequencies may be reduced by the presence of certain elements of symmetry in the arrangement of the atoms. The number of these frequencies which may be expected to appear in the Raman or infra-red spectra is still further reduced by the existence of certain selection rules based on the symmetry of the vibration and the change of polarizability for Raman spectra or the change of dipole moment for infra-red spectra. In spite of these reductions, the complexity of Raman spectra has made the complete

analysis and assignment of frequencies and force constants extremely difficult except in the case of the simpler and more symmetrical organic molecules. But a tremendous number of organic compounds have been examined, and in many cases the persistence of a particular line through a series of compounds, together with the rules given above, has made it possible to assign certain characteristic frequencies to particular bonds. This sort of empirical analysis has proved very

TABLE 18
CHARACTERISTIC GROUP VIBRATIONAL FREQUENCIES
R = Alkyl

Group	$\Delta\tilde{\nu}$(cm.$^{-1}$)	Molecule
C≡C	1973	HC≡CH
	~2118	*R*C≡CH
	~2235	*R*C≡C*R*
C≡N	~2245	*R*C≡N
N≡N	2329	N_2
C=C	1621	$H_2C{=}CH_2$
	~1642	*R*CH=CH$_2$
	~1658	*R*CH=HC*R cis*
	~1674	*R*CH=HC*R trans*
	1676	$R_2C{=}CR_2$
C=O	1650-1800	Various
C=N	1560-1660	"
N=O	~1640	*R*ONO
C=S	~1523	CS_2
O—H	~3400	*R*OH
N—H	3310-3370	*R*NH$_2$
	~3330	R_2NH
	~3335	$R_2C{=}NH$
S—H	~2575	*R*SH
C—H	2700-3000	*R*CH$_3$
	3000-3100	$R_2C{=}CH_2$
	3213	HCN
	~3310	*R*C≡CH
	~3062	C_6H_6

Group	$\Delta\tilde{\nu}$(cm.$^{-1}$)	Molecule
C - C	750-1100	Open chains
	992	C_2H_6
	802	Cyclohexane
	886	Cyclopentane
	~960	Cyclobutane
	1184	Cyclopropane
C—OH	1032	CH_3OH
C—Cl	~570	R_3CCl
	~610	R_2CHCl
	~650	*R*CH$_2$Cl
	710	CH_3Cl
C—SH	About the same as the C—Cl series.	
C—Br	~510	R_3CBr
	~530	R_2CHBr
	~560	*R*CH$_2$Br
	594	CH_3Br
C—I	~480	R_3CI
	~490	R_2CHI
	~500	*R*CH$_2$I
	522	CH_3I

helpful in the determination of structure and even in qualitative and quantitative analysis of mixtures of organic substances. In Table 18, compiled by Kohlrausch, are given some of the frequencies which have been identified as belonging to a particular bond, together with the type of compound in which they have been observed.

19a. Force constants. The force constants f, characteristic of a bond and independent of the masses of the bonded atoms, are derived quantities whose values depend upon the type of analysis which is made of the possible vibrations of the molecular model. As a result

they are available only from the simpler molecules although a fair approximation is obtained by simply using the assigned frequency together with the masses of the two atoms concerned in the bond, in the relation

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{M}}.$$

In Table 19 are given the stretching force constants for a number of bonds together with the molecules in which they were determined.

TABLE 19

FORCE CONSTANTS CHARACTERISTIC OF BONDS IN SOME POLYATOMIC MOLECULES

Bond	f(dynes/cm. $\times 10^{-5}$)	Molecule or Group
C≡C	15.7	C_2H_2
C≡N	17.9	HCN
	16.7-16.9	Cl-, Br-, ICN
	17.5	$(CN)_2$
N≡N	14.6	N_2O
	15.0	N_3^-
	22.0	N_2
C=C	9.5	C_2
	8.2-9.8	C_2H_4
C=O	13.4	CH_2O
	14.2	COS
	15.3	CO_2
	19.0	CO
N=O	9.1	NO_2
	13.7	N_2O
S=O	10.0	SO_2
C=S	7.6	CS_2
	8.0	COS
O—H	7.0	H_2O
N—H	6.4	NH_3
S—H	4.0	H_2S
F—H	8.6	HF
H—H	5.1	H_2

Bond	f(dynes/cm. $\times 10^{-5}$)	Molecule or Group
C—H	5.9	C_2H_2
	5.8	HCN
	5.0, 4.9	CH_4
	5.0	C_2H_4
	4.8	$-CH_2-$
	5.0	C_6H_6
	5.0	C_2H_6
C—C	4.8	$(CN)_2$
	7.6	C_6H_6
C—O	4.5	$(CH_3)_2O$
C—S	3.0	$(CH_3)_2S$
C—F	5.8, 5.04	CH_3F
C—Cl	3.4, 3.6	CH_3Cl
	5.2	ClCN
C—Br	2.9	CH_3Br
	4.2	BrCN
C—I	2.3	CH_3I
	3.0	ICN
C—N	4.9	CH_3NH_2
N—N	3.6	$H_2N—NH_2$
$N^+—N$	4.5	$H_2N—NH_3^+$
$N^+—N^+$	5.4	$H_3N—NH_3^+$

Although the values for each type of bond vary a good deal from compound to compound and even for the same compound by different investigators, there is some regularity for bond multiplicity. Single bonds have values below 7×10^5; double bonds lie between 7 and 15×10^5; and triple bonds have values above 15×10^5. We thus have again evidence for the triple bond resonance in CO, whose force constant is 19.0×10^5, and even for CO_2, whose force constant is

15.3×10^5. The value of 7.6×10^5 for the aromatic C—C bond lies between those for ethane, 5×10^5, and ethylene, 9×10^5.

It is of interest to know the energy required for the stretching or deformation of bonds, since these quantities will be involved in our considerations of chemical reactivity and various kinds of steric effects. The energy required to stretch a bond from its equilibrium position is given by $\Delta E = \frac{1}{2}f(\Delta x)^2$, where Δx is the displacement from equilibrium. In order to stretch a carbon-carbon single bond .1 Å (which is the order of magnitude of the amplitude of a vibration), the energy required, per mole, is approximately 3600 cals. On the other hand, since the force constants for deformation, i.e. displacement in a direction normal to the axis of the bond, are about one-tenth those of stretching, the energy for an equal displacement in this direction would be only about 360 cals./mole. Thus we see that at room temperature, where $RT = 600$ cals., these deformation vibrations will be highly excited and the angles between bonds, of which we have already spoken, can be hardly more than an average of rather large displacements. Furthermore, in considering the mechanisms by which molecules react, it must be kept in mind that it is much easier to avoid a repulsion between atoms or groups by permitting an angle change than by most other mechanisms.

20. COLOR

So far we have considered in some detail the equilibrium positions of the atoms in the molecule and their displaceability from these equilibrium positions (force constants and vibration frequencies). Further, we have considered the equilibrium configuration or distribution of the electrons within the molecule (dipole moments, electron density maps, and, for simple molecules, the spectroscopic description of the ground electronic states of molecules). We now have left a consideration of the displaceability of these electrons from their equilibrium configurations in their ground states. We have already encountered a term which is in effect a measure of this displaceability, namely the polarizability (see section 18). Since the molecule as a whole and especially its electrons must be subject to the quantum restrictions, the electrons cannot be considered as continuously displaceable but rather as capable of existing only in a series of different electronic states, $\psi_0, \psi_1, \psi_2, \cdots \psi_j$, each of whose energies will be denoted by $E_0, E_1, \cdots E_j$, where the subscript 0 refers to the state of lowest energy, i.e. the ground state, and the other subscripts 1, 2, $\cdots j$ refer to the several possible excited states

in the order of increasing energy. With each state will be associated a frequency, $\nu_0, \nu_1, \nu_2 \cdots \nu_j$, given by the Bohr relationship $\nu_j = \frac{E_j}{h}$. Now, the classical dispersion formula of Drude, which gives the relationship between the polarizability α and the characteristic frequencies of the molecule, can be expressed in these terms by

$$\alpha_\nu = \frac{e^2}{m} \sum_{j \neq 0} \frac{f_{j0}}{(\nu_j - \nu_0)^2 - \nu^2}. \tag{22}$$

In this equation α_ν is the polarizability of the molecule when subjected to an alternating field of frequency ν; e and m are the electronic charge and mass, respectively; f_{j0} is a measure of the probability that the molecule will undergo the transition from the electronic state ψ_0 to the electronic state ψ_j. Now, the term

$$\nu_j - \nu_0 = \frac{E_j - E_0}{h} = \nu_{j0}$$

is simply the frequency of the light which is absorbed by the molecule in going from state ψ_0 to state ψ_j. Therefore, the problem becomes one of determining the absorption bands of the molecule.

TABLE 20
ABSORPTION WAVE LENGTH AND VISIBLE COLOR

Wave-length region, Å	Color Absorbed	Complementary or Visible Color
4000–4350	Violet	Yellow green
4350–4800	Blue	Yellow
4800–4900	Green blue	Orange
4900–5000	Blue green	Red
5000–5600	Green	Purple
5600–5800	Yellow green	Violet
5800–5950	Yellow	Blue
5950–6050	Orange	Green blue
6050–7500	Red	Blue green

When these absorption bands are in the range of visible light (about 4000–7500 Å), the molecule appears colored. If the absorption is a single band, the visible color will be approximately the complementary color of the one absorbed. In Table 20 is given a series of wave-length regions together with the color absorbed and the complementary color or the visible color. It should be remembered that, in the first place, these designations of color are purely subjective and, secondly, that the absorption is very frequently not a single band, or it may stretch throughout the visible region with varying

intensity, in which case it is impossible to say what color will appear to the eye.

20a. Older theories. The correlation between the color of an organic compound and its structure has interested chemists almost from the very inception of organic structural formulas. It was very early recognized that some sort of unsaturation was necessary in order that a compound be colored, i.e. absorb visible light.[22] This idea was further elaborated by Witt,[23] who designated certain unsaturated groups as chromophores, with the stipulation that their presence was required in order that a compound be colored. Further, he designated another set of groups, generally saturated, i.e. containing no double bonds, as auxochromes, and their presence enhanced the chromophoric properties of the chromophores. These ideas of unsaturation and chromophoric and auxochromic character have undergone many developments and ramifications until in recent years they find their culmination in the theories of Dilthey and Wizinger, so ably expounded by Wizinger.[24] We will not pursue these theories any further, since they cannot yield any quantitative correlations, and very complete expositions of them may be found in a number of comparatively recent reviews.[25]

20b. Quantum mechanical calculations. Absorption of light by organic compounds in any region but the far ultra-violet is certainly associated with the phenomenon of resonance in systems containing multiple bonds.[26] This is especially true of dyestuffs, which contain many double bonds and aromatic groups in conjugation, and a number of attempts have been made to calculate the absorption spectra from almost first principles for a number of simpler conjugated systems.[27] The method that is used is exactly the one illustrated in the case of benzene in Chapter IV. It will be recalled that the solution of the secular equation given there had two roots: $W_g = Q + 2.4\alpha$ and $W_e = Q$. $W_g = Q + 2.4\alpha$ was designated as

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[22] Graebe, C., and Liebermann, C., *Ber.*, **1**, 106 (1868).

[23] Witt, O. N., *Ber.*, **9**, 522 (1876).

[24] Wizinger, R. K., *Organische Farbstoffe*. Ferd. Dummlers Verlag, Berlin u. Bonn, 1933.

[25] (a) Martinet, J., "Couleur et constitution chimique," *Traité de Chimie Organique*; sous la direction V. Grignard; Secretaire Général, Paul Band. Tome II, Fascicule II, 653 (1936).

(b) Ramart-Lucas, P., "Structure des molécules et spectres d'absorption," *ibid.*, Tome II, Fascicule I, 59 (1936).

[26] Bury, C. R., *J. Am. Chem. Soc.*, **57**, 2115 (1935).

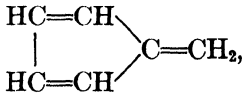
[27] Sklar, A. L., *J. Chem. Phys.*, **5**, 669 (1937); Förster, T., *Z. Elektrochem.*, **45**, 548 (1939).

the energy of the ground state, and it is suggested that $W_0 = Q$ is the energy of the first excited state. Thus the frequency of the first absorption band of benzene should be $\frac{2.4\alpha}{h}$. Now the same calculation has been carried out for a number of other condensed ring system hydrocarbons with the results shown in the second column of Table 21. If the value of α is taken as 49 kcals./mole,

TABLE 21
CALCULATED ABSORPTION OF SOME HYDROCARBONS

Molecule	Excitation Energy	Wave Length of the First Absorption Band in Å	
		Calc. with α = 49 kcals./mole	Observed
Benzene	2.40α	2450	2550
Naphthalene	1.97α	2950	2750
Anthracene	1.60α	3650	3700
Naphthacene	1.31α	4500	4600
Pentacene	1.08α	5450	5800
Phenanthrene	1.94α	3000	2950
Pyrene	1.70α	3450	3300

which is simply the best value for these particular data and is somewhat larger than the value used in the bond energy calculation, the results given in the third column of the table are obtained and are to be compared with the experimental values given in the last column. Similar calculations have been carried out for the simple conjugated polyenes and for fulvene,



with fair agreement if the value of α is somewhat adjusted. While it is true that eventually some such calculation as this will probably be found which will give the correct results, it seems useful to try to find a point of view which will permit the consideration of the more complex and important substances such as the dyestuffs, recognizing the overwhelming importance of the resonance phenomenon in the production of color in organic molecules. Such an attempt has been made by Lewis and Calvin,[28] and the following short presentation is based upon the suggestions made there in some detail.

[28] Lewis, G. N., and Calvin, M., *Chem. Rev.*, **25**, 273 (1939).

20c. Complexity of spectra. By far the largest amount of data on the absorption spectra of organic compounds has been obtained for solutions. These spectra are rarely lines; usually they are spread over rather wide regions of wave length. They may be recorded as a plot of the molar extinction coefficient ϵ as ordinate against the wave length λ or the frequency ν, or better yet the wave-number $\tilde{\nu}$ as abscissa. The molar extinction coefficient is given by

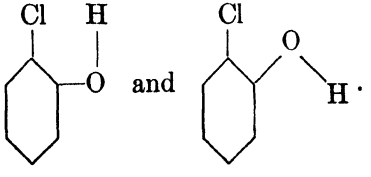
$$\epsilon_\lambda = \frac{1}{md} \log \frac{I_{0\lambda}}{I_\lambda},$$

where $I_{0\lambda}$ is the intensity of the light of wave length λ which penetrates a thickness d in cm. of the pure solvent, and I_λ is the intensity of the light of wave length λ which penetrates a thickness d of a solution of molarity m.

It must be recognized at the outset that the absorption spectrum of an organic compound may be complex for any of a number of reasons not directly concerned with the complexity of the electronic states associated with the isolated molecule, and that it will be necessary at first to distinguish and eliminate these complications, which for the moment are secondary, before any serious attempt at correlation can be made.

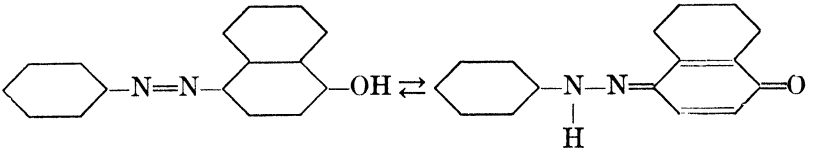
One of the most important and widespread sources of this sort of complication is the presence in the solution of more than a single molecular species even though an analytically pure solute is used. There are at least five different ways in which this can come about:

1. There may be easily converted isomers present whose absorptions may be quite different from each other. For example, some of the complexity of the spectrum of azobenzene has been resolved by the discovery and isolation of the *cis* and *trans* forms of the compound. Similarly, the presence of two bands in the infra-red spectrum of *o*-chlorophenol has been doubtlessly correctly interpreted as being due to the presence of the two isomers



As an example of a tautomeric equilibrium which makes itself evident in the spectrum, we may recall the benzene azo-α-naphthol

in which both forms



are present in sufficient quantity to make their respective absorption bands appear in the spectrum.

2. The solute may exist in solution not only as a single molecule, but also in the form of certain very definite polymers (dimers, trimers, etc.), each of which has its own characteristic absorption. A great many aromatic molecules exhibit this phenomenon and considerable care must be exercised in the interpretation of their spectra.[29]

3. The solute may form definite solvates with a certain number of solvent molecules—e.g., chloral hydrate—and in certain cases these may exist in equilibrium with the unsolvated solute, thus producing more than one absorption region.

4. The colored substance may and frequently does have acid or basic properties, and it may be capable of combination with acid or basic solvents so as to give new molecular species with different absorption spectra. Many such cases have been analyzed, among the first of which is that of crystal violet, studied by Adams and Rosenstein.[30]

5. The solute may be capable of dissociation to produce differently colored ions in equilibrium with the undissociated substance as, for example, triphenylmethyl chloride in chlorobenzene solution.

Having considered all of these possibilities of more than a single molecular species, there still may be present a number of absorption maxima. Some of these have been correlated with a number of vibrational states in either or both electronic states involved in the particular region of absorption concerned. They are usually more sharply defined if the samples are cooled to very low temperatures. Such vibrational structure is well exemplified by the various maxima in the absorption spectra of the diphenylpolyenes[31] at low temperatures, shown in Figure 26. It is to be noted that each vibrational band still has a very appreciable width. This broadening may be

[29] Scheibe, G., *Kolloid Zeit.*, **82**, 1 (1938).

[30] Adams, E. Q., and Rosenstein, L., *J. Am. Chem. Soc.*, **36**, 1452 (1914).

[31] Hausser, K. W., Kuhn, R., and Seitz, G., *Z. physik. Chem.*, **B29**, 391 (1935).

due to any or all of a number of reasons. There may be such a high density of very low-frequency vibrational states in the upper electronic state as to appear almost as a continuum of energy within a certain range. Or the probability of transition from the initial excited vibrational state to another excited vibrational state may be very high, so that the mean life of the initial excited state is very low, of the order of 10^{-13} to 10^{-14} sec. By the uncertainty principle

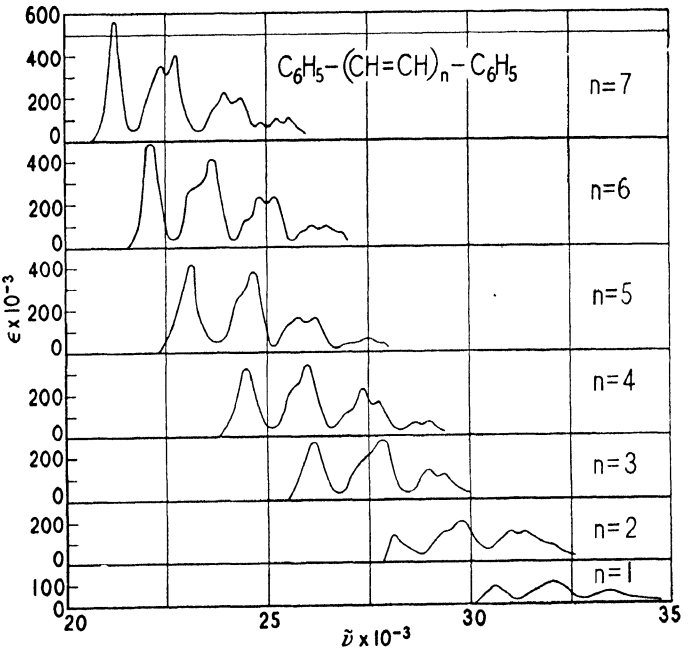


Figure 26. Absorption curves of diphenylpolyenes in ether-alcohol mixtures at −196°.

of Heisenberg, which states that the uncertainty in the energy (ΔE) and life (τ) of a molecular state are connected by the relationship $\Delta E \times \tau \simeq h$, the energy of the initial excited state would be indeterminate to within several hundred wave numbers. This type of broadening has been called the natural width of the band. Lastly, the presence of the solvent molecules produce perturbing electric and magnetic fields around the absorbing molecules so as to greatly increase the number of excited states close together (analogous to the pressure broadening of spectral lines of gases due to Zeeman and Stark effects).

20d. Electrons as quantized oscillators. Even after all of the above-mentioned sources of complexity have been eliminated or accounted for, we still frequently find in an absorption spectrum, taken through the visible and well into the ultra-violet, a number of separate electronic bands. It has been possible to classify and interpret, in some cases quantitatively, these spectra on the basis of the assumption that the electrons in the molecule are acting as oscillators subject to the simple rules of quantization, and whose types of oscillation are indicated by certain of the resonance forms contributing to the state of the molecule.

The principles can best be introduced in terms of the isolated single and double bonds although, as will be seen, these are the cases for which this type of approximation is least applicable. Consider first the single bond, and we will use here only the carbon bonds although exactly analogous considerations apply for others as well, as represented in a molecule such as ethane. On the basis of the ideas developed in Chapters III and IV, we write for the structure of ethane the one major form A and the two very minor polar forms B and C:

$H_3C : CH_3$	$H_3C \quad :CH_3$	$H_3C: \quad CH_3$
$H_3C—CH_3$	$H_3\overset{+}{C} \quad \overset{-}{C}H_3$	$H_3\overset{-}{C} \quad \overset{+}{C}H_3$
A	B	C

It is to the excitation of electronic oscillations whose extremes are represented by B and C that the absorption of light is attributed. If it is assumed that these oscillations are those of a linear harmonic oscillator, the energy states associated with it are given by $E_n = (n + \frac{1}{2})h\nu_0$; ν_0, the fundamental frequency, is given by $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$, where k is the restoring force constant for the oscillator and m is its reduced mass (see equation 6). Exactly similar considerations apply to the isolated double bond, which may be written in terms of three resonance states: a major homopolar one A and two minor polar ones B and C:

$R_2C{=}CR_2$	$R_2\overset{+}{C}—\overset{-}{C}R_2$	$R_2\overset{-}{C}—\overset{+}{C}R_2$
A	B	C

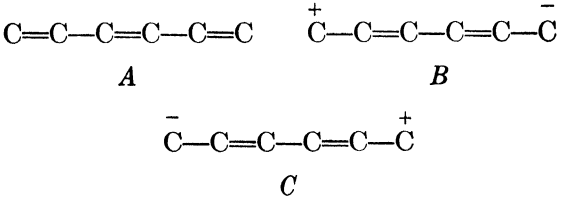
The polarization of the second bond of the double bond is neglected, since a state involving the polarization of both bonds, in the sense here indicated, would have an extremely high energy. In other

words, the restoring force constant k would be very high and hence its absorption would appear only in the far ultra-violet. A similar difference in the restoring force constant between the single and the double bond may also be construed as the essential difference between them, giving the single bond an absorption in the far ultra-violet, while the double bond has its characteristic absorption at considerably lower frequencies. Further, the varying chromophoric power of the different double bonds can then be considered as the different value of k for each type of double bond. The order of decreasing k, or increasing chromophoric activity, is:

$$R_2C{=}CR_2, \quad R_2C{=}NR, \quad R_2C{=}O, \quad RN{=}NR, \quad R_2C{=}S.$$

However, a molecule must contain more than one oscillator of any of the first three types in order that its absorption reach down into the visible region. This then, in general, will lead to an oscillator in more than one co-ordinate, usually in two and sometimes in three. We will consider first the case in which these multiple oscillators are arranged in a molecule in such a manner that the molecule can be considered as a system of linear oscillators all having the same direction, or as a single linear oscillator.

20e. Approximately linear oscillators. There are at least three different types of linear oscillators, represented by (1) the diphenylpolyenes whose absorptions are shown in Figure 26, (2) the cyanines, and (3) the para-polyphenyls. Most linear oscillator types of molecules belong to one of these three classes or to some type intermediate between them. The diphenylpolyenes can be represented by the following type structures, omitting the terminal groups:



A *B* *C*

of which *A* is the major form and *B* and *C* are the minor forms. The essential characteristic of these molecules is the fact that they consist of a chain of conjugated double bonds. The forms *B* and *C* represent merely the limits toward which the oscillation tends; these limits are certainly never actually attained. The molecule may be considered as a whole and thus be a single linear oscillator, or it may be considered as a system of three oscillators moving exactly in phase.

The final result can be made the same, but it is somewhat simpler to consider it from the latter point of view. In that case the net result of the concerted motion of all the oscillators, each having the same force constant k, is simply that of an oscillator of force constant k and mass nm, where n is the number of oscillating units and m is the

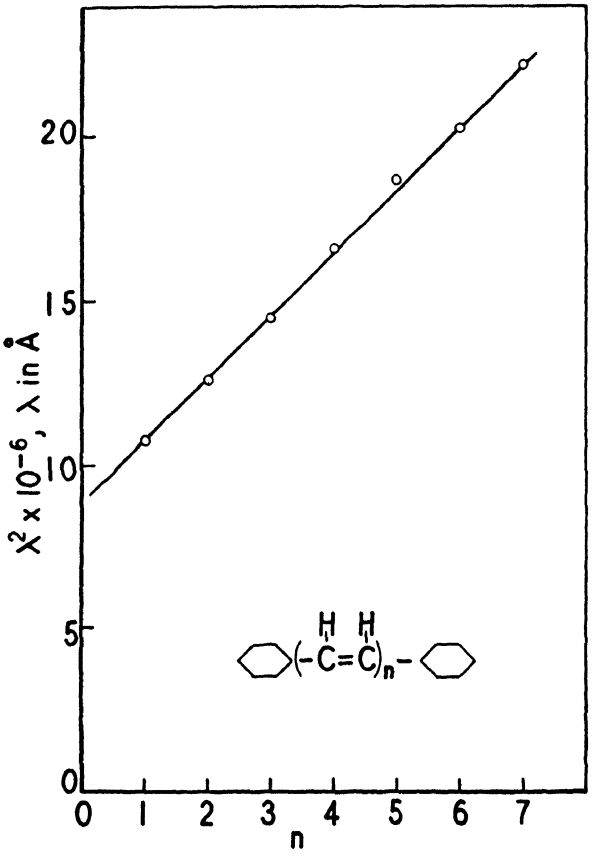
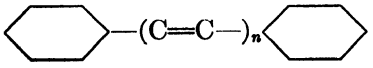


Figure 27. Plot of the square of the wave length of the first absorption band of the diphenylpolyenes against the number of units of the polyenic chain.

mass of each unit. It should be noted that in this case the main source of the restoring force is still the neighboring nuclei bounding each unit. There is comparatively little overlapping of the electron density of one unit on the next. Only a very small perturbation is required in order that the several units oscillate in phase. Thus, the

characteristic frequency for the series of molecules represented by



is given by

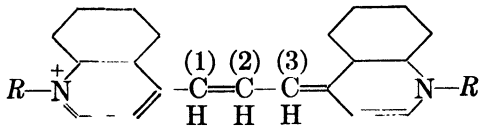
$$\nu_0 = \frac{1}{2\pi}\sqrt{k/nm}.$$

The wave length of the first absorption band corresponding to the transition, $E_1 - E_0 = h\nu_0$, is given by

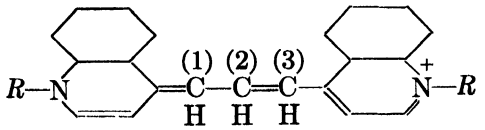
$$\lambda_0 = \frac{2\pi c}{\sqrt{k/nm}},$$

and by including all the constant terms in a new constant we get $\lambda_0^2 = k'n$. In Figure 27 are plotted the data of Hausser, Kuhn, and Seitz (Figure 26), with λ_0^2 as ordinate and the number of double bonds between phenyl groups as abscissa. The very close approach of the individual points to a straight line is excellent verification of the linear relationship. From the intercept on the $n = 0$ axis, we find that, in order to make λ_0^2 not only linear with n but actually proportional to it, a value of 2.35 double bond units must be assigned to each terminal phenyl group. There are other ways of formulating this end effect, so that this evaluation is not critical.

There is another type of linear oscillator whose characteristic frequency ν_0 depends on the size of the oscillator in quite a different manner from the one just discussed. This type is best exemplified by the ion of cyanine, for which the two equally contributing identical energy structures, *A* and *B*, may be written:



A



B

In contrast to the diphenylpolyenes, in this case, the electron distribution between carbon atoms (1) and (2) and between carbon atoms

(2) and (3) is the same. In fact, the electron density distribution between the two terminal nitrogen atoms is without doubt not an oscillatory one, although not necessarily constant. The restoring force on these electrons arises primarily from the presence of the neighboring electrons, and hence the analogous model is that of the elastic string undergoing longitudinal vibrations, and for which the

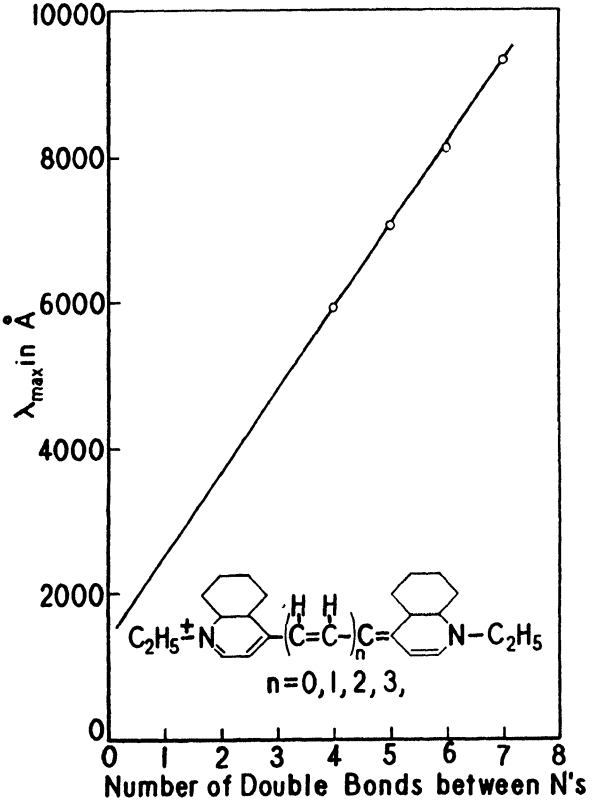
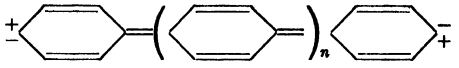


Figure 28. Plot of the wave length of the first absorption band against the number of double bonds between the nitrogen atoms for a series of carbocyanines.

frequency is inversely proportional to the length. Thus we have to expect the wave length of the first absorption maximum to increase linearly with the number of double bonds between the nitrogen atoms. Such a plot is shown in Figure 28 for the longest series of carbocyanines for which measurements are available. Here again the agreement is excellent.

The third type of molecule which may be classed as a linear oscillator, but different from those already mentioned, is that represented by the para-polyphenyls, the absorption of a series of which has been measured by Gillam and Hey.[32] In this case the two structures concerned in the absorption of light are represented by the formulas:



It should be noted that these forms contribute only at the expense of the Kekule resonance. When the number of phenyl groups is small, the percentage increase in length for an additional phenyl group is sufficiently great to outweigh the additional energy required to break the Kekule resonance; but, as the number of phenyl groups increases, the percentage increase in length becomes smaller until it is no longer sufficient to outweigh the loss of the Kekule forms. Hence we may expect an increase in the wave length of maximum absorption for each additional phenyl group, which gradually decreases as the length of the chain increases. These molecules may be considered as oscillators of the same general character as the diphenylpolyenes; but they differ in that there is not only an increase in m as the length of the chain increases but also an increase in k, so that finally a maximum wave length is reached beyond which additional phenyl groups have only the effect of increasing the probability of absorption without changing the wave length. The results of Gillam and Hey are exactly these, and Figure 29 shows a plot of the

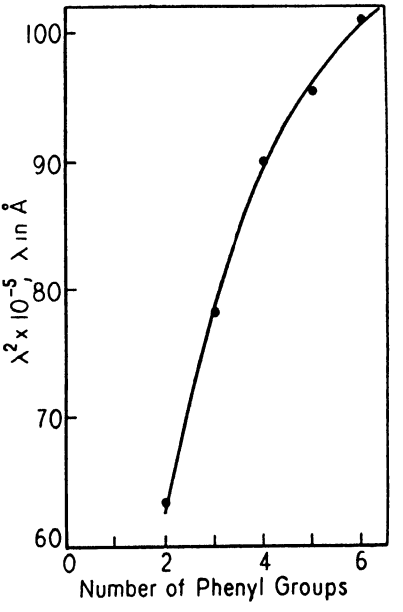


Figure 29. Plot of the square of the wave length of the first absorption band against the number of phenyl groups for a series of para-polyphenyls.

[32] Gillam, A. E., and Hey, D. H., *J. Chem. Soc.*, 1170 (1939).

square of the wave length of the first absorption maximum against the number of phenyl groups in the chain.

20f. Conjugation, insulation, partials. One of the directly apparent deductions from this concept of the absorption of light by approximately linear molecules is the effect of a break in the conjugation through the chain. This break in the conjugation has been

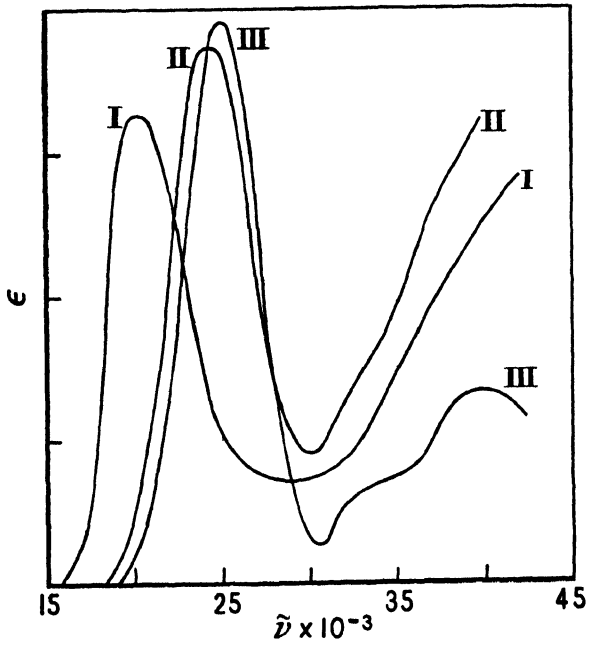


Figure 30. Absorption curves of some azo dyes in alcohol.

I. $(CH_3)_2N-C_6H_4-N=N-C_6H_4-C_6H_4-N=N-C_6H_4-N(CH_3)_2$

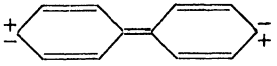
II. $(CH_3)_2N-C_6H_4-N=N-C_6H_4-CH_2-C_6H_4-N=N-C_6H_4-N(CH_3)_2$

III. $(CH_3)_2N-C_6H_4-N=N-C_6H_4-CH_3$ $(2 \times \epsilon)$

called an insulation effect, since the conjugated chain acts as a conductor of electricity and the break in the conjugation as an insulation between the two conjugated parts. It is to be expected then that a completely conjugated system will have an absorption characteristic of the molecule as a whole, but if that conjugation is broken, by the insertion of a CH_2 group for example, the absorption will be more nearly characteristic of the two independently conjugated parts. An excellent example of this is afforded by the measure-

ments of Piper and Brode[33] on some azo dyes. In Figure 30 are shown the absorption spectra of the fully conjugated molecule (I); of the molecule (II) containing an insulating CH_2 group which divides the molecule into two equivalent, insulated, but internally completely conjugated halves; and of the molecule (III) which corresponds very closely to one of these halves. The molar absorption of the insulated molecule (II) corresponds well with twice that of the smaller molecule (III). That of the completely conjugated molecule (I) shows a new absorption band at a lower frequency.

There are other ways in which such an insulation between parts of a molecule may be effected, though not in general so completely as by the insertion of a CH_2 group. It will be recalled that in order that the resonance of diphenyl



occur, the two rings must be coplanar. If, however, a number of large ortho groups be inserted, this coplanarity cannot occur without a large expenditure of energy, and hence this type of resonance, which is so important for the absorption of light, will be considerably inhibited. This effect is well illustrated by the measurements of Pickett, Walter, and France[34] on substituted diphenyls containing four chlorine atoms or four methyl groups in the ortho position. The conjugation bands are entirely absent from the spectra of these substances. The same effect is apparent in the work of Müller and Neuhoff[35] on some more complex substituted diphenyls which they encountered in their work on the demonstration of this steric effect on the possibility of the existence of diradicals. This work is discussed in Chapter VII.

In certain molecules the steric requirements may be such as to reduce the conjugation without completely inhibiting it. In this case the conjugation resonance absorption will appear, but with diminished intensity or at a higher frequency, or both. Such is the case for *cis*- and *trans*-stilbene. For *trans*-stilbene the molecule is entirely coplanar and the optically important resonance discussed in the section on the diphenylpolyenes can readily occur. For *cis*-

[33] Piper, J. D., and Brode, W. R., *J. Am. Chem. Soc.*, **57**, 135 (1935).

[34] Pickett, L. W., Walter, G. F., and France, H., *J. Am. Chem. Soc.*, **58**, 2296 (1936). A more detailed study of this effect is to be found in the publication by O'Shaughnessy, M. T., and Rodebush, W. H., *J. Am. Chem. Soc.*, **62**, 2906 (1940); its use in a special case is described by Calvin, M., and Wood, C. L., *J. Am. Chem. Soc.*, **62**, 3152 (1940).

[35] Müller, E., and Neuhoff, H., *Ber.*, **72**, 2063 (1939).

stilbene, on the other hand, a model to scale will show, exactly as in the case of the isomers of azobenzene discussed in Chapter VII, that the ortho hydrogen atoms will interfere to such an extent as to prevent the complete coplanarity of the molecule. This will inhibit the optically important resonance and have the effect just mentioned, as is shown in Figure 31,[36] where the absorption of the *cis* compound is both reduced in intensity and shifted to higher frequencies with respect to the *trans*.

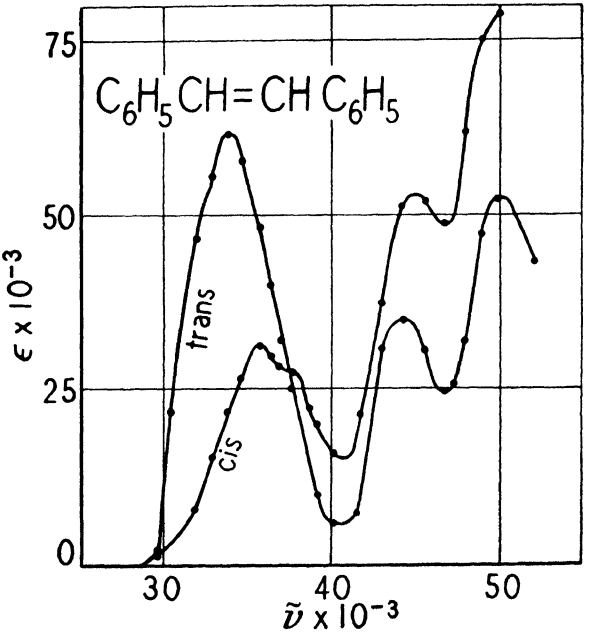
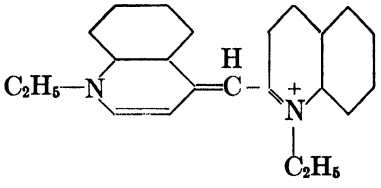


Figure 31. Absorption curves of the *cis* and *trans* forms of stilbene.

For some of the more complex molecules, in which there exist parts which in themselves contain excellent resonance systems, it is sometimes possible to observe absorption bands which are almost certainly due to oscillations within these parts but somewhat perturbed by the rest of the molecule, together with an absorption band attributable to an oscillation throughout the molecule as a whole. In order to observe these bands of partial oscillation, which have been called "partials," it is not necessary to have complete insulation or even any immediately obvious partial insulation, although, owing to

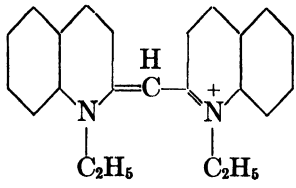
[36] Smakula, A., and Wasserman, A., *Z. physik. Chem.*, **A155**, 353 (1931).

the complexity of the molecule, it is not possible at present to say definitely whether or not some insulation, steric or otherwise, is necessary. Such an observation has been made by Brooker and Smith[37] on the series of cyanines represented by:



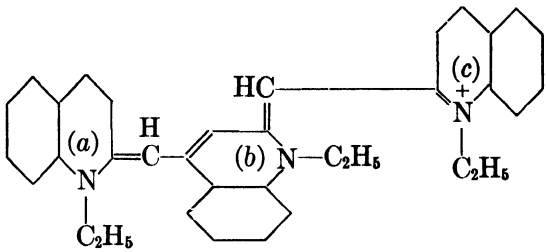
Isocyanine ion

I



Pseudoisocyanine ion

II



2,4-Di [(1-ethyl-2(1)-quinolylidene)methyl] (1) ethyl quinolinium ion

III

It is apparent that (III) contains, in a sense, both (I) and (II). In all three cases only one of the resonance forms has been shown. In (III) the three nitrogen atoms are not exactly equivalent, but (*a*) and (*c*) are more nearly similar than is either of them to nitrogen atom (*b*). It is possible, then, to conceive that the forms having the positive charge on nitrogen atoms (*a*) and (*c*) represent the oscillation through the molecule as a whole, while those having the positive charge on (*a*) and (*b*) or on (*b*) and (*c*) represent partial oscillations. The absorption of these three substances is shown in Figure 32, in which curves 1 and 2 correspond to compounds I and II while curve 3, corresponding to III, shows a new band at lower frequency (on the left) and a band very similar to those of I and II at higher frequency (on the right). It seems reasonable to ascribe the lower frequency band to an oscillation through the molecule as a whole and the higher frequency band to a partial oscillation in that part of the molecule similar to I or II, or a coincidence of both. The fact that this partial is at a frequency higher than that of either of the constituent mole-

[37] Brooker, L. G. S., and Smith, L. A., *J. Am. Chem. Soc.*, **59**, 67 (1937).

cules is probably due to the phenomenon of cross-conjugation discussed in some detail in Chapter VI. It is essentially due to the condition that when two resonances in the same molecule are mutually exclusive, neither one of them can exert its full effect.

This phenomenon of partial oscillation may appear in simple molecules as well, although not quite so readily assignable, and corresponds somewhat to the older ideas of assigning to a particular group a characteristic frequency which may be recognizable in a number of differently constituted molecules, provided they are not too different in their resonance characteristics.

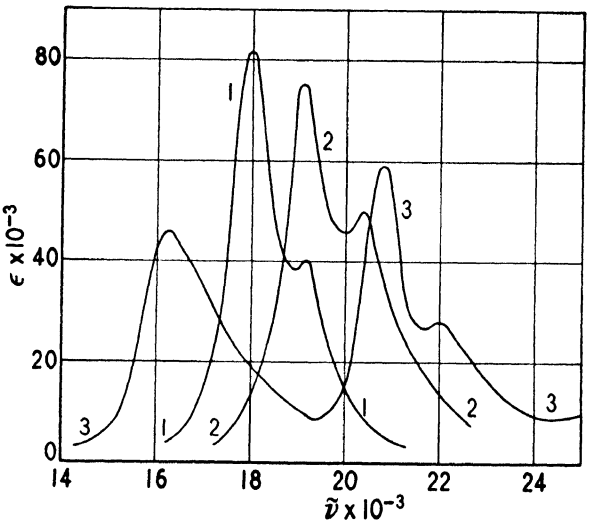
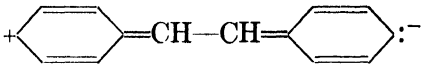


Figure 32. Absorption curves of three cyanines in alcohol. Curve 1, isocyanine ion; curve 2, pseudoisocyanine ion; curve 3, 2,4-di[(1-ethyl-2(1)-quinolylidene)methyl]-1-ethyl quinolinium ion.

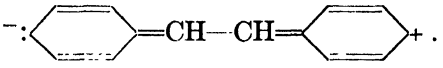
20g. The function of auxochromes. On the basis of the present theory, the function of those groups which have been designated as auxochromes, and of most other groups for that matter, is readily understood. Any group which is capable of enhancing the optically important resonance forms should increase the color of the substance. Generally that increase takes the form of a shift in the absorption to lower frequencies, but it may also be accompanied by an increase in intensity as well. The whole question of the intensity of absorption bands is very complex and is far from satisfactorily answered. For this reason we will restrict ourselves to considerations of the position

of the bands and hope that the questions of intensity may be answered some time soon.

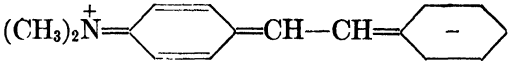
Consider the resonance forms which are held responsible for the absorption of light by a molecule of stilbene:



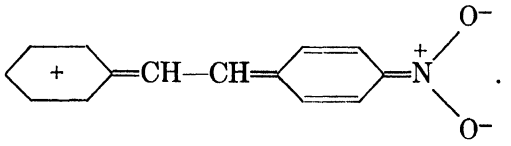
and



The positive and negative charge may be written on any of the three ortho and para carbon atoms. These states are of comparatively high energy. The substitution of any group which will provide atoms which can carry positive or negative charge more readily than carbon will lower the energy of these states and hence permit them a greater contribution to the state of the molecule. The best examples of such groups are the amino or dimethylamino groups which provide the nitrogen atom to carry the positive charge by losing its extra electron pair, and the nitro or carboxyl groups which provide the oxygen atom to carry the negative charge by accepting an extra electron pair. Thus *p*-dimethylaminostilbene will have a considerable contribution of the form



and *p*-nitrostilbene a considerable contribution of the form



When the two substituents are both present in the same molecule, the effect will be greater than the sum of the two. These considerations are exactly analogous to the ones made in an earlier section on the dipole moment. The absorption spectra of this series of stilbenes have been measured by Hertel and Lührmann[38] and are shown in Figure 33. The shift in frequency accomplished by the *p*-NO_2 group is 3.7×10^3 cm.$^{-1}$; that by the *p*-$(CH_3)_2N$ group is 2.7×10^3

[38] Hertel, E., and Lührmann, H., *Z. physik. Chem.*, **B44**, 261 (1939).

cm.$^{-1}$. That accomplished by both groups together is 9.4×10^3 cm.$^{-1}$. From such measurements as these one obtains the usual order of effectiveness of the various groups, an order which will appear again and again when considerations are made of chemical equilibria and rates in later chapters.

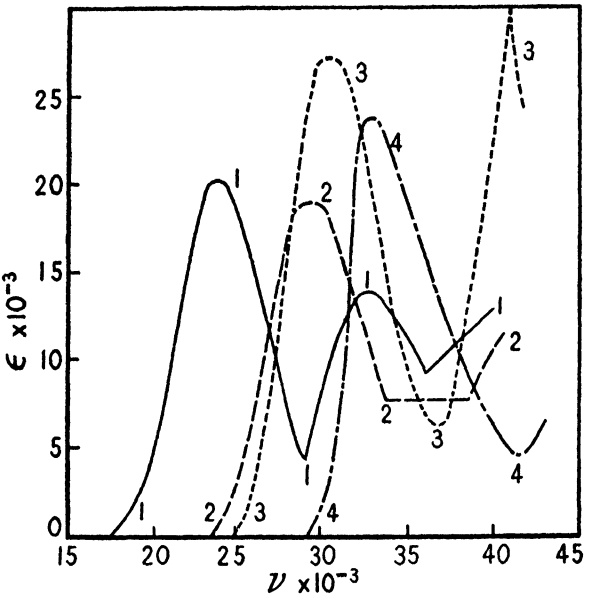


Figure 33. Absorption curves of four stilbenes in alcohol. Curve 1, *p*-nitro-*p'*-dimethylaminostilbene; curve 2, *p*-nitrostilbene; curve 3, *p*-dimethylaminostilbene; curve 4, stilbene.

20h. Oscillators in more than one direction. So far we have been considering molecules in which there was only one axis along which the polarizability was very large, the other two components of the polarizability being relatively small and hence concerned with absorptions far in the ultra-violet. If, however, the conjugated system has an appreciable extension in two dimensions, there will exist two axes of appreciable polarizability; and in some special cases it is possible to have extension in three dimensions, and hence three axes of large polarizability. The absorption bands associated with these three axes have been called the x, y, and z bands, the x and y bands being the ones associated with planar molecules and the z band appearing only in certain special cases. Further, the convention is adopted, for the planar molecules having x and y bands, of calling

the band of longest wave length the x band and the corresponding direction the x direction.

The correlation of the observed absorption bands with the two directions in the molecule is not so readily done directly. For a few of the simpler nearly linear molecules having only an x band and for which the orientation of the molecule in the crystal has been determined by means of X-rays, it has been possible to show from observations with plane polarized light that a molecule absorbs the wave length of the x band only when the direction of polarization (the electric vector) of the incident light is roughly parallel to the length

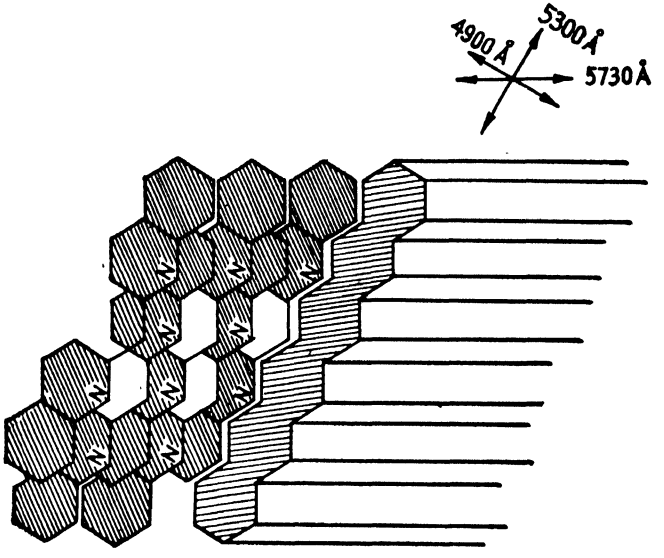
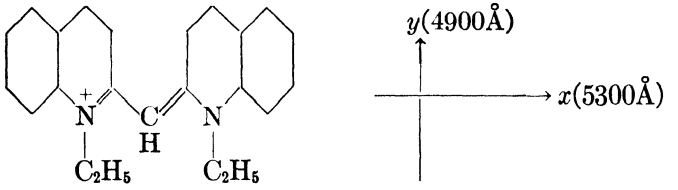


Figure 34. Absorption and structure of the polymer of pseudo-isocyanine.

of the conjugated chain: e.g., diphenyloctatetraene, diphenyldodecahexaene, and *p*-azoxyanisole. It has also been possible to show in the case of some large planar molecules that absorption is at a maximum when the plane of polarization of the light is in the plane of the molecule, and at a minimum when the plane of polarization of the light is normal to the plane of the molecule; e.g., azobenzene, quinone, perylene, chrysene.[39] There is only one case, however, in which the x and y bands have been unequivocally assigned by direct physical measurements. This is also one of the two cases for which

[39] The measurements on chrysene were reported by Krishnan, K. S., and Seshan, P. K., *Raman Jubilee Volume, Ind. Acad. Sci.*, 487 (1938).

z bands have been assigned and measured. Scheibe and his co-workers[40] have studied the absorption spectra of pseudoisocyanine and other related dyestuffs under a great variety of conditions. The work on the pseudoisocyanine is most complete, and the x, y, and z bands have been assigned as shown in Figure 34. The same result was reported somewhat earlier by Jelley.[41] The band at 5300 Å is the x band; the x direction is then the long axis of the molecule, while the band at 4900 Å is the y band.



These two absorption bands are characteristic of the single molecule, but in aqueous solutions these flat molecules polymerize face to face to form long threads (Figure 34), and a third absorption band appears (5730 Å) whose direction of polarization is along the length of the thread, and this we call the z band. It is indicative of an electronic resonance between molecules, which is probably responsible for the very extensive molecular compound formation between aromatic molecules, which has long been known.[42]

There is another set of molecules whose absorption bands can be very definitely assigned as x and y bands, but only on the basis of the general principles of color and molecular structure which we have so far developed. There exists as yet no direct experimental determination of these directions, but the interpretation of the existing data in these terms is so clear that it is practically certain that when such experiments are performed it will be found that the correlation of the bands with the molecular symmetry, which we are about to make, is true. The best examples of this set of triphenylmethane dyes are the three molecules, crystal violet (I), malachite green (II), and methoxymalachite green (III), shown opposite.

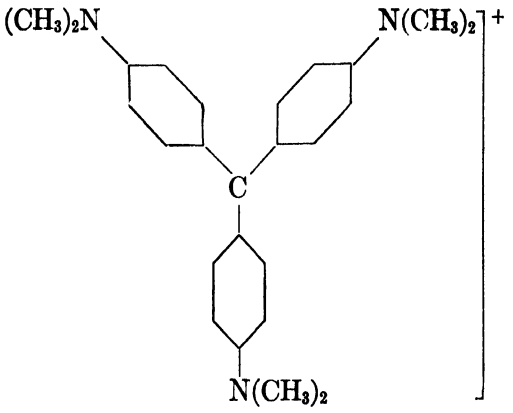
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[40] Scheibe, G., *Angew. Chem.*, **52**, 631 (1939).

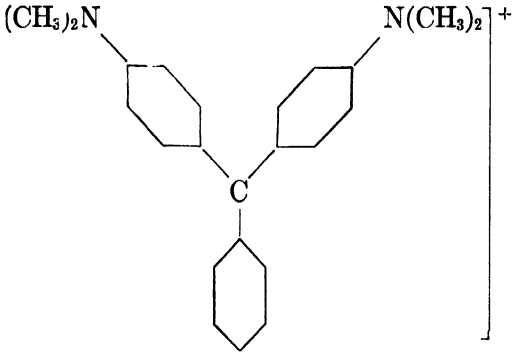
[41] Jelley, E. E., *Nature*, **139**, 631 (1937).

[42] Pfeiffer, P., *Organische Molekülverbindungen.* Ferdinand Enke, Stuttgart, 1934.

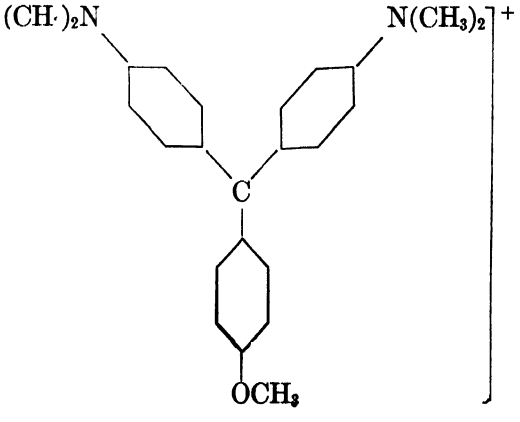
I



II



III



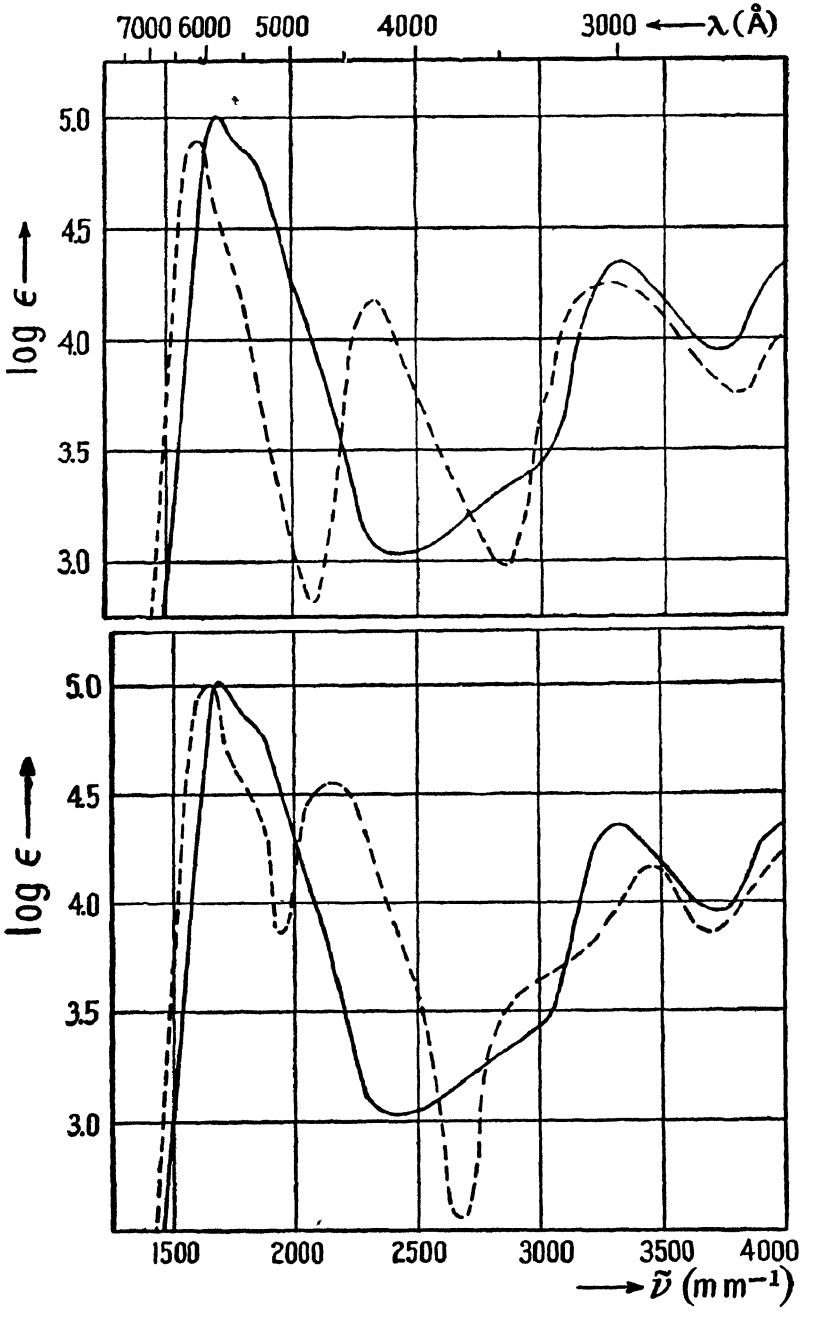
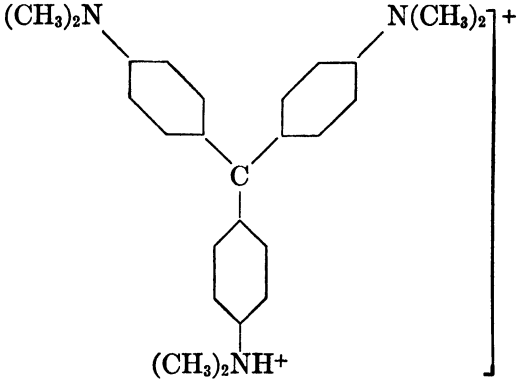


Figure 35. Absorption spectra of crystal violet (solid line), of malachite green (upper dotted line), and of methoxymalachite green (lower dotted line). After Hantzsch and Auskaps.

Their absorption spectra are shown in Figure 35. The crystal violet molecule, which is symmetrical in the plane (i.e., the x and y directions are identical) has only a single band in the visible at about 6000 Å. The malachite green molecule, however, is not symmetrical and hence the x and y bands do not coincide, the x band being the one at about 6200 Å and the y band the one at about 4200 Å. Furthermore, the x direction can be fairly certainly assigned as the direction of oscillation having the greatest contribution from the two dimethylamino groups, while the y direction is the one involving largely the unsubstituted phenyl group. If an auxochrome other than $(CH_3)_2N$—e.g., CH_3O—is substituted into the para position of this third phenyl group of malachite green to form methoxymalachite green, the greatest effect should be the shifting of the y band to longer wave lengths without much change in the x band. This is actually the case, as is seen in Figure 35, the y band being shifted from about 4200 Å to about 4700 Å and log ϵ being increased from about 4.2 to about 4.6.

20i. Acid-base indicators. On the basis of the present theories, the changes of color undergone by acid-base indicators are readily understood in terms of the blocking or freeing, by the protons, of the participation of auxochromic groups in the oscillating system and from the symmetry properties of the limiting states. For example the changes in color of crystal violet in acid solutions were analyzed in 1914 by Adams and Rosenstein,[43] and they were able to assign an absorption spectrum to the ion very similar to that of

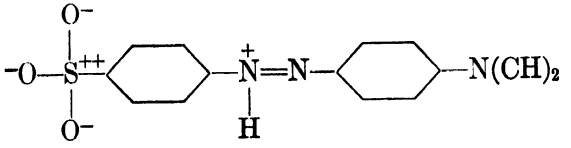


malachite green, and corresponding spectra for the successive addition of protons to the crystal violet ion.

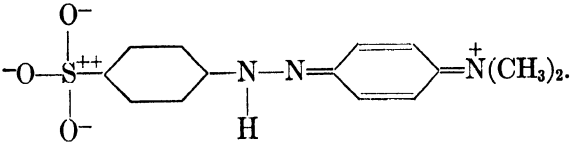
The action of the proton on a different type of dye may be exem-

[43] Adams, E. Q., and Rosenstein, L., *J. Am. Chem. Soc.*, **36**, 1452 (1914).

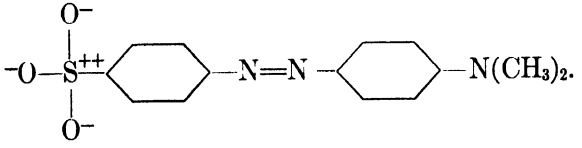
plified by methyl orange which is yellow in solutions of *p*H above 4.4 and red in solutions of *p*H below 3.1. The red form, in acid solution, may be described as the ion



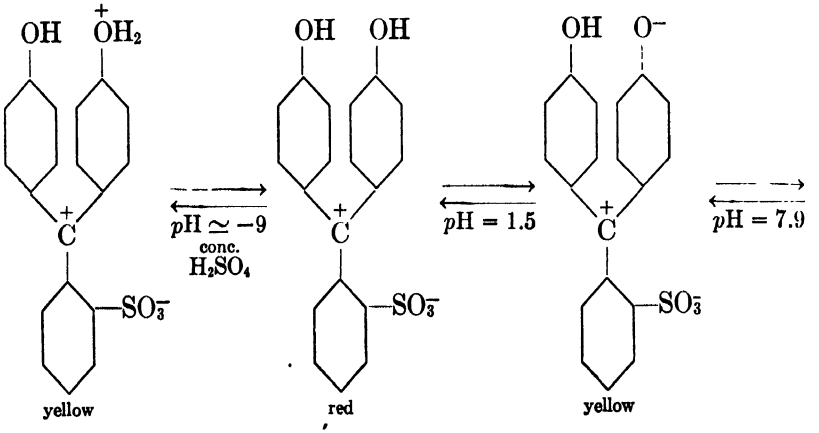
in which the oscillation toward the other extreme form occurs:



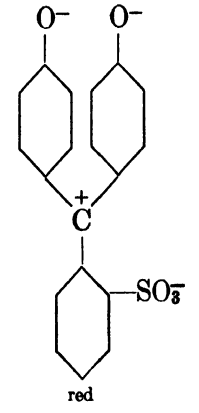
The yellow form in alkaline solution is simply the azo form, with the oscillation involving a separation of charge:



Another example, taken from the work of Schwarzenbach,[44] is that of the phenol- and anilinesulfonphthaleins:

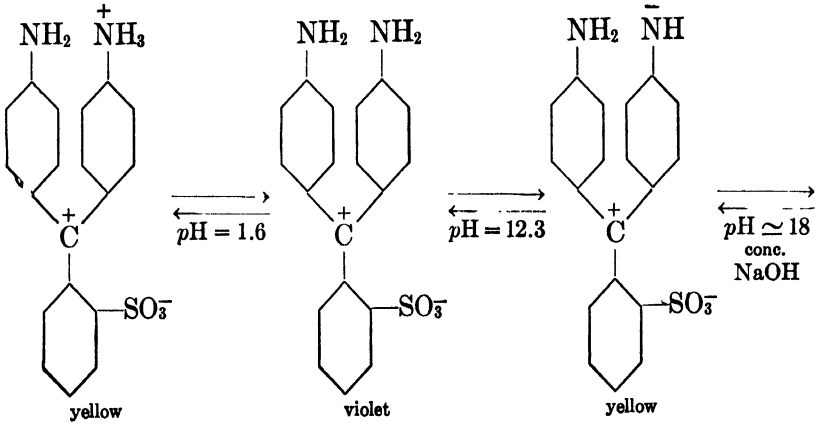


[44] Schwarzenbach, G., and Ott, G. H., *Helv. Chim. Acta*, **20**, 627 (1937).

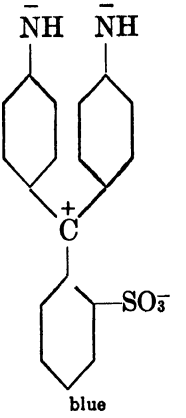


red

Phenolsulfonphthalein



yellow violet yellow



blue

Anilinesulfonphthalein

Another interesting observation to be made from these data is the relatively high range of *p*H over which the symmetrical highly colored forms may exist. This is to be understood in terms of the high resonance energies available for stabilizing the symmetrical forms of the molecule.

CHAPTER VI

EQUILIBRIUM—ACID STRENGTH

The chemical properties of a substance can be defined in two terms: how that substance stands in equilibrium with any other substances which may be formed from it, and how fast that equilibrium state is approached from some unstable initial state. In this and the following chapter we shall be concerned only with the first of these terms; i.e., what relationships can be found between the structure of a compound and the equilibria in which it may take part. In order to do this we shall first examine briefly the language and notation which has been developed to express the experimental results most concisely and explicitly. This is the language of thermodynamics.

21. EQUILIBRIUM

Consider in general any reaction in which a moles of A and b moles of B react to give c moles of C and d moles of D:

$$aA + bB \rightleftarrows cC + dD.$$

If the initial mixture of A and B is allowed to stand under given conditions of temperature, pressure, solvent, etc., until no more C and D are formed, a certain relationship between the amounts of A, B, C, and D will be found in the resulting mixture. The same relationship could be obtained by starting with C and D and permitting them to react under the same conditions to form A and B. When this condition of no further change is attained, the system is said to have reached equilibrium, and the relationship between the amounts of the several molecular species present in the equilibrium mixture is expressed by the equilibrium constant $K_{\text{conc.}}$:

$$K_{\text{conc.}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

$[C]$ represents the concentration of C in the equilibrium mixture and the other brackets have the corresponding significance. One of the most important characteristics of this constant is that it is inde-

pendent of the path by which the equilibrium is attained, i.e. of the mechanism of the reaction, and independent of the time required to achieve that equilibrium.

In order that the equilibrium constant be properly related to the other thermodynamic functions for the substance, such as free energy F, heat content H, and entropy S, it should be expressed in terms of the activity rather than the concentration. For the type of system with which we will be most concerned, namely, reactions between dissolved solutes, the activity is defined so that it becomes equal to the concentration in very dilute solutions. Another type of system with which we shall occasionally be concerned is the reaction between gases or vapors. In this case the activity is defined so that it becomes equal to the pressure at very low pressures. Thus for a perfect gas the activity would always be equal to the pressure, while for any actual gas the departure from equality would be commensurate with the departure of the gas from the condition of the perfect gas.

The thermodynamic equilibrium constant for a reaction is given by

$$K = \frac{a_C^c a_D^d \cdots}{a_A^a a_B^b \cdots}$$

where a_C^c represents the activity of the component C raised to the power c, and the other terms have the corresponding significance. It is expressed so that the activities of the products of the reaction as written from left to right appear in the numerator and the activities of the reactants appear in the denominator. The relation between this equilibrium constant and the free energy of the reaction is given by

$$\Delta F^\circ = -RT \ln K \qquad (1)$$

where $\Delta F^\circ = F_P^\circ - F_R^\circ$. F_P° is the free energy of the products when they are at unit activity, and F_R° is the free energy of the reactants when they are at unit activity. ΔF° is known as the standard free energy of the reaction, and henceforth we shall omit the superscript, since we shall be concerned only with such standard free energy changes.

For the purposes of this book, the use of concentrations or pressures, where activities are not available, in the expression for the equilibrium constant, will be a sufficiently close approximation. In order to predict from structural considerations what the equilibrium

concentrations for a given reaction will be, we have now to calculate the difference in free energy between the product and reactant molecules. This is still very largely an impossible task in the ultimate sense. There is, however, a process of comparison which is somewhat more hopeful and perhaps slightly nearer attainment. This amounts to comparing the effect of various substituents upon some particular equilibrium.

Suppose K_u is the equilibrium constant for some reaction in which an unsubstituted or standard molecule takes part, and K_σ is the equilibrium constant for the same reaction in which a molecule made from the standard molecule by some substitution or other structural change, takes part. Then

$$\Delta F_u = -RT \ln K_u ; \qquad \Delta F_\sigma = -RT \ln K_\sigma$$

$$RT \ln \frac{K_\sigma}{K_u} = \Delta F_u - \Delta F_\sigma$$

or

$$\ln K_\sigma = \ln K_u + \frac{1}{RT} (\Delta F_u - \Delta F_\sigma), \tag{2}$$

and it becomes possible to predict K_σ from a knowledge of K_u and the difference in the ΔF values for the two reactions. At first sight this does not seem to have helped matters much, but a more detailed consideration of some special cases will make the general difficulties and special simplifications apparent.

In comparing any series of equilibria involving molecules related as we have just described, there is often at least one reactant and often some product molecule which is common throughout the series. By selecting one member of this series as a standard and comparing all the others with it, the necessity of knowing the free energies of these common reactants or products is eliminated. These considerations apply equally well to acid-base neutralization, substitution, addition hydrolysis, oxidation-reduction reactions, and the like. The only condition which must be fulfilled is that an equilibrium condition is indeed being measured and that it is the *same* reaction within any given series.

One such reaction in which equilibrium is very quickly and easily attained is the electrolytic dissociation of an acid or a base, or what is equivalent, the neutralization of an acid by a base. Because of

this and the relatively large quantity of experimental material that has been accumulated on this type of reaction, we shall consider in detail acid-base reactions as an example of the effect of structure upon equilibrium.

22. ACIDS AND BASES

Long before the development of modern chemistry it was observed that many substances could be assigned to one or another of two opposed classes, the basis of the classification being the ability of members of opposed classes to react rapidly with each other, forming compounds that belonged to neither class. These two types of substances were called acids and bases, and the reaction between an acid and a base was called a neutralization. At first it was supposed that acids and bases were restricted to oxygen compounds, but this could not be maintained when it became evident that the halogen acids contain no oxygen.

After the discovery of the existence of ions in solution, it was found that the acids produce hydrogen ion and the bases hydroxide ion on solution in water. As these two ions combine vigorously to form water, this process was accepted as the explanation of neutralization, and the acids were defined as ionizable hydrogen compounds and the bases as ionizable hydroxides. This definition excluded certain substances previously considered as acids and bases from this classification. Common examples are carbon dioxide, sulfur trioxide, ammonia, and the organic bases. The apparent acidities or basicities of these substances were assumed to be due to their reaction with water to form true acids and bases. Thus the acid anhydrides mentioned above add water and form carbonic and sulfuric acid, respectively, while ammonia and the amines combine with water to form ammonium hydroxide or one of its derivatives.

This idea of acids and bases was generalized to include solvents other than water. An acid was then defined as a substance that ionizes to form the positive ion of the solvent, and a base was a substance that ionizes to form the negative ion. A substance is then an acid or base only with respect to some solvent. One cannot help feeling that the older idea of acids and bases is more fundamental than the definition in terms of water in particular, or the solvent in general. The effectiveness of these definitions lies in the fact that the positive and negative ions of the solvent are themselves acids and bases in the older sense.

In *Valence and the Structure of Atoms and Molecules,* Lewis[1] returns to the older idea of acids and bases, and defines a base as a substance furnishing a pair of electrons for a chemical bond, and an acid is one that accepts such a pair. Sidgwick[2] has used the same idea, calling the base the donor and the acid the acceptor. Thus trimethylamine and boron trimethyl are respectively a base and an acid, or a donor and acceptor, and their combination is a neutralization.

The base trimethylamine is effectively neutralized, both in its reaction with hydrogen chloride and in its reaction with methyl chloride, yet only hydrogen chloride is considered an acid. The essential difference between these two reactions is that there is no energy barrier between the systems trimethylamine plus hydrochloric acid and trimethylammonium ion plus chloride ion, the intermediate condition with the hydrogen ion forming a bridge between the bases trimethylamine and chloride ion being at a lower energy level than either extreme. On the other hand, there is an energy barrier between the systems trimethylamine plus methyl chloride and tetramethylammonium ion plus chloride ion. The lack of an energy barrier in the reactions between the members of the two opposed classes of substances and the giving and accepting of a pair of electrons are probably the best criteria of the acid-base reaction. According to these criteria, the readily ionizable hydrogen compounds are true acids.

A salt may or may not be found among the products of the neutralization reaction. Thus ammonia and acetic acid neutralize each other, forming the salt ammonium acetate, but when trimethylamine neutralizes boron trifluoride, the product $(CH_3)_3\overset{+}{N}—\overset{-}{B}F_3$ is not an ordinary salt but what is called an inner salt.

Some substances show their full acidic or basic properties only after some reconstruction of the molecule that needs an activation energy. Such substances may be called pseudo-acids or pseudo-bases. Phenylnitromethane is a pseudo-acid, its ion a pseudo-base. It is sometimes convenient to class pseudo-acids and pseudo-bases with the true acids and bases. Except at a low temperature, phenylnitromethane behaves as an acid, with a dissociation constant between 10^{-11} and 10^{-12}. At 0°C., however, it takes an appreciable

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[1] Lewis, G. N., *Valence and the Structure of Atoms and Molecules.* The Chemical Catalog Co., New York, 1923.

[2] Ref. (1), Chapter I.

time for it to neutralize a base to the extent corresponding to an acid of this strength.

It is unusual for carbon, oxygen, or nitrogen atoms to have six electrons, or, when bonded, to accept the electrons of a base without activation, so that a large majority of organic acids are hydrogen compounds. On the other hand, the basicity of organic compounds nearly always arises from the presence of unshared electron pairs. For these reasons it has become popular to restrict bases to molecules or ions having unshared electron pairs and to restrict acids to the hydrogen ion compounds of the bases. With this restriction, acids and bases occur in pairs, the members of a pair being said to be conjugate to each other. Thus NH_4^+ and NH_3, CH_3COOH and $CH_3CO_2^-$, H_2O and OH^-, H_3O^+ and H_2O, HCO_3^- and $CO_3^=$ are examples of conjugate pairs of acids and bases.

The K_a or K_b of an acid or base in any solvent which can act as a hydrogen acid is the product of the activities of the conjugate base and positive ion of the solvent divided by the activity of the acid or the product of the activities of the conjugate acid and negative ion of the solvent divided by the activity of the base. In any conjugate pair these constants are related to each other and the dissociation constant of the solvent, by the equation $K_a \times K_b = K_s$.

23. ACID STRENGTH AND STRUCTURE

When two bases compete for an insufficient supply of an acid, one combines with more of the acid than the other, even though the two bases have the same concentration. This leads to the concept of relative strengths in bases; a similar inequality in the competition of two acids for a base leads to the concept of relative strengths of acids. The base that obtains the major share of the acid is the stronger, and the acid obtaining the major share of the base is the stronger.

23a. Mechanism of comparison of acid strength. The order of strengths is rigorously maintained only when the conditions are rigorously alike. That is, in the case of bases, the acid competed for, the solvent, temperature, and concentrations, except in very dilute solutions, must be fixed. Generally hydrogen ion is chosen as the test acid. The relative strengths in any solvent and at any temperature can then be defined from the equilibrium $B_1 + HB_2 \rightleftarrows HB_1 + B_2$ by the equation

$$\frac{C_{HB_1} \times C_{B_2}}{C_{HB_2} \times C_{B_1}} = \frac{\beta_1}{\beta_2} = \frac{\alpha_2}{\alpha_1},$$

in which β_1 and β_2 are the basic strengths of B_1 and B_2, respectively, and α_1 and α_2 are the acidic strengths of HB_1 and HB_2, respectively. C is the concentration of the substance described by the subscript. To obtain values for β and α it is necessary to fix arbitrarily the values for some acid and base. A convenient standard to use for water solutions is

$$\beta_{OH^-} = M \quad \text{and} \quad \alpha_{H_2O} = \frac{K_w}{M},$$

where M is the molarity of water and $K_w = 10^{-14}$. Then

$$\alpha_{HB} = K_{aHB}, \qquad \beta_B = \frac{K_w}{K_{aHB}} = K_{bB},$$

$$\alpha_{H_3O^+} = M \quad \text{and} \quad \beta_{H_2O} = \frac{K_w}{M},$$

where K_a and K_b are acidic and basic dissociation constants. Similar standards can be used for other solvents if so desired. The above standards are convenient, for α and β can be identified with K_a and K_b, and only one of these constants need be measured. It should be noted that the stronger the acid the weaker its conjugate base, and vice versa.

The ionization of an acid BH in a solvent S may be represented by the equilibrium

$$B{:}H + {:}S \rightleftharpoons B{:} + H{:}S$$

and the equilibrium constant is

$$K = \frac{[B{:}][H{:}S]}{[B{:}H][{:}S]}.$$

As $[{:}S]$ for any given solvent is constant, it is usual to use

$$K_a = \frac{[B{:}][H{:}S]}{[B{:}H]}.$$

This reaction can be considered as the sum of the processes $B{:}H \rightarrow B{:} + H^+$, $H^+ + {:}S \rightarrow H{:}S$, the separation of $B{:}$ and $H{:}S$ and the changes in solvation that accompany these processes. In general, the solvent molecules, especially if the solvent, like water, has unshared electrons and bonded hydrogen atoms, are strongly associated with each other and also with the acid. This system changes on ionization to strong association of solvent with $B{:}$ and $H{:}S$ mole-

cules. The action of the solvent is very much more than that of a dielectric medium for the separation of electrically charged particles.

The dissociation constant of an electrically neutral acid, especially in water, increases with the temperature, reaches a maximum, and then diminishes.[3] The decrease of the dissociation constant with temperature has been attributed to the decrease in the dielectric constant of water with increase in temperature.[4] This makes it increasingly difficult to separate oppositely charged ions, while the increase in the constant before reaching the maximum is attributed to the normal rise of equilibrium constant with temperature for an endothermic reaction. It is doubtful whether this explanation is sound.

A dissociation constant that rises to a maximum and then diminishes shows a reaction for which $\Delta\bar{H}$ (the heat absorbed) is positive at low temperature and diminishes with increasing temperature. At the maximum value of the dissociation constant, $\Delta\bar{H} = 0$. At higher temperatures $\Delta\bar{H}$ acquires a negative value.[5] However, a decrease in the dielectric constant does not explain a decrease in $\Delta\bar{H}$ for the separation of oppositely charged ions.

When ions are solvated by water, the process breaks down the associations of the water molecules among themselves to form new complexes around the ions. As the temperature is increased, the associations between the water molecules are broken down and the energy of solvation of the ions is increased to the extent that heat energy has been expended on the breaking up of the water complexes. Thus it seems that the temperature variation of acid strength should be considered as an effect of the ions on the water rather than an effect of the water on the ions.

The thermodynamic equation $-RT \ln K = \Delta F = \Delta H - T\Delta S$ connects the equilibrium constant, the free energy change, the heat content change, and the entropy change of a reaction. A relation between any of these quantities and the structure of the reacting molecules may be sought. In the dissociation of acids it would seem that the free energy change is probably the easiest to correlate with the structure of the molecules. It has been suggested that these correlations should not be attempted at a fixed temperature, but

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[3] Harned, H. S., and Embree, N. D., *J. Am. Chem. Soc.*, **56**, 1050 (1934).

[4] Baughan, E. C., *J. Chem. Phys.*, **7**, 951 (1939); Gurney, R. W., *J. Chem. Phys.*, **6**, 499 (1938); Kirkwood, J. G., and Westheimer, F. H., *J. Chem. Phys.*, **6**, 506, 513 (1938).

[5] Pitzer, K. S., *J. Am. Chem. Soc.*, **59**, 2365 (1937).

that a separate temperature should be used for each acid, namely the temperature at which the dissociation constant has a maximum value.[3] To be useful, the correlation would have to be both for the value of the maximum dissociation constant and the temperature of this maximum, for these quantities are not simply related to each other. On the whole the simple correlations between structure and acidic strength at a fixed temperature are more practical and informative.

When the strengths of hydrogen acids are compared in the same solvent and at the same temperature, one obtains a fairly good estimate of the relative strengths of the bonds between the protons and the unshared electron pairs of the conjugate bases, towards an ionic break. In general, some acid is chosen as a reference acid, and the difference between the free energy of ionization of a derived acid and that of the reference acid is used as a measure of the influence of the substituent groups on the ionization.

This difference,

$$RT \ln K_{B_u:H} - RT \ln K_{B:H},$$

is the free energy for the reaction

$$B{:}H + {:}B_u \rightleftarrows B{:} + B_u{:}H,$$

in which B_u:H stands for the chosen reference acid and B:H for the derived acid, and equals

$$(\bar{F}^\circ_{B:} + \bar{F}^\circ_{B_u:H}) - (\bar{F}^\circ_{B:H} + \bar{F}^\circ_{:B_u}) = (\bar{F}^\circ_{B:} - \bar{F}^\circ_{B:H}) + (\bar{F}_{B_u:H} - \bar{F}^\circ_{:B_u}).$$

It no longer contains the free energies of hydrogen ion and the solvent. But the influence of the solvent has not been entirely eliminated.

At a fixed temperature, $RT \ln K$ is proportional to $\log_{10} K$, so that the effect of structural changes can be expressed in terms of $\Delta \log_{10} K_\sigma$, where the subscript σ, indicates the structural change, when comparisons are all made at the same temperature.[6] Sometimes the symbol pK is used to indicate the strength of an acid. The equation is

$$pK = -\log K_a.$$

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[6] In the future we shall use log when the base of the logarithm is 10, and ln for natural logarithms.

The effect of a structural change can then be measured by ΔpK. Then

$$\Delta pK_\sigma = \log K_u - \log K_\sigma = -\Delta \log K_\sigma .$$

The value of ΔpK is negative when the structural change increases the acidic strength. We shall use $\log K$ and $\Delta \log K$ rather than pK and ΔpK; and when any quantity is used to indicate the effect of a structural change, we shall define it so that it has a positive value when the structural change increases the strength of the acid, or in general has the effect of a positive charge.

The value of $\Delta \log K_\sigma$ does not depend solely on the structural change. It depends also on the temperature and solvent, and if, as it is often convenient to do, we consider the substitution of one group for another as a sufficiently defined structural change, $\Delta \log K_\sigma$ depends on the acid chosen for reference, and the position of the substitution in the molecule of this acid. Often these variations do not change the relative values of $\Delta \log K_\sigma$ for a set of structural changes, but only their magnitudes. In such cases $\Delta \log K_\sigma$ can be expressed as a product of two quantities, one characteristic of the structural change and the other of the temperature, solvent, reference acid, and position of substitution. Thus, if we consider that a structural change is sufficiently defined by the substitution of a group for a hydrogen atom, a set of groups has a one-to-one correspondence to a set of structural changes. If the reference acids are various fatty acids, the $\Delta \log K_\sigma$ values depend on the reference acid and more particularly on the position of the substitution with respect to the carboxyl group, but their relative values for the set of groups are fairly constant as we change the position of substitution, and a common factor of the $\Delta \log K_\sigma$ characteristic of the structural changes can be found. The other factor is determined by the temperature, solvent, reference acid, and position of substitution. However, in other cases the relative values of $\Delta \log K_\sigma$ for a set of structural changes sometimes vary considerably with the choice of solvent, reference acid, and position of substitution, and hence the sign of a $\Delta \log K_\sigma$ may be changed by these variations. For instance, substitution of chlorine for iodine has a positive $\Delta \log K_\sigma$ in hypoiodous acid, but a negative one in *p*-iodobenzoic acid.

23b. Mechanism for the description of intramolecular action; division into contributing factors. The lack of consistency in $\Delta \log K_\sigma$, and other effects produced by structural changes, leads one to the conclusion that these effects arise from more than one cause. These different factors all influence the free energies of the acids and their

ions or conjugate bases, and the sum of their individual effects is the net effect of the structural change on the free energy. The $\Delta \log K_\sigma$ value is proportional to sums and differences of the free energies involved, so that it may be expressed as the sum of the effects of the various factors of intramolecular action. The most important of these component effects are those due to (1) a polarizing source in the molecule arising from a formal charge or unevenly shared bond electrons, (2) resonance in the molecule, (3) the repulsion between atoms that are close together but not bonded, (4) the polarizability of bonds, and (5) the interaction with solvent molecules. They may be named and symbolized as follows: (1) the polar or inductive effect, **I**, (2) the resonance effect, **R**, (3) the steric hindrance effect, **H**, (4) the polarizability effect, **P**, and (5) the solvent effect, **S**. Then

$$\Delta \log K_\sigma = \mathbf{I}_\sigma + \mathbf{R}_\sigma + \mathbf{H}_\sigma + \mathbf{P}_\sigma + \mathbf{S}_\sigma . \qquad (3)$$

This subdivision of $\Delta \log K_\sigma$ into various effects is to a large extent artificial. Thus from the treatment of resonance in Chapter IV it is apparent that the separation of polar and resonance effects depends on the method of approaching the problem, and whether the bond dipole is taken as a property of the bond or the result of resonance. Further, any of these effects are themselves affected by other factors, e.g., the dependence of polar effects on polarizability, and of resonance on steric factors. Nevertheless the subdivision of $\Delta \log K_\sigma$ into the various effects is of some value in clarifying our ideas and bringing out the relationships between $\Delta \log K_\sigma$ and structural changes. For this purpose the most important effects are the polar and resonance ones, so that in our treatment we shall, very largely, use $\Delta \log K_\sigma = \mathbf{I}_\sigma + \mathbf{R}_\sigma +$ other effects, using the other effects to explain many of the anomalies that are observed. At present $\mathbf{I}_\sigma$ and $\mathbf{R}_\sigma$ can be given only semiquantitative connotations.

For any given structural change the sign given to a component effect depends on how it is defined. As before, we shall define an effect so that its sign is positive if it increases the strength of the acid. The inductive effect was first defined in England and, unfortunately, it is there used so that it is negative when it increases acidic strength. This usage is not universal in America.[7] Apart from any question of nationality, we shall continue to use inductive and all other effects so that they are positive when they are acid-strengthening.

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[7] Johnson, J. R., "Modern Electronic Concepts of Valence", p. 1617 of *Organic Chemistry*, by H. Gilman. John Wiley & Sons, New York, 1938.

The *polar* or *inductive effect* tends to make an acid stronger than the reference acid when the structural change increases the positive potential at the point of dissociation. When the structural change is the addition of a group to a pair of unshared electrons on an atom in the reference acid, the formal charge of this atom is increased. For such a change $\mathbf{I}_\sigma$ is positive. For instance, the structural changes

$$:\overset{+\,-}{S}O(OH)_2 \rightarrow \overset{-\,+\,+\,-}{O}:\overset{+\,+}{S}O(OH)_2,$$

$$:NH_2—CH—COOH \rightarrow H:\overset{+}{N}H_2—CH_2—COOH,$$

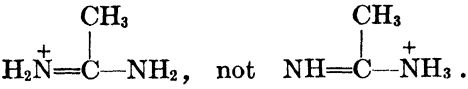
$$\text{and } :\overset{-}{O}—\overset{O}{\overset{\|}{C}}—COOH \rightarrow H:O—\overset{O}{\overset{\|}{C}}—COOH$$

are all acid-strengthening. The opposite type of addition, in which the reference acid is the acceptor and the addend the donor, has the reverse effect. For the removal of atoms from a reference acid, $\mathbf{I}_\sigma$ is positive or negative, according to whether the removed atom carries the pair of bond electrons with it or leaves them on the acid. In substitutional changes, $\mathbf{I}_\sigma$ is positive or negative according to whether the new bond dipole is more or less positive towards the point of dissociation than the old one. Thus $ClCH_2COOH$ is stronger than CH_3COOH because the bond dipole of Cl—C is more positive at the carbon pole than that of H—C.

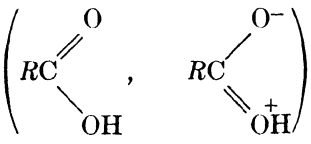
The *resonance effect* makes an acid stronger when the resonance energy introduced with the structural change is greater in the ion than in the acid. One of the most important resonance effects on acid strengths occurs when the structural change introduces a double or triple bond next to the atom from which the proton dissociates. The resulting structure is $A{=}B{-}C{:}H$ for the acid and $A{=}B{-}C{:}$ for the conjugate base, and the latter is always a triad resonating structure. The sign of $\mathbf{R}_\sigma$ for this type of structural change is positive except when A has an unshared electron pair. In this case the acid $:A{=}B{-}C{:}H$ is in tautomeric equilibrium with $H{:}A{=}B{-}C{:}$. The latter is a strongly resonating structure. The proportion of this tautomer and its resonance energy can be so great that, on the average, there is more resonance in the acid than in its conjugate base, in which case there is a negative $\mathbf{R}_\sigma$ term in the observed $\Delta \log K_\sigma$. For instance, the change from

$$CH_3—CH_2—NH_2 \text{ to } HN{=}\overset{CH_3}{\overset{|}{C}}—NH_2$$

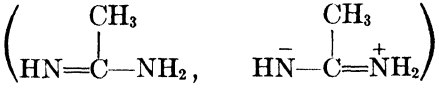
does not produce a weaker base, as the ion of the amidine is



Whether a resonance of the triad type strengthens or weakens the acid can be deduced from the position of formal charges in the resonating structures. For this purpose either the acid or its conjugate base may be used. When the secondary resonating forms show positive formal charges nearer to the dissociating proton than the negative ones, the resonance strengthens the acid. Thus in



the positive formal charge in the secondary form is nearer the proton than the negative one, and the resonance strengthens the acid. On the other hand, in



the proton adds to the imino nitrogen, which has a negative formal charge in the secondary form, and the resonance is base-strengthening.

Steric hindrance effects arise when the bonding together of the atoms into a molecule imposes spatial relationships on atoms that are not bonded to each other. In this way atoms are sometimes brought so close together as to encounter large repulsive forces. The free energy of the molecule includes terms for the potential energies resulting from these forces. The change in these terms accompanying a change in structure may be different in the acid and in the ion or conjugate base. Consequently $\Delta \log K_\sigma$ for a structural change may include steric terms. This effect can be considered as a pure steric hindrance effect, for which a separate term, $\mathbf{H}_\sigma$, in $\Delta \log K_\sigma$ is needed. However, steric hindrance often acts indirectly through its influence on polar and resonance effects.

Resonance and its effects depend to a great extent on spatial configuration and this is governed by the repulsions between groups. Examples of the effect of steric hindrance on resonance are given in the sections on dipole moment and on color, and examples of similar effects on acid strength are mentioned later in this chapter.

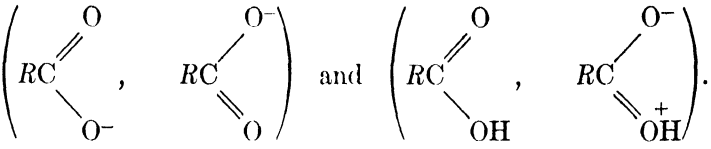
Polar effects are transmitted through space as well as inductively through the atomic chain. These effects depend on the distance between the polar group and the dissociating proton. This distance varies with the various configurations produced by rotation about the single bonds. When rotation is sufficiently free to prevent the isolation of isomers, the different configurations exist in an equilibrium which largely favors forms in which the repulsions between non-bonded atoms are small. When these favored configurations bring highly polar groups near the dissociating protons, the directly transmitted polar effects are large. In this way steric hindrance can change the value of I_σ.

Polarizability effects can to a great extent be identified with the transmission of polar effects through the molecule. Hence, if a strongly polar group is present and a structural change increases the polarizability of that part of the molecule between the polar group and the dissociating proton, the effect of the polar group is increased. This increase can easily be considered as part of the polar effect and included in I_σ. However, quite apart from the effect of a polar group, a change in the polarizability of a molecule affects the dissociation constant. When the polarizing power of the acidic group is greater in the conjugate base than in the acid, increase of polarizability increases acidic strength. It is not, however, always clear whether the effects of highly polarizable groups are due to this cause or to their own polarizing power.

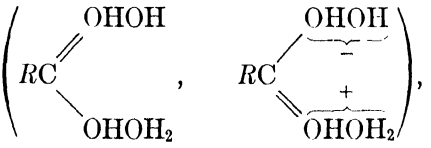
Double and triple bond groups are more polarizable than saturated groups. Resonance can enhance polarizability.

The *solvation effect* on the dissociation of an acid is very great, but its importance is greatly diminished when the relative dissociations of acids is considered, more especially when all the dissociation constants are measured in the same solvent.

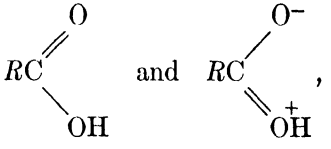
The difference in solvation energy of an acid and its ion is not the same for all acids, so that $\Delta \log K_\sigma$ may be considered to have a solvation term. This term varies markedly with the solvent and is very important when comparisons of $\Delta \log K_\sigma$ values are made in different solvents. However, when comparisons are restricted to a single solvent, the solvent effect may be included to a large extent in one of the other effects. When a structural change introduces a resonance, as for instance the change from CH_3OH to HCOOH, the effect of this resonance on $\Delta \log K_\sigma$ depends on the solvent. The resonance effect is the difference in the energy of the resonances



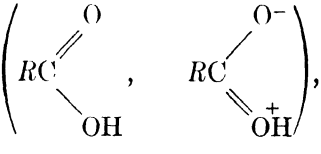
If the molecules are dissolved in water, the resonating structures are solvated. The resonance in the acid might be depicted as



or between even more hydrated forms. The energy difference between these forms is not the same as that between



and the resonance energy is also different. But as long as no other solvent is considered, and the structural change necessitates this solvation, there is no need to separate the effect of the resonance into the resonance itself,



and the effect of solvation on this resonance.

Similarly, when a structural change is the replacement of one polar group by another, the old and the new groups are solvated, and there is a change in these solvations with conjugation. But the structural change can be considered as the replacement of one solvated group by another. This influence of the solvent can be included in the polar effect for the exchange of groups as long as the comparisons are restricted to a single solvent. Even then some anomalous effects can be attributed to solvation. The solvation of a group in an acid is affected by the rest of the acid, and may be different for the same group in different acids even though the same solvent is used.

The *effect of tautomerism* on the observed dissociation constant of an acid is to introduce a complicating reaction whose equilibrium is established in addition to that of the dissociation. The measured equilibrium constant involves the sum of concentrations of tautomers in place of concentrations of definite compounds. Structural changes may not affect the equilibria of the tautomerisms in the same way as that of the acidic dissociations, and hence the observed dissociation constants show very anomalous effects of the groups. For instance, $H_2N—CH_2—COOH$ is a tautomeric substance, and if its measured dissociation constant is compared with that of CH_3COOH, the substitution of NH_2 for H appears to be a structural change for which $\Delta \log K_a$ is about -5. In a comparison between $H_2N\overset{+}{N}H_3$ and $H\overset{+}{N}H_3$ the same structural change has a $\Delta \log K_a$ value of about $+1$.

The general theory of the dissociation constants for tautomeric acids is the same as that for any equilibrium constant of tautomeric substances. The observed constant is given by

$$K = \frac{[H^+]\{[\text{ion}] + [\text{ion}']\}}{[\text{acid}] + [\text{acid}']},$$

and the two tautomeric equilibrium conditions are

$$K_1 = \frac{[\text{ion}']}{[\text{ion}]} \quad \text{and} \quad K_2 = \frac{[\text{acid}']}{[\text{acid}]}.$$

The true dissociation constants are

$$K_a = \frac{[H^+][\text{ion}]}{[\text{acid}]} \quad \text{and} \quad K_a' = \frac{[H^+][\text{ion}']}{[\text{acid}']}.$$

The true dissociation constant can then be expressed in various ways as a function of the other constants: e.g.,

$$K_a = K\frac{1 + K_2}{1 + K_1},$$

or more generally, if many tautomers exist:

$$K_a = K\frac{1 + K_2 + K_2' + \cdots}{1 + K_1 + K_1' + \cdots}. \tag{4}$$

Often, in the dissociation of tautomeric acids, either K_2 or K_1 can be neglected with respect to unity, and

$$K_a = K(1 + K_2) \quad \text{or} \quad K_a = \frac{K}{1 + K_1}.$$

Thus in the dissociation of H_2NCH_2COOH the tautomerism is restricted to the acid, and $K_a = K(1 + K_2) = KK_2$, as K_2 is very large $\left(K_2 = \frac{[\overset{+}{H_3}NCH_2CO_2^-]}{[H_2NCH_2CO_2H]}\right)$. The true dissociation constants can be calculated from the observed constants when there is any method of obtaining the tautomeric equilibrium constant. The method[8] of obtaining the true dissociation constants of aminoacetic acid is interesting. The true equilibrium constant of the reaction

$$\overset{+}{H_3}NCH_2COOH \rightleftarrows H^+ + H_2NCH_2COOH$$

by the same reasoning as above is

$$K_{at} = \frac{K_i}{1 + K_2}$$

where K_{at} and K_i are the true and observed equilibrium constants for this reaction, but K_2 is the constant of the same tautomerism

$$H_2NCH_2COOH \rightleftarrows \overset{+}{H_3}NCH_2COO^-$$

that is involved in the dissociation of the amino acid. K_{at} is taken as equal to the dissociation constant of

$$\overset{+}{H_3}NCH_2COOCH_3 \rightleftarrows H^+ + H_2NCH_2COOCH_3,$$

by assuming that $\Delta \log K_\sigma$ is negligible for the structural change,

$$\overset{+}{H_3}NCH_2COOH \rightarrow \overset{+}{H_3}NCH_2COOCH_3.$$

The value of K_2 can then be used to calculate K_a for aminoacetic acid from the observed dissociation constant.

Exactly the same methods can be used when equilibrium reactions for combination with the solvent or with added substances are involved. In this way it can be shown that when an added substance combines more completely with the ion than the acid, it increases the observed acid strength. Thus glycerol or mannitol combines more completely with $B(OH)_2O^-$ than with $B(OH)_3$, and so increase the apparent acidity of boric acid. Whether dealing with a group interaction or one between molecules, the same rule applies. A potential-energy-diminishing interaction is acid-strengthening if it is greater in the ion than in the acid. This rule also applies to the

[8] Ebert, L., *Z. physik. Chem.*, **121**, 385 (1926).

effects of the component factors of group interaction—inductive, resonance, steric hindrance, polarizability, and solvation effects, or any other better or worse subdivision of the interaction.

There is a special type of tautomerism that can be called imaginary tautomerism, in which the two isomers are indistinguishable; e.g.,

$$HO—CH=O \rightleftarrows O=CH—OH.$$

The equilibrium constant is necessarily unity. For these acids

$$K_a = K(1 + 1)$$

or

$$K_a = K\frac{1}{1+1},$$

according to whether the tautomerism exists in the acid or its conjugate base. More generally,[9]

$$K_a = K\frac{m}{n}, \tag{5}$$

where m is the number of equivalent forms of the acid and n that of the ion. The ratio of the number of forms of the acid to the number of forms of the ion is equal to the ratio between the number of equivalent atoms in the ion to which the proton can return and the number of equivalent protons in the acid. For this reason m can be redefined as the number of equivalent atoms in the ion to which the proton can return and n as the number of equivalent protons in the acid. The effect of group interaction is on K_a, so that, when necessary, $\Delta \log K_\sigma$ should be corrected for the effects due to any change in the numbers of the equivalences produced by the structural variation. Thus $\Delta \log K_\sigma$ for the change CH_3COOH to $CH_2(COOH)_2$ is not a true measure of the effect of substituting a carboxyl group for a hydrogen atom on the dissociation of acetic acid. The measured $\Delta \log K_\sigma$ is equal to

$$\mathbf{I}_\sigma + \mathbf{R}_\sigma + \mathbf{H}_\sigma + \mathbf{P}_\sigma + \mathbf{S}_\sigma + \log 2.$$

In general,

$$\Delta \log K_\sigma = \mathbf{I}_\sigma + \mathbf{R}_\sigma + \mathbf{H}_\sigma + \mathbf{P}_\sigma + \mathbf{S}_\sigma + \log\frac{n}{m}.$$

[9] Bjerrum, N., *Z. physik. Chem.*, **106**, 219 (1923).

24. ACIDS WITHOUT RESONANCE

In general, acids with no double bonds have little resonance in either the acid or its ion. There are a large number of acids of this type whose dissociation constants in water have been measured, and this collection of data covers the range from $K = 10^{-16}$ to $K = 10^{-1}$—a change of about 20 kcals. of free energy. If we content ourselves with an accuracy of about 1 kcal., this work is available for a study of polar effects by neglecting resonance, steric hindrance, and other effects. Solvation effects are to a large extent eliminated by confining comparisons to the single solvent, water, but as these acids involve such a large variety of elements and relative solubilities, the solvent effect must still remain a large perturbation. However, when this becomes very large it may result in chemical combination, and independent evidence of this may be obtained. Thus for H_2TeO_4 there is a very large S_σ, but there is ample evidence that in aqueous solution telluric acid is H_6TeO_6 and for this formula S_σ is negligible.

When the acids become strong ($K = 10^{-1}$), the reaction with the solvent,

$$B{:}H + {:}OH_2 \rightleftarrows B{:} + H{:}\overset{+}{O}H_2,$$

is so complete that group-interaction effects are negligible. This limits the range of acid strengths at one end. The other end is also limited by a solvent reaction,

$$B{:} + H{:}OH \rightarrow B{:}H + {:}OH^-.$$

The concentration of B: cannot be raised to measurable values without using such high concentrations of B:H and OH^- that the solvent has been greatly changed. These limits apply to all types of acids in aqueous solution.

The inductive effect arises from the ionic contribution to a bond. If it is assumed as a first approximation that the substitution of a hydrogen atom by another element always changes the polar character of the bond to the same extent, each element may be given an inductive effect relative to hydrogen as a standard. The element replacing the hydrogen is assumed to have its other bonds attached to hydrogen atoms, so that the inductive effect of further substitution can be evaluated from the nature of the next substituent. Thus if we start with H_nA and change to $H_mB{-}AH_{n-1}$, an inductive effect characteristic of B is introduced, and when $H_mB{-}AH_{n-1}$ is changed to $H_oC{-}BH_{m-1}{-}AH_{n-1}$, another inductive effect characteristic of C is introduced. However, the effect of C at any point

past B is reduced in passing through B, the reduction being dependent on the polarizability of B and the nature of the bonds from B. The effect of C on points past B arises from the polarization induced in the B-to-A bond by C. In a chain of similar atoms this reduction is by the same fraction for each member of the chain.

If in one of these compounds a hydrogen ion is added or removed, a positive or negative formal charge is put on the atom, and an inductive effect characteristic of the formal charge is added. Presumably the magnitude of the effects of positive and negative formal charges are the same, but the signs are opposite. The inductive effects of formal charges on any distant atom will diminish in the same way as those of substituent groups with each intervening atom.

When the kernel charge of the atom is high, the bonding electrons will be drawn toward that atom more than they are by a hydrogen. Such an atom is said to have a high positive I effect. Further, as the electronegative character of the elements tends to decrease with the number of electron shells, the positive inductive effect should decrease in the same way. Thus fluorine, with its high kernel charge and small size, should be the most effective element in producing an inductive effect in which electrons are drawn towards it.

In general, inductive effects should be additive, though this must be limited by saturation effects, and be less than additive as they assume very large proportions.

In a hydroxyl compound, the inductive effects of substituent atoms and formal charges tend to change the polar character of the oxygen to hydrogen bond. As the hydrogen-ion character of the bonded hydrogen atom increases, the acid becomes stronger. Multiplied by 2.3 RT, an inductive effect becomes a potential and has the dimensions of free energy, and may be added to the free energy of ionization of the parent acid to give the free energy on ionization of the derived acid. Or, if the acids are compared at the same temperature, the inductive effects may be given such relative values that they may be added to the logarithm of the dissociation constant of the parent acid to give that of the derived acid.

In view of the complexity of solvent effects on relative strengths of acids, and the common occurrence of complex resonances in the acids and their ions, it is not of much value to attempt to separate the inductive and the direct effects of formal and kernel charges, or to attempt to consider the consequences of saturation of the inductive effect. Further, inductive effects assumed for the calcula-

tion of the strengths of acids in any particular solvent are characteristic of the solvent as well as of the groups producing them, for no bond can be exactly the same in all environments. We shall not attempt to introduce different polarities for different intervening atoms, but assume the transmission across singly bonded atoms to be always the same, and to be much feebler than those across double bonds and resonating groups.

It is, however, possible to calculate the strengths of a large variety of saturated acids derived from water on the above assumptions with an accuracy of a power of ten. This degree of accuracy is of some practical importance, but its chief value is to suggest that some other important factor is present in those cases in which the calculation fails.

If an acid derived from water is taken as

$$H_pD—CH_o—BH_m—AH_n—O—H,$$

or any branched chain, the free energy of dissociation is approximately given by taking that of water and adding a term characteristic of A for the inductive effect due to the replacement of a hydrogen atom by A, then adding another term characteristic of B multiplied by a fraction for its transmission through a saturated atom, then adding another term characteristic of C twice multiplied by the above fraction, and similarly, terms for the inductive effects of D and any other substituent groups. If any of the atoms have formal charges, then terms characteristic of a formal charge, multiplied by the transmission fraction for each intervening atom, must also be added. If all the terms are divided by 2.3 RT, the sum becomes the common logarithm of the dissociation constant and each term becomes a dimensionless inductive constant. This process leads to the equation

$$\log K = \log K_{H_2O} + \sum_{\text{atoms}} I_a \alpha^i + \sum_{\text{charges}} I_c \alpha^i \qquad (6)$$

in which I_a is an inductive constant for each atom other than hydrogen, α is the fraction that reduces the inductive effect for each transmission across an atom, i is the number of atoms separating the inducing atom from the hydroxyl group, and I_c is the inductive constant for a formal charge.

In this equation the dissociation constant for water should have the same form as that of other acids, so that K_{H_2O} is $\frac{[H^+][OH^-]}{[H_2O]}$ and

its value at 25°C. is not 10^{-14} but 2×10^{-16}. In the preceding section it was shown how the number of equivalent ionizing hydrogen atoms in the acid and the number of equivalent atoms to which it can return in the ion affect the dissociation constant. As there are two ionizable hydrogen atoms in a water molecule, log K_{H_2O} can be replaced by log $\frac{1}{2}K_{H_2O}$, which is equal to -16, and a correction added to the equation to take care of this multiplicity effect in the derived acid.

When this correction is introduced into equation 6, it becomes:

$$\log K = -16 + \sum I_a \alpha' + \sum I_c \alpha' + \log \frac{n}{m} \qquad (7)$$

in which n is the number of ionizing hydrogen atoms in the acid and m is the number of equivalent charged oxygen atoms in the ion.

The following table gives the inductive constants for water at 25°C. and the value of α.

TABLE 22

INDUCTIVE CONSTANTS FOR ELEMENTS AND FORMAL CHARGE

α	$= \frac{1}{2.8}$	I_S	$= +3.4$
		I_{Se}	$= +2.7$
I_{charge}	$= \pm 12.3$	I_{Te}	$= +2.4$
I_{Cl}	$= +8.5$	I_N	$= +1.3$
I_{Br}	$= +7.5$	I_P	$= +1.1$
I_I	$= +6$	I_{As}	$= +1.0$
I_O	$= +4$	I_C	$= -0.4$

Since these constants are valid in resonating compounds when the substituent group is insulated from the resonating acidic group, their values are not chosen from a study of non-resonating acids only. The chief difference this makes is that the values chosen for the halogens are more nearly equal than they would be if only non-resonating acids had been considered.

Using the constants given in Table 22, and equation (7), which assumes that resonance, steric hindrance, polarizability, and solvation effects either are negligible or can be included in the polar effect, we have calculated the log K values for a wide range of acids derivable from water. Except in a few instances the acids chosen are those whose accepted formulas would indicate no resonance. Where we have deviated from this rule the formula given for the acid is a form without double bonds, and the log K is calculated from the formula shown. The results of these calculations and the observed values

of log K are shown in Table 23.[10] In general, the agreement between calculated and observed value is sufficiently close to justify the assignment of empirical constants for the effective polarities of various elements and of a formal charge. There are, however, some striking anomalies that warrant further discussion.

24a. Discussion of special cases. The dissociation constants of strong acids are not strictly comparable with those of weak ones. The levelling effect of the solvent makes a solution of a strong acid one in which the solvent, acting as a base, has practically completely neutralized the acids to form a salt. The dissociation of the acid is then the same as that of any other strong electrolyte. The calculated values are not limited in this way, and show large differences in the strengths of strong acids. Thus the calculations show that perchloric acid is much stronger than sulfuric acid. This difference cannot be observed in water solution, but in the more acidic solvent, acetic acid, perchloric acid is more highly dissociated than sulfuric acid.

The calculations exaggerate the differences between strong acids. There should be a tendency for polar effects of groups to increase less rapidly than the calculated values when the sum of the inductive constants of the component parts becomes very great (a saturation effect). The polarity of the A—O bond in A:OH depends on the relative contributions of the ionic forms, $A\overset{-}{:}\overset{+}{O}$ and $\overset{+}{A}:\overset{-}{O}$. When the polarity of A is very great, the contribution of the ionic form $\overset{+}{A}:\overset{-}{O}$ disappears, and further increase in the polarity of A has a diminished effect on the bond. As oxygen is a strongly electronegative element, the contribution of the ionic form $\overset{+}{A}:\overset{-}{O}$ is normally great and a considerable polarity of A is needed for saturation. The agreement between calculated and observed values suggests that this saturation effect is not reached for oxygen before the levelling

[10] With very few additions and corrections, the experimental values have been taken from Landolt and Börnstein's Tables. The formulas given are those from which the calculated values are obtained. In some instances unsatisfactory formulas $\left(\text{e.g., } \begin{matrix} & & & \overset{+}{C} & \\ H-O- & & & | & -O^- \\ & & & H & \end{matrix}\right)$ have been chosen for purposes of comparison. Except where especially noted, the calculations are made on the assumption that the hydroxylic hydrogen atom marked with a bond, and those equivalent to it, dissociate.

effect of water sets in, but in the strong acids it would be expected. For the bonds of less electronegative elements than oxygen, this saturation of polar effects should be noticeable in weaker acids. It will be seen later that there are phenomena which point to this saturation effect existing in carbon bonds.

In a strong acid derived from water there may be two or more positive formal charges on the atom attached to the hydroxyl group. Where this atom can increase its valence shell beyond eight electrons, which is possible for all known strong acids of the type $(O^-)_nA^{+n}(OH)_p$, the atom A has strong acidic properties, and, apart from the dissociation of the proton, the acid can be neutralized by water. The reaction is

$$(O^-)_nA^{+n}(OH)_p + mH_2O \rightleftarrows (O^-)_{n-m}A^{+(n-m)}(OH)_{2m+p}.$$

The effect of this reaction must be considered to be beyond the range of solvation effects that are included in the sum of the inductive constants for the solvated component parts of the group $(O^-)_nA^{+n}(OH)_{p-1}$. When the compound formed with any particular value of m is the predominant form of the acid, the dissociation constant can be calculated from the formula of this compound. Thus telluric acid would be assumed to be strong were its dissociation constant calculated from the formula $(O^-)_2Te^{+2}(OH)_2$; but the observed value corresponds to the formula $Te(OH)_6$.

This tendency for the central atom to be neutralized by water increases with its formal charge, and with the size of the valence shell. It can therefore result in the acid of an element in a higher state of oxidation being weaker than a less oxidized acid. Thus telluric acid is weaker than tellurous, and periodic acid is weaker than iodic acid.

Even when the hydroxylation of a positively charged atom has not proceeded to an extent beyond the formation of four equivalent bonds, it is to be expected that the interaction with water becomes very large, and tends to limit the inductive effect as the formal charge is increased. Thus the second dissociation of H_2SO_4 is less than that calculated for $(O^-)_3S^{+2}OH$, but greater than that calculated for $(O^-)_2S^+(OH)_3$. This cannot be attributed to an equilibrium between the two forms, since the exchange of heavy oxygen between sulfate ion and water is slow.[11]

Nitrous and formic acids have higher dissociation constants than those calculated for them. These acids are not generally classed with the oxygen acids of heavier elements. A distinction is generally

[11] Datta, S. C., Day, J. N., and Ingold, C. K., *J. Chem. Soc.*, 1968 (1937); Mills, G. A., *J. Am. Chem. Soc.*, **62**, 2833 (1940).

made in the formulas of these two classes of acids. Nitrous and formic acids are represented with neutral atoms and doubly bonded oxygen. In the formulas of phosphoric, sulfurous, cacodylic acids, etc., the double bond is replaced by a semipolar double bond. According to the theories developed in Chapters III and IV, the distinction between these two classes of acids is one of degree and not of kind. Both classes of acids and their respective ions can be represented by the resonances

$$(^{-}O—A^{+}—OH,\ O{=}A—OH,\ ^{-}O—A{=}\overset{+}{O}H)$$

and

$$(^{-}O—A^{+}—O^{-},\ O{=}A—O^{-},\ ^{-}O—A{=}O).$$

TABLE 23

DISSOCIATION CONSTANTS OF NON-RESONATING ACIDS

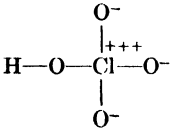
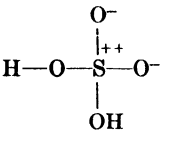
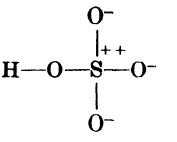
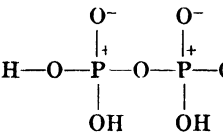
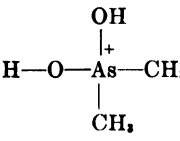
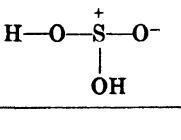
Acid	Log K_a (Observed)	Log K_a (Calculated)
	strong	+20.0
	strong	+7.4
	−1.7	+2.5
	−1.0	−0.7
	−1.5	−1.1
	−1.8	−1.8

TABLE 23—*Continued*

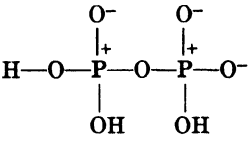
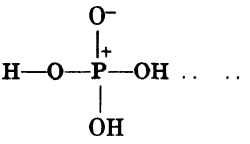
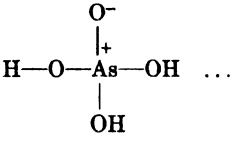
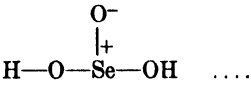
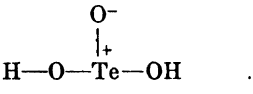
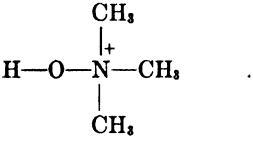
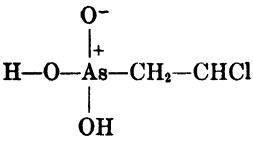
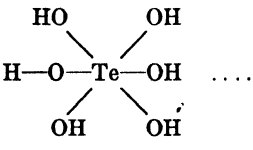
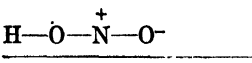
Acid	Log K_a (Observed)	Log K_a (Calculated)
	−2.0	−1.9
	−2.1	−2.5
	−2.4	−2.6
	−2.5	−2.5
	−2.5	−2.8
	−3 ± 1[a]	−2.8
	−3.8	−4.0
	−6.2	−5.7
	−3.3	−5.6

TABLE 23—*Continued*

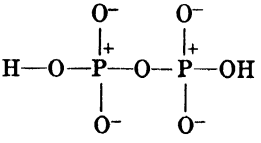
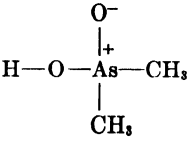
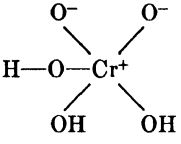
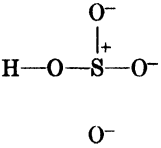
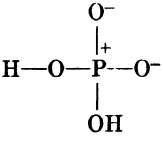
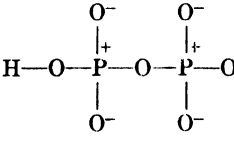
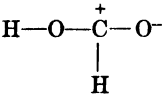
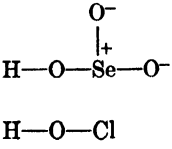
Acid	Log K_a (Observed)	Log K_a (Calculated)
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	−6.2	−6.2
	−6.2	−6.6
	−6.9[b]	−6.7
	−6.9	−7.3
	−8.4	−7.3
	−3.8	−7.3
	−7.4	−7.4
	−7.3	−7.5

TABLE 23—*Continued*

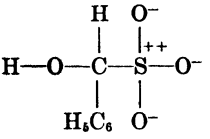
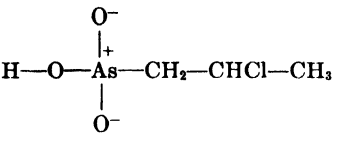
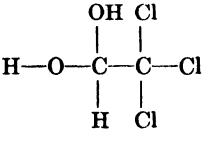
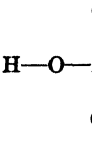
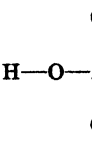
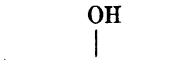
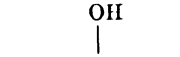
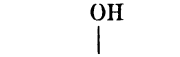
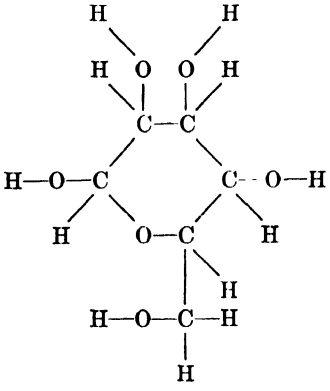
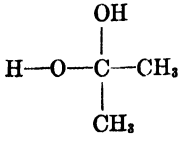
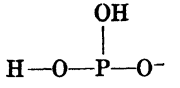
Acid	Log K_a (Observed)	Log K_a (Calculated)
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	−8.7	−8.5
	−9.5[c]	−8.9
	−8.4	−8.9
	−10.5	−10.0
	−1.2	−11.6
	−11.2	−11.6
	−9.2	−11.7
	−11.7	−11.7
	−12	−12.1
	−11.5	−12.2

TABLE 23—*Concluded*

Acid	Log K_a (Observed)	Log K_a (Calculated)
	−9.2	−12.6
	−13	−12.6
	−1.5	−13.2
	−12.4	−13.5[d]
	−14	−14.8
	−4.7	−16.4

[a] Estimated from the general properties of the base.

[b] The value −5 3 in the tables has been ignored. This value is taken from Kolthoff, I. M., *Chem. Wiekbl.*, **16**, 1154 (1918), and is the only value that agrees with the measurements of Donnally and Stewart.

[c] Donnally, L. H., and Stewart, T. D., *J. Am. Chem. Soc.*, **54**, 3559 (1932). The calculated value includes a polar constant of 2 for the phenyl group.

[d] The inductive effects have been assumed to act through both sides of the ring. The calculation includes the contributions from all the hydroxyl hydrogen atoms. The hydrogen atom at the extreme left of the formula dissociates more than any other.

However, double bonds are very much less stable for atoms having more than two electron shells than for atoms of the second period of elements. Again, when A is a second-period element, A has only six electrons in $^{-}O—A^{+}—OH$ and $^{-}O—A^{+}—O^{-}$, but completes its octet when the double bond is formed, whereas for the higher elements the atom A has an octet in $^{-}O—A^{+}—OH$ or $^{-}O—A^{+}—O^{-}$, and obtains more than eight electrons when the double bond is formed. For these reasons, in formic and nitrous acids, the main forms for acid and ion are the resonating couples ($O{=}A—OH$, $^{-}O—A{=}\overset{+}{O}H$) and ($O{=}A—O^{-}$, $^{-}O—A{=}O$), while in phosphoric, sulfurous, and similar acids the forms $^{-}O—A^{+}—OH$ and $^{-}O—A—O^{-}$ are more stable than those with double bonds, and fairly adequately represent the molecules. The latter class of acids can then all be treated alike as non-resonating acids, whereas nitrous and formic acids belong to the resonating acids. This type of resonance increases the strength of the acid, in fact, even more than would formal charges, for their actual dissociation constants are greater than those calculated from formulas of the type $^{-}O—A^{+}—OH$.

Boric acid has an anomalously high dissociation constant in comparison with the closely related acid $Al(OH)_3$. Both acids can be represented by the type formula

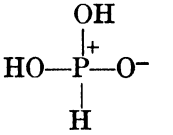
$$\left(\begin{array}{c} OH \\ | \\ HO—A—OH, \end{array} \quad \begin{array}{c} OH \\ |^{-} \\ \overset{+}{H}O{=}A—OH, \text{ etc.} \end{array}\right).$$

The double bond to the heavier atom, Al, is much less stable than that to the lighter atom, B. Hence for aluminum hydroxide the formula $Al(OH)_3$ is adequate, but boric acid must be considered as a resonating acid. A resonance of the type suggested for boric acid strengthens the acid beyond that which would be calculated from the formula $B(OH)_3$. This can be predicted from the resonating formula which tends to charge the hydroxyl groups positively with respect to the boron atom. The actual strength of boric acid is therefore greater than the value calculated from the classical formula $B(OH)_3$.

Phosphorous and hypophosphorous acids have long been considered much too strong to correspond to the formulas $P(OH)_3$ and $HP(OH)_2$ respectively. They have therefore been assigned the formulas

$$\begin{array}{c} OH \\ | \\ HO—P^{+}—O^{-} \\ | \\ H \end{array} \quad \text{and} \quad \begin{array}{c} H \\ | \\ HO—P^{+}—O^{-}. \\ | \\ H \end{array}$$

On this basis it must be assumed that the hydrogen ion dissociates from the oxygen rather than the phosphorus atom. If the hydrogen ion dissociated from the phosphorus atom of



the resulting ion would be the same as that of $P(OH)_3$, which is a tautomeric form of phosphorous acid.

The equilibrium constant of the tautomerism

$$\overset{+\ -}{H}PO(OH)_2 \rightleftarrows P(OH)_3$$

is given by the equation

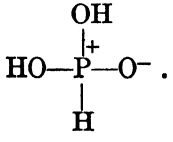
$$K = \frac{[P(OH)_3]}{[\overset{+\ -}{H}PO(OH)_2]} = \frac{K_a'}{K_a},$$

in which the square brackets represent the concentrations of the enclosed molecular species, K_a the acidic dissociation constant of $P(OH)_3$, and K_a' that of $\overset{+\ -}{H}PO(OH)_2$, assuming that the hydrogen attached to the phosphorus is dissociated. The observed dissociation constant for the acid would be given by the equation:

$$K_a^0 = \frac{[H^+][PO_3H_2^-]}{[P(OH)_3] + [\overset{+\ -}{H}PO(OH)_2]} = \frac{[H^+][PO_3H_2^-]}{[P(OH)_3] + [P(OH)_3]\dfrac{K_a}{K_a'}}$$

$$= \frac{K_a}{1 + \dfrac{K_a}{K_a'}}.$$

The dissociation constant would then have to be less than that expected from the formula $P(OH)_3$. Hence it is impossible to account for the high dissociation constant of phosphorous acid by assuming a dissociation of the hydrogen ion from the phosphorus in the tautomer



If one assumes that the hydrogen ions dissociated from $\overset{+\ -}{H}PO(OH)_2$ and $H_2\overset{+\ -}{P}O(OH)$ come from the hydroxyl groups, these structures

would explain the large discrepancies between observed and calculated values, even though they would not explain why these acids are stronger than the more oxygenated acid, phosphoric.

There is also a fundamental difficulty in explaining why $\overset{+-}{H}PO(OH)_2$ and $H_2\overset{+-}{P}O(OH)$ are stable with respect to $P(OH)_3$ and $HP(OH)_2$. The structure $\overset{+-}{H}PO(OH)_2$ represents phosphorous acid as a derivative of a very strong acid, phosphonium ion. This ion is so strong an acid that it needs a high pressure of HCl to prevent phosphonium chloride, PH_4Cl, from decomposing into PH_3 and HCl at room temperatures. Although the acidic strength of phosphonium ion would be reduced by the introduction of a negatively charged oxygen atom, as in $\overset{+-}{H}PO(OH)_2$, it is not conceivable that this process alone could make it a weaker acid than the simple trihydroxy acid $(HO)_3P$. But if the dissociation of hydrogen from the phosphorus atom of $\overset{+-}{H}PO(OH)_2$ is much greater than the dissociation of hydrogen ion from $P(OH)_3$, the tautomer $\overset{+-}{H}PO(OH)_2$ can exist only as a small fraction of the phosphorous acid, for

$$[\overset{+-}{H}PO(OH)_2] = [P(OH)_3]\frac{K_a}{K_a'},$$

and $\frac{K_a}{K_a'}$ is a very small fraction.

In order to explain the strength of phosphorous and hypophosphorous acids, it seems that it is necessary to assume a resonance that favors the attachment of hydrogen ion to phosphorus or a resonance that assists the dissociation of $P(OH)_3$. The possibility of both of these resonances exists.

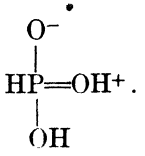
As has been explained previously, the semipolar bond is in resonance with a homopolar double bond, so that $\overset{+-}{H}PO(OH)_2$ is stabilized with respect to $P(OH)_3$ by the resonance

$$\left(\begin{array}{cc} O^- & O \\ | & \| \\ \overset{+}{H}P(OH)_2, & HP(OH)_2 \end{array} \right).$$

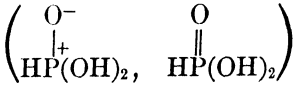
This resonance is exaggerated in the ions by additional forms: e.g.,

$$\left(\begin{array}{ccc} O^- & O & O^- \\ | & \| & | \\ \overset{+}{H}P-O^-, & HP-O^-, & HP=O \\ | & | & | \\ OH & OH & OH \end{array} \right).$$

In the acid, additional forms would also exist, but they would be less important, being forms of the type

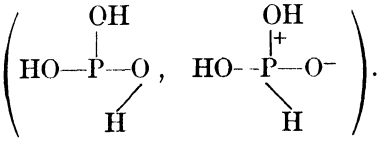


The greater number of these additional forms in the undissociated phosphoric acid than in phosphorous acid might account for the former being slightly weaker than the latter. The chief objection to the formula



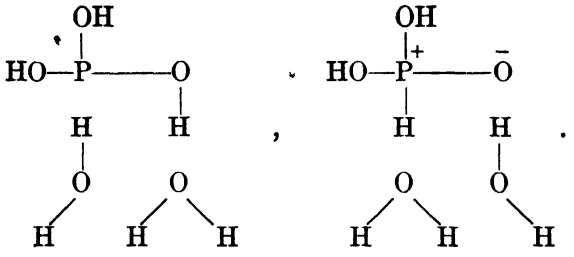
is that the weight of evidence seems to be against any marked contribution of the homopolar double bond in elements beyond the first period of eight. (See the discussion on the strengths of nitrous, formic, and boric acids, page 206.)

The alternate theory for the strengths of phosphorous and hypophosphorous acids is that a resonance exists in which a hydrogen ion is alternately bonded to an unshared pair of electrons on an oxygen atom and to a similar pair of electrons on the phosphorus atom: e.g.,



This resonance would be acid-strengthening, as the dissociating proton is nearer to the positive pole of the imposed dipole than to its negative pole. The third dissociation constant of phosphorous acid and the second one of hypophosphorous acid would be very small, as hydrogen atoms left in these ions would be tied up in the resonance. This type of resonance could not exist in phosphoric acid or sulfurous acid, the former having no free pair of electrons on the phosphorus, and the already positively charged sulfur atom of the latter not having much combining power for a proton.

In this simple form, the theory is not tenable owing to the lack of any single position for the hydrogen ion which would allow ready bonding to both oxygen and phosphorus atoms. However, this difficulty could be overcome by means of a bridge of water molecules or any amphoteric solvent. The resonance could then be represented by



In this formula two water molecules have been used; probably three are better.

It may be noted that these two resonance interpretations of the anomalous strength of phosphorous and hypophosphorous acids agree with each other, and with the older explanation, in attributing the great strengths of these acids to the combining power of the unshared pair of electrons on the phosphorus atom. They all agree on the paradox of an essentially basic configuration increasing acidic strength.

In arsenious acid the unshared pair of electrons on the arsenic atom has much less combining power than that on a phosphorus atom, and the enhancement of the acidic strength in arsenious acid is necessarily much less than that in phosphorous acid. In terms of log K, the difference between arsenious and phosphorous acids must be much greater than that between arsenic and phosphoric acids. These differences are, respectively, 8.0 and 0.3. The dissociation constant of arsenious acid is about a hundred times the calculated value. It would appear that even in arsenious acid a little of the anomaly noticed in phosphorous acid persists.

24b. The electrostatic method. Other methods for calculating the strengths of non-resonating acids have been devised. These attempt direct calculations of the effects of the formal charges on the potential at the point of dissociation. Thus Kossiakoff and Harker[12] assume a curve for the abnormally low dielectric constant in the neighborhood of the acid and calculate the work of removing the proton from the formal charges, using tetrahedral models of the atoms and accepted bond distances. Although these calculations give a variable factor for the different acids, there are also common factors such as the breaking of the O—H bond. These are obtained from the dissociation constant of phosphoric acid. They ignore all effects other than those of formal charges. For oxygenated acids

[12] Kossiakoff, A., and Harker, D., *J. Am. Chem. Soc.*, **60**, 2047 (1938).

with formal charges, their calculated values and the observed dissociation constants agree about as well as ours, but for less oxygenated acids their calculated values are less reliable. Thus their methods give almost identical values for H_3AsO_4, H_2RAsO_3, and HR_2AsO_2. This series of acids has a range of dissociation constants from $10^{-2.4}$ to $10^{-6.2}$. Similarly the methods of Kossiakoff and Harker give almost identical values for acids without formal charges, such as ClOH, BrOH, IOH, HOOH, HOH, and C_2H_5OH. The dissociation constants[13] of these acids vary from $10^{-7.3}$ to less than 10^{-16}.

25. THE FATTY ACIDS

In a study of the relative strengths of fatty acids, Derick[14] observed (1) as a first approximation, that $\Delta \log K_\sigma$ for a substitution of a group for a hydrogen atom depended on the group and position of substitution; (2) that $\Delta \log K_\sigma$ for a substitution is a third of that for a similar substitution, one atom nearer to the carboxyl group; (3) as a second approximation, that $\Delta \log K_\sigma$ for a group is not completely independent of the reference acid, but tends to decrease as the acidic strength increases, being roughly proportional to the negative of the logarithm of the dissociation constant of the acid resulting from the substitution. The first and second of these observations can be expressed by the equation

$$\Delta \log K_\sigma = \sum_\sigma D_{\sigma\alpha}(\tfrac{1}{3})^{i_\alpha} \tag{8}$$

where $D_{\sigma\alpha}$ is a constant for the group and is equal to $\Delta \log K_\sigma$ for the substitution of the group on the α-carbon atom, and i_α is the number of atoms between the group and the α-carbon atom. The third observation makes

$$D_{\sigma\alpha}(\tfrac{1}{3})^{i_\alpha} = d_{\sigma\alpha}(\tfrac{1}{3})^{i_\alpha}(-\log K_\sigma),$$

where $d_{\sigma\alpha}$ is determined by the group alone, and when only one group is introduced into a fatty acid. The strength of the acid resulting from several substitutions can then be calculated by the repeated use of the equation

$$\log K_\sigma = \frac{\log K_u}{1 + d_{\sigma\alpha}(\tfrac{1}{3})^{i_\alpha}}, \tag{9}$$

---

[13] For other direct calculations of acid strengths, see Kirkwood, J. G., and Westheimer, F. H., *J. Chem. Phys.*, **6**, 506 (1938).

[14] Derick, C. G., *J. Am. Chem. Soc.*, **33**, 1152 (1911).

where K_σ and K_u are the dissociation constants of the substituted and unsubstituted acids, respectively. Derick also suggested that the equation could be used by making a summation of $d_{\sigma\alpha}(\frac{1}{3})^{i\alpha}$ instead of repeating the calculation for each substitution. These two methods are not identical, but with respect to agreement with fact are about equally valid. These methods of calculating the strengths of fatty acids are fairly accurate.

The similarity between equation 8 and equation 6, which was used to calculate the strengths of non-resonating acids, is apparent. The constant $\frac{1}{3}$ in equation 8 is the constant α in equation 6, for which the value chosen, $\frac{1}{2.8}$, is equal to $\frac{1}{3}$ within the accuracy warranted by the approximations made. The quantity $\sum D_{\sigma\alpha}(\frac{1}{3})^{i\alpha}$ is proportional to $\sum I_a\alpha^i + \sum I_c\alpha^i$ when the groups introduced have neither resonance nor high polarizability. Both quantities are the polar effect in $\Delta \log K_\sigma$; the former may, however, include parts of the resonance effect that can be conveniently treated as polar in character.

Equation 9 expresses the fact that the effectiveness of polarity diminishes as the polarity becomes great. In the preceding section we pointed out that polar effects should exhibit a saturation phenomenon, and that this should be more marked in carbon than in oxygen bonds to any atom A on account of the greater contribution of the ionic form $\overset{-}{\mathrm{O}}\mathrm{:}\ \overset{+}{A}$ in the latter bonds than of the ionic form $\overset{-}{\mathrm{C}}\mathrm{:}\ \overset{+}{A}$ in the former. It is also more important to introduce a saturation effect in the calculation of the strength of fatty acids than in that of the non-resonating acids, because the former calculations should aim at a higher degree of accuracy than the latter. The fatty acids are a class of acids closely related in structure and strength. The non-resonating acids discussed in the preceding section cover an enormous range in structure, composition, strength, and interaction with the solvent. They have little in common except the hydroxyl group and only small amounts of resonance.

The change from equation 8 to 9 is an empirical method of introducing a correction for a saturation effect. This method is not suited for a comparison of polar effects in fatty and non-resonating acids. To do this it is easier to make such an empirical change in equation 7 as to limit the effects of strongly polar groups. The simplest method is to combine the summations of polar effects of groups and charges into one summation (i.e., to make $\sum I_a\alpha^i + \sum I_c\alpha^i = \sum I\alpha^i$) and to assume the net polar effect to be given by the equation

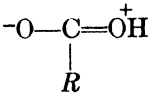
$$\mathrm{I}_\sigma = \frac{\sum I\alpha^i}{1 + |B\sum I\alpha^i|} \qquad (10)$$

where B can be taken as a constant for a class of sufficiently closely related acids, and the absolute magnitude of $B \sum I\alpha^i$ is used since a saturation effect will occur for either sign of the induction. This equation can be only an approximate one. Further, it makes the saturation effect symmetrical for groups with more positive and more negative polarities than a hydrogen atom. This cannot be true, but it is not important for the fatty acids, as in these we do not deal with groups that greatly reduce the acidic strength below that of acetic acid. For non-resonating acids we made B equal to zero, a simplification that was warranted just as much as making α constant and neglecting resonance, steric hindrance, polarizability, and solvation effects. For fatty acids we expect a higher degree of accuracy, and we shall not neglect the saturation effect, i.e. $B > 0$.

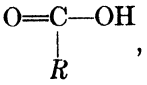
If we consider the fatty acids as derivatives of water and neglect steric hindrance, polarizability, and solvation effects, the dissociation constant is given by the equation

$$\log K = -16 + \frac{\sum I\alpha^i}{1 + |B \sum I\alpha^i|} + \mathbf{R}_\sigma + \log \frac{n}{m}. \qquad (11)$$

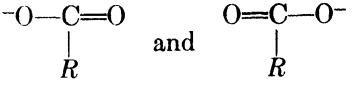
The resonance effect, $\mathbf{R}_\sigma$, is chiefly due to the difference between the resonance energy of the carboxyl group and that of the carboxylate ion group. The resonance energy of the latter group is much greater than that of the former, as the energy level of



is higher than that of



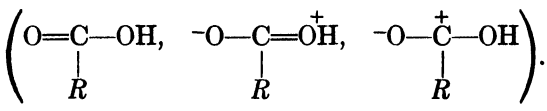
while



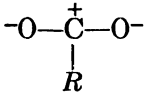
are equivalent. From an empirical value of the polar effect of the carbonyl group and the dissociation constants of fatty acids, $\mathbf{R}_\sigma$ can be estimated at about 6, which is equivalent to 8.5 kcals. of free energy.

However, the value of $\mathbf{R}_\sigma$ is not independent of the polarity of

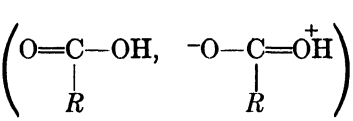
substituent groups. There are two ways of seeing that this is so. The full resonance of the carboxyl group can be expressed as



The relative stability of the third form depends on the polarity of the group R, becoming less stable as the polarity of the group increases. As this effect is more important in the acid than in the ion, where the form



is of very minor importance, $\mathbf{R}_\sigma$ increases with the polarity of the substituent groups. The other point of view is simpler. The resonance



gives the bond between carbon and the hydroxyl group a certain amount of double-bond character and consequently a higher polarizability than a simple single bond. In consequence, the polarity of a substituent group has a greater effect than it would have if separated from the ionizable proton by a singly bonded chain of atoms of the same length. It is therefore apparent that this effect can be treated as an enhancement of the polar effects of the substituent groups by multiplying $\mathbf{I}_\sigma$ by an appropriate constant; then equation 11 becomes

$$\log K = -16 + \frac{A \sum I\alpha'}{1 + |B \sum I\alpha'|} + \mathbf{R}_\sigma + \log \frac{n}{m}. \qquad (12)$$

This equation contains constants that can be evaluated only by comparison of the dissociation constants of various fatty acids. This is simplified by assuming the solution of the equation for acetic acid to be -4.75, the observed value of $\log K_{\text{acetic}}$. That is, that

$$-16 + \mathbf{I}_\sigma + \mathbf{R}_\sigma + \log \tfrac{1}{2} = -4.75,$$

where $\mathbf{I}_\sigma$ is the net inductive effect of the groups HC=O and CH_3 that must successively replace hydrogen to change from water to acetic acid, and $\mathbf{R}_\sigma$ is the resonance effect of the carboxyl group apart

from the enhancement of the polar effects by resonance in this group. Log K_{acetic} can be substituted for

$$-16 + \mathbf{I}_\sigma + \mathbf{R}_\sigma + \log \tfrac{1}{2}$$

in equation 12; and since, in acids derived from acetic, all substitutions occur at the α or some more distant position, i_α can be substituted for i, with a corresponding change of A to A_α and B to B_α. The equation is then

$$\log K = -4.75 + \frac{A_\alpha \sum I\alpha^{i_\alpha}}{1 + |B_\alpha \sum I\alpha^{i_\alpha}|} + \log \frac{n'}{m'}, \qquad (13)$$

where n' and m' are the numbers of equivalent carboxyl and carboxylate groups in the acid and its ion, respectively. In this equation, A_α and B_α are constants only for structural changes of acetic acid into another carboxylic acid with no conjugation between the carboxyl and any other group; and i_α is the number of atoms intervening between a substituent group and the α-carbon atom of a carboxylic acid. On the other hand, I and α are not restricted to carboxylic acids. Their values, given in Table 22, have already been used in the calculation of the strengths of non-resonating acids given in Table 23. However, the inductive constant I for a group is constant only when the group is substituted for a hydrogen atom in a position in which it is not conjugated with another group, and when some solvent is chosen. The use of a single value for α is restricted to a chain of atoms connected by single bonds.

By plotting $\Delta \log K_\sigma$ against $\sum I\alpha^{i_\alpha}$ for those fatty acids for which $\sum I\alpha^{i_\alpha}$ can be calculated from the inductive constants obtained from non-resonating acids, one can obtain a curve whose slope in the neighborhood of the origin is A_α. The value of B_α can be obtained from the bending over of the curve as the polar effect increases. The best curves correspond to the values 0.3 and 0.03 for A_α and B_α, respectively.

Except for certain polarization factors in bond dipole moments and for solvation effects included in inductive constants, the fundamental causes of the two properties are similar. Consequently, if the dipole moment of a bond is corrected for its distance from the α-carbon atom, and an arithmetic sum rather than a vector sum is taken for the net action of the bond dipoles on acidic strength, it is possible to estimate the effect of a group on the strength of a fatty acid from the dipole moment of its bond to carbon. Nathan and Watson[15] plotted the logarithms of the dissociation constants of

[15] Nathan, W. S., and Watson, H. B., *J. Chem. Soc.*, 894 (1933).

XCH_2COOH against the dipole moments of XCH_3 in the vapor phase and obtained a curve that is approximately a straight line at the start, but bends over for very strong polar effects, such as would be obtained by introducing two halogen atoms. The curve can be expressed by the equation $\log K_\sigma = \log K_u + a\mu + b\mu^2$. When $a\mu$ and $b\mu^2$ have different signs, the latter term corrects for a saturation effect.

When a resonating or highly polarizable group is separated from the carboxyl group by a saturated chain, it affects the strength of the acid because its resonance or polarization energy is different in the acid from what it is in the ion, owing to the different polarities of COOH and COO^-. This effect is transmitted in the same way as any other polar effect. Hence the resonance or polarizability effect of such an insulated substituent group can be included in its polar effect. However, the polar effect of any group back of this substituent, or in any way conjugated with it, is affected by this type of substituent. In consequence, a terminal resonating or highly polarizable group can be assigned an inductive constant, and this constant, when multiplied by α'^α for the group, can be included in the summation $\sum I\alpha'^\alpha$. When, however, the group has some polar group back of it, or is part of a conjugated system, one cannot obtain the effect of the compound system by addition, but can assign a new inductive constant to the whole group. Thus one can assign inductive constants to the phenyl, *p*-chlorophenyl, and phenoxy groups, but a combination of the inductive constants of phenyl, Cl, and O cannot be used to obtain the effects of the *p*-chlorophenyl and phenoxy groups. Table 24 gives the inductive constants for some of these complex groups in a terminal and insulated position.

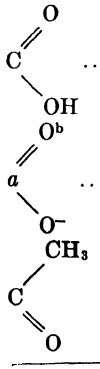
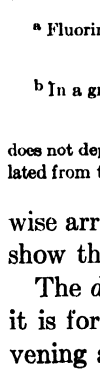
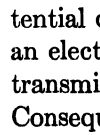
Table 25 shows the calculated and observed values of the logarithms of some fatty acids. No attempt has been made to make a complete table, but a wide range of acids has been chosen. The observed values are in general taken from Landolt and Bornstein and from The International Critical Tables. The calculations are made from the inductive constants given in Tables 22 and 24 and from equation 13, using the values 0.3 and 0.03 for the empirical constants A_α and B_α, respectively. These values can both be lowered or both raised a little without introducing much error in the calculations.

While, in general, the calculated and observed values shown in Table 25 agree fairly well, an exact correlation cannot be expected, nor is it obtained. The calculation neglects all resonance, polarizability, and solvation effects that cannot be included in the polar

effect, and completely neglects steric hindrance. Further, it assumes that polar effects are all transmitted inductively. It would appear from the table that these somewhat gross approximations do not as a rule lead to errors greater than 0.3 in log K, which is equivalent to about 0.4 kcals. in free energy. One can, however, find greater differences than these between calculated and observed values. These anomalies are not isolated instances but occur in certain types of acids. We have included examples of all these types with which we are familiar, placing them at the end of the table, which is other-

TABLE 24

INDUCTIVE CONSTANTS FOR RESONATING AND POLARIZABLE GROUPS

Group	Inductive Constant, I_g	Group	Inductive Constant, I_g
F[a]	9	$H_2C{=}CH$	1.4
	6.5	C≡N	10
		C_6H_5	1.5
		p-ClC_6H_4	2.0
		m-ClC_6H_4	2.3
		C_6H_5O	6.5
		$RCH{=}CH$	0.8
	$I_a - 1.5$		
	5.0		

[a] Fluorine was not included in Table 22 because the dissociation constant of F—OH is not known.

[b] In a group having the general structure , the resonance from the shift of the double bond does not depend on the nature of the atom a. The inductive constant for such a group can be calculated from the inductive constant of the atom a, I_a.

wise arranged in order of calculated strengths. We shall attempt to show the causes of these anomalies in the following discussion.

The *direct transmission* of a polar effect of a charge is better than it is for an electric dipole. Further, the addition of another intervening atom in a long chain has a relatively small effect on the potential of the point of ionization when that potential is produced by an electric charge on the other end of the chain; but an inductively transmitted potential would fall off to about a third of its value. Consequently, the calculated value of any acid with a charged atom

TABLE 25

DISSOCIATION CONSTANTS (log K) OF FATTY ACIDS

Acid	Log K (Observed)	Log K (Calculated)
Cl_3CCOOH	strong	−0.4
$F_2CHCOOH$	−1.1	−1.2
$ClCH(COOH)_2$	−1.4	−1.4
$Cl_2CHCOOH$	−1.3	−1.4
CH_3CBr_2COOH	−1.5	−1.7
$COOHCHBrCHBrCOOH$	−1.4	−1.8
$(CH_3)_2\overset{+}{N}HCH_2COOH$	−1.9	−1.9
$(CH_3)_3\overset{+}{N}CH_2COOH$	−1.8	−1.9
$Cl_3CCH(OH)COOH$	−2.3	−2.0
$C_6H_5CHClCOOH$	−2.4	−2.4
$NCCH_2COOH$	−2.4	−2.4
$COOHCH_2CHBrCOOH$	−2.3	−2.4
$C_6H_5CHBrCOOH$	−2.5	−2.6
FCH_2COOH	−2.7	−2.6
$COOHCH(OH)CH(OH)COOH$ (racemic)	−3.0	−2.7
$ClCH_2COOH$	−2.8	−2.7
$C_6H_5CH_2CHClCOOH$	−2.6	−2.7
$CH_2(COOH)_2$	−2.8	−2.8
$CH_3CH(COOH)_2$	−3.0	−2.9
$C_6H_5CH_2CHBrCOOH$	−2.8	−2.9
$BrCH_2COOH$	−2.9	−2.9
$\overset{-}{C}O_2CHBrCHBrCOOH$	−2.8	−2.9
$(CH_3)_2C(COOH)_2$	−3.2	−3.0
$C_6H_5OCH_2COOH$	−3.1	−3.1
ICH_2COOH	−3.0	−3.2
$C_6H_5CH(OCH_3)COOH$	−3.1	−3.3
$H_2C{=}CHCH(OH)COOH$	−3.3	−3.3
$S(CH_2COOH)_2$	−3.3	−3.4
$HOCH_2CH(OH)(COOH)$	−3.6	−3.5
CH_3COCH_2COOH	−3.6	−3.5
$NO_2CH_2CH_2COOH$	−3.8	−3.6
$HOCH_2COOH$	−3.8	−3.7
$\overset{+}{H_3}N\overset{-}{C}H(CO_2)CH_2COOH$	−3.8	−3.8
$COOHCH_2CH_2COOH$	−4.2	−3.9
$HSCH(C_2H_5)COOH$	−3.7	−3.9
$Cl(CH_2)_2COOH$	−4.0	−4.0
$COOHCH(CH_3)CH(CH_3)COOH$ (m.p. 209°C.)	−3.8	−4.0
$BrCH_2CH_2COOH$	−4.0	−4.1
m-$ClC_6H_4CH_2COOH$	−4.1	−4.1
p-$ClC_6H_4CH_2COOH$	−4.2	−4.2
$C_6H_5OCH_2CH_2COOH$	−4.3	−4.2
$CH_3COCH_2CH_2COOH$	−4.6	−4.3
$C_6H_5CH_2COOH$	−4.3	−4.3
$\overset{-}{C}O_2CHBrCH_2COOH$	−4.4	−4.3
$COOHCH_2CH_2CH_2COOH$	−4.3	−4.4
$CH_2{=}CHCH_2COOH$	−4.4	−4.4
$Cl(CH_2)_3COOH$	−4.5	−4.6

TABLE 25—*Concluded*

Acid	Log K (Observed)	Log K (Calculated)
$Br(CH_2)_3COOH$	−4.6	−4.6
$(C_6H_5CH_2)_2CHCOOH$	−4.6	−4.6
m-$ClC_6H_4CH_2CH_2COOH$	−4.6	−4.6
p-$ClC_6H_4CH_2CH_2COOH$	−4.6	−4.6
$C_6H_5CH_2CH_2COOH$	−4.7	−4.6
$H_2C{=}CHCH_2CH_2COOH$	−4.7	−4.7
$CH_3CO(CH_2)_3COOH$	−4.7	−4.7
CH_3CH_2COOH	−4.9	−4.9
$(CH_3)_3CCOOH$	−5.0	−5.1
$C\bar{O}_2CH_2CH_2COOH$	−5 5	−5.3
$C\bar{O}_2CH(CH_3)CH(CH_3)COOH$	−5.9	−5.5
$C\bar{O}_2CH_2COOH$	−5.7	−5.6
$C\bar{O}\,CH(CH_3)COOH$	−5.8	−5.7
$\overset{+}{H_3}N(CH_2)_4COOH$	−4.2	−4.7
$C\bar{O}_2(CH_2)_4COOH$	−5.5	−5.2
$COOHC(C_2H_5)_2COOH$	−2.1	−3.0
$C\bar{O}_2C(C_2H_5)_2COOH$	−7.3	−5.9
$\overset{+}{H_3}NCH_2COOH$	−2.3	−1.9
$CH_3SO_2CH_2COOH$	−2.3	−0.8
$HCOOH$	−3.8	−4.4

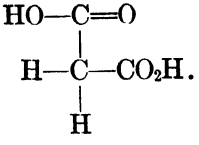
widely separated from the carboxyl group is too low when the charge is positive and too high when it is negative. This principle has been illustrated, in the table, by the dissociation of the positive ion of δ-aminovaleric acid, when log K is 0.5 units greater than the calculated value, and by the dissociation constant of the ion of adipic acid, $COOH(CH_2)_4COO^-$, where log K is 0.3 units less than the calculated value.

Steric hindrance imposes certain shapes on the molecules. At first sight this would not appear to be a very important factor governing the strengths of fatty acids, as the steric repulsions would be expected to be practically the same in an acid and in its ion. Outside of the carboxyl group there is little resonance in a saturated fatty acid, and an inductively transmitted polar effect would be practically independent of the shape. However, directly transmitted polar effects depend on the distance between ionizing proton and polarizing group, and so the shape of the molecule affects the strength of an acid.

In general, a chain of carbon atoms is most stable when the carbon atoms form a zigzag. In this way, in any four-atom segment of the chain, the outer carbon atoms are *trans* to each other. Branching of a chain can therefore change the distances between atoms.

One of the most striking anomalies in the strengths of saturated fatty acids is the great increase in strength produced by substituting two alkyl radicals greater than methyl for the two α-hydrogen atoms of malonic acid. The inductive constants of the introduced groups are negative, and a single group or even two methyl groups do not produce the effect. The substitution of two alkyl groups greater than methyl for the α-hydrogen atoms of hydrogen malonate ion produces the opposite effect to an even more exaggerated degree. That is, these substitutions increase the first dissociation constant and decrease the second. The phenomenon was experimentally observed a long time ago and has been fully substantiated. It is difficult to imagine that anything but a change in the spatial relationship between the carboxyl groups or their component parts can account for the phenomenon.

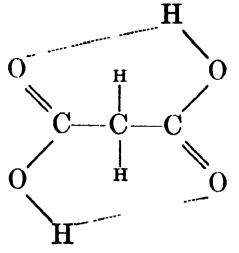
Owing to the repulsive forces, the most stable configuration of malonic acid is probably that with the hydroxyl group of one carboxyl *trans* to the other carboxyl, as represented in the formula



In this position the ionizable proton is at its maximum distance from the carboxyl, and the repulsion between the proton and the positively polar group is at a minimum, while in the ion the attraction between the remaining proton and the negatively polar group is also least. When both α-hydrogen atoms are replaced by groups large enough to exert repulsive forces as great as that of a carboxyl group, the above structure is no longer uniquely favored. Steric hindrance diminishes the distance between the hydroxyl group and the carboxyl group in a dialkylmalonic acid, and the distance between the hydroxyl group and the carboxylate ion group in the first ion of a dialkylmalonic acid, when the alkyl groups are larger than methyl groups. The result of the substitution is therefore to increase the first and decrease the second dissociation.

In the preceding paragraph the hydrogen of the carboxyl group has been assumed to be *cis* to its carbonyl oxygen atom, corresponding to the configuration previously assumed for esters (see Figure 21). If the *trans* position of the hydrogen atom of the carboxyl group is permitted, another interpretation becomes apparent. In this case,

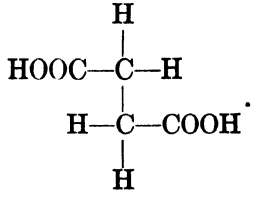
for the unsubstituted malonic acid, the most stable configuration would probably be one in which the two hydroxyl groups tend to form hydrogen bonds with the opposite carbonyl oxygen atoms as represented in the formula



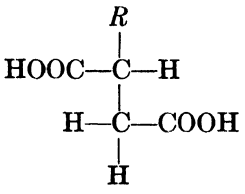
in which the small H's extend below the plane of the paper. The O—H . . .O distance is still rather large for a good hydrogen bond, but does permit a fair polar interaction. When groups larger than methyl (e.g., ethyl) are introduced, this configuration cannot easily be attained. An examination of the Stuart models shows that the carboxyl groups must be rotated so as to bring one hydroxyl closer to the opposite carbonyl oxygen atom and the other hydroxyl further from its corresponding carbonyl oxygen atom. The effect on the dissociation constants is thus the same as was deduced from the preceding considerations.

There is a somewhat similar anomaly in the effect of introducing alkyl groups into succinic acid. This anomaly is much smaller than that noticed in the malonic acids, but it is quite regular and appears to be due to steric hindrance. The introduction of alkyl groups into both α positions markedly increases the first and decreases the second dissociation. The effect is noticeable with methyl groups, but is larger with ethyl and most striking when all four α-hydrogen atoms have been replaced. The replacement of hydrogen atoms of only one α position does not have much effect.

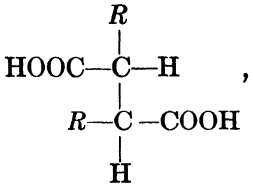
In succinic acid steric hindrance makes the *trans* configuration of the carboxyl groups the most stable:



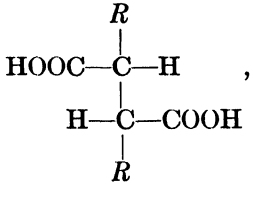
The introduction of an α-alkyl group giving



does not greatly alter the predominance of *trans*-carboxyl configurations. The addition of another alkyl on the α' position gives the meso compound,



or



the racemic mixture. In the first, a repulsion between carboxyl and R is introduced; in the second, a repulsion between R and R. These repulsions decrease the predominance of the *trans*-carboxyl configuration. If this configuration is the least acidic one, the introduction of the second alkyl group has a positive, or acid-strengthening, steric term in $\Delta \log K_\sigma$. This steric term is not the same in the meso and racemic acids, and in general meso and racemic derivatives of succinic acid have different dissociation constants. In the dimethyl succinic acids this difference is small, being about 0.17 in $\Delta \log K$ units. As might be expected, the second dissociation constant of the succinic acid is greater than those of the dialkyl succinic acids. The *trans*-carboxyl configuration of the first ion is the most acidic configuration.[16]

Solvation effects cannot be included in the polar effect when they

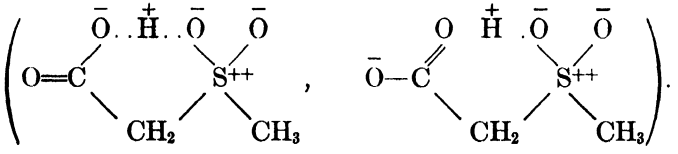
[16] For further discussion of the relationship between the dissociations of dicarboxylic acids and the separation of the carboxyl groups, see Gane, R., and Ingold, C. K., *J. Chem. Soc.*, 2158 (1931).

become so strong that they amount to bond formation, even though a single solvent is used. Thus it was shown in the preceding section that the strength of telluric acid in water could not be calculated from the formula H_2TeO_4; that it was necessary to use the formula of its compound with water, H_6TeO_6. The formation of divalent hydrogen seems to be more than an electrostatic attraction, and an inductive constant for hydrogen should depend on its situation. Yet a constant value of zero has been assumed in all these calculations, and this assumption must lead to some error. Since the solvation of bonded hydrogen atoms by water is the neutralization of an acid by a base, this error should be greatest when a highly acidic hydrogen atom is replaced by a group whose hydrogen atoms have very little acidity. This is the case when hydrogen atoms are replaced in an $\overset{+}{N}H_3$ group by alkyl groups.

The solvation of an acidic hydrogen atom by the base, water, tends to decrease the acidic strength. There is more energy evolved by this solvation in the acid than in the ion, where the acidity of the hydrogen atom is reduced by negative charge. Consequently, when the hydrogen atoms of $H_3\overset{+}{N}CH_2COOH$ are replaced by alkyl groups, the acidity is increased although the alkyl groups have negative polarities. The effect is quite regular and the order of decreasing strength is $R_3\overset{+}{N}CH_2COOH$, $R_2\overset{+}{N}HCH_2COOH$, $R\overset{+}{N}H_2CH_2COOH$, and $H_3\overset{+}{N}CH_2COOH$. In the last-mentioned substance the solvation effect has become so large that it is apparent even in this approximate calculation.

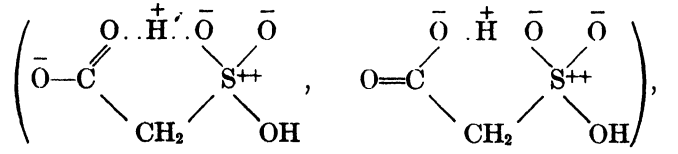
Resonance effects are not explicitly included in equation 13, but some of them are implicitly included in the term log K for acetic acid, in the value chosen for the constant A_α, and in the polar constants assigned to insulated resonating groups. Consequently, the equation can be used only to calculate the dissociation constants of carboxylic acids in which the carboxyl group is attached to an atom having all its valences satisfied by single bonds. Even these restrictions do not entirely exclude the possibility of choosing an acid with a significant resonance effect that has not been accounted for in equation 13. The structural restrictions placed on the choice of acids do not eliminate the resonance effects of chelation and the resonance due to the possibility of more than one electron distribution in the ionic component of a bond. The latter has been called "no-bond" resonance.

The calculated value for the dissociation constant of methylsulfonacetic acid, $CH_3SO_2CH_2COOH$, is thirty times the observed value. There is a discrepancy in the same direction and of approximately the same magnitude between the calculated and observed values of all α-sulfonacetic acids. The dissociation constants of the α-sulfoxyacetic acids (RSOCH$_2$COOH) are also smaller than the calculated values, but these discrepancies are very much less. The greatest anomaly in the strengths of sulfonic derivatives of acetic acid is that of the sulfonic acid, $HOOCCH_2SO_3H$. The first and second dissociation constants of this acid are 5.8×10^{-3} and 8.9×10^{-5}. The first dissociation constant is very much less than those of other sulfonic acids. In general, sulfonic acids are strong acids, their dissociation constants being greater than 10^{-1}. From these facts it would appear that the sulfonic acid group, the sulfone group, and to a less extent the sulfoxide group can interact in some way with the carboxyl group when the groups are separated by one carbon atom. The most probable interaction is the formation of a chelate ring:

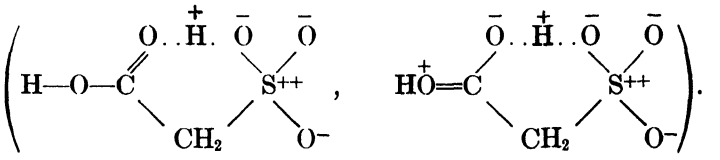


The bond distances and angles are such that the sulfone and carboxyl groups can be brought to a suitable chelation distance without the expenditure of much energy. Another requirement for chelation through a proton is that the attached groups shall not differ too widely in basicity. This condition is fulfilled by means of the resonance in the carboxylate ion group. When a resonance in a group helps to meet the condition of not too widely separated basicities of the chelated groups, the same resonance can be shown in the formula for the chelate ring. The carboxylate ion resonance is shown in the formula assigned above to the chelated methylsulfonacetic acid. The chelation weakens the strength of the acid, as it cannot occur in the ion.

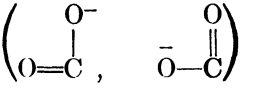
The similarly chelated form of carboxymethylsulfonic acid,



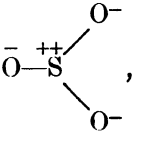
is in tautomeric equilibrium with another chelated form:



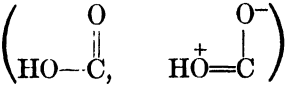
The former is a sulfonic acid and the latter a carboxylic acid. The ions of both acids are identical; therefore the weaker acid, presumably the latter form, is the more stable, and the overall strength must be less than that of the less acidic tautomer. In consequence the dissociation constant would be that of a carboxylic acid, not that of a sulfonic acid. The chelation in this acid is probably acid-weakening. The decrease in free energy on chelation with a proton bridge goes to a maximum as the alternative groups to which the proton may be attached approach equality in basicity. The group



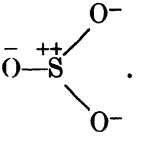
is certainly more basic than



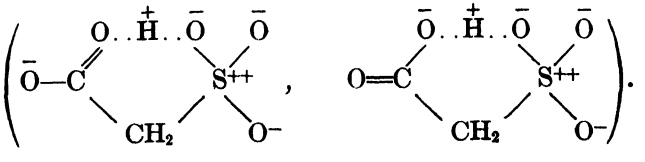
and the group



is probably no less basic than

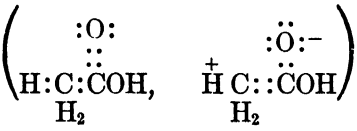


Hence, in the acid the alternative groups are more nearly equal in basicity than in the ion:

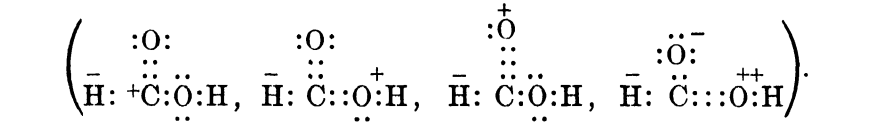


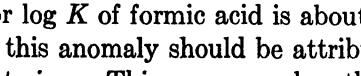
The dissociation constant should be less than that calculated from the formula HO_3SCH_2COOH, with the assumption that the proton dissociates from the carboxyl group.

There are resonance forms of acetic and formic acids in which the carbon-attached hydrogen atoms have no covalent bond to the carbon atom. These forms are the "no-bond" resonance contributions. The hydrogen atoms of acetic acid are alpha to a carbonyl group, so that the resonance



tends to give a positive charge to the hydrogen atom, and this charge is enhanced by solvation. This resonance is reduced by ionization, and is an acid-weakening resonance. In formic acid the removal of the hydrogen atom as hydride ion is increased by the possibility of the unshared electrons of the oxygen atom completing the octet of the carbon atom as this atom loses its electrons to the hydrogen. The resonance is



This resonance is greatly assisted by the removal of a proton from the hydroxyl group, and is therefore acid-strengthening. It is also assisted by solvation in water, as the acidity of the water neutralizes the basicity of the hydride ion, $\bar{H}$:. To ignore these possible resonances and to give the same I_σ value for the replacement of a hydrogen by a methyl group in acetic acid, as for a similar replacement in formic acid, introduces an error. In Table 25 this has been done, and the calculated value for log K of formic acid is about 0.6 units too low. The major part of this anomaly should be attributed to the hidden resonance of formate ion. This resonance has the same form as in carbon dioxide  . The resonance energy of carbon dioxide is estimated by Pauling as 31 kcals./mole. When this energy is compared to the resonance effect in formate ion, equivalent to 0.8 kcals./mole, one gets some idea of how greatly resonance is hindered by the formation of a single bond.

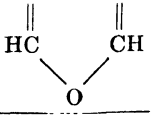
26. UNSATURATED ACIDS

The unsaturated acids differ in many important ways from the saturated ones. Since we shall discuss these differences, the logarithms of the dissociation constants of a few unsaturated acids have been collected in Table 26. Only acids directly mentioned in the discussion or very closely related to them have been included.

A double bond in the carbon chain of a fatty acid enhances the polarizability of the chain. In consequence, the effect of a group separated from the acidic group by a chain containing a double

Table 26

DISSOCIATION CONSTANTS OF A FEW UNSATURATED ACIDS

Acid	Log K
$CH_2{=}CHCOOH$	−4.25
$CH_3CH{=}CHCOOH$	−4.69
$C_2H_5CH{=}CHCOOH$	−4.69
$(CH_3)_2C{=}CHCOOH$	−5.12
$CH_3CH_2CH_2CH{=}CHCOOH$	−4 70
$C_2H_5C(CH_3){=}CHCOOH$ (*trans*)	−5.13
$C_2H_5C(CH_3){=}CHCOOH$ (*cis*)	−5.15
$CH_2{=}CHCH_2COOH$	−4 35
$CH_3CH{=}CHCH_2COOH$	−4.51
$C_2H_5CH{=}CHCH_2COOH$	−4.52
$CH_2{=}CHCH_2CH_2COOH$	−4 68
$CH_3CH{=}CHCH_2CH_2COOH$	−4 72
$(CH_3)_2C{=}CHCH_2CH_2COOH$	−4.80
$COOHCH{=}CHCOOH$ (*cis*)	−1.92
$COOHCH{=}CHCOOH$ (*trans*)	−3.02
$CO_2^-CH{=}CHCOOH$ (*cis*)	−6.22
$CO_2^-CH{=}CHCOOH$ (*trans*)	−4.38
	−7.52

bond is greater than it is when the chain is saturated. Thus $\Delta \log K_a$ for the substitution of a methyl radical for a hydrogen atom on the γ-carbon of $CH_2{=}CH{-}CH_2{-}COOH$ is -0.16, and for a similar substitution of the β-carbon atom of $CH_2{=}CH{-}COOH$ it is -0.44. The $\Delta \log K_a$ for similar substitutions in saturated acids are hardly significant, being $+.01$ and $+.06$ respectively. The slopes of the cinnamic and β-phenyl propionic acid lines in Figure 36 also illustrate this point.

The direct transmission of polar effects also is different in saturated and unsaturated carboxylic acids. In saturated acids the direct

transmission depends on the shape imposed on the molecule by the repulsions between the groups; in unsaturated acids the positions of the groups are more precisely fixed by the lack of rotation about the double bond. The directly transmitted effects are much larger in a *cis* than in a *trans* acid. This is very clearly seen in a comparison of the dissociation constants of maleic and fumaric acids. The polarity of the carboxyl group is positive, so the first dissociation constant of maleic acid, the *cis* form, is greater than that of fumaric acid, the *trans* form.

On the other hand, the second dissociation constant of maleic acid is smaller than that of fumaric, since the direct effect of the carboxylate ion group decreases the acidic strength. The direct effect of an electrically charged group is larger than that of a neutral group, so the difference in the log K values for the second dissociation is greater than that for the first dissociation. Thus $\log K_{1_{(\text{maleic})}} - \log K_{1_{(\text{fumaric})}} = 1.1$, but $\log K_{2_{(\text{maleic})}} - \log K_{2_{(\text{fumaric})}} = -1.9$.

The double bond, being more polarizable than the single bond, should produce a polarizability effect. However, it also seems to have a polarizing power of its own. The fact that propylene has a dipole moment suggests this to be so. The structure of propylene is such that the dipoles of the C—H bonds would neutralize each other if dipoles for $H—C_{alkyl}$ and $H—C_{vinyl}$ bonds were the same. Since toluene has a dipole for which the methyl group is the positive end, but phenylethylene has practically no moment, the methyl-vinyl dipole is methyl plus and vinyl minus, and the polarity of the $CH_2{=}CH$ group is positive.

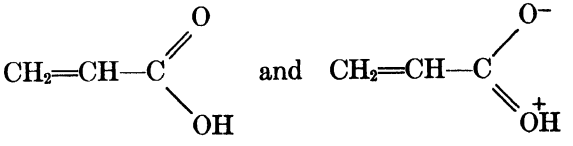
The vinyl group attached to an atom with unshared electrons is a resonating group, and in many unsaturated carboxylic acids there is a resonance effect over and above that due to the carboxyl group. In general this resonance effect will not be identical for *cis* and *trans* isomers, as it alters the bond distances and the repulsions between groups.

When we are dealing with a vinyl group that is separated by a saturated chain from the carboxyl group, and we include all groups that are conjugated with the vinyl group or are attached to the far end from the carboxyl group, the composite group can be assigned an inductive constant that expresses its polarity. Different inductive constants for the *cis* and *trans* forms must be assigned. Table 24 includes an inductive constant for the vinyl group, and Table 25 includes acids containing this group. The strengths of these acids agree with the calculated values. When the vinyl group is attached

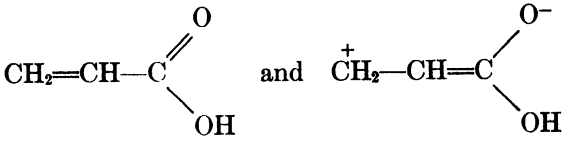
to the carboxyl group, there is an additional resonance beyond that due to the carboxyl group.

26a. Cross-conjugation. In acrylic acid the carbonyl group is conjugated with both the hydroxyl and vinyl groups, but the hydroxyl and vinyl groups are not conjugated. The reaction we are considering is the dissociation of the hydroxyl group, and the conjugation of the carbonyl group directly affects this dissociation, but the conjugation of vinyl and carbonyl groups has only an indirect action, which we shall call a cross-conjugation effect.

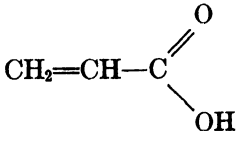
The cross-conjugation in acrylic acid decreases the strength. This is a special case of the following theorem for cross-conjugation effects in general. When a reaction of a group A is affected by a resonance of A with another group, B, the introduction of a third group, C, that resonates with B but not with A produces a cross-conjugation effect. The cross-conjugation effect decreases the magnitude but does not change the sign of the effect of the original resonance between B and A. A resonance between two groups means that there are two or more bonding arrangements for the molecule that differ only within the groups considered. Thus in acrylic acid the formulas



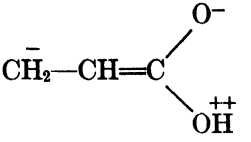
differ only in the bonds and charge distributions of the C=O and OH groups; while the formulas



differ only in the bonds and charge distributions of the groups CH_2=CH and C=O. When we say that there is no resonance between the vinyl and hydroxyl groups, we mean that there is no alternative bonding arrangement that changes only the bonds of these groups. There are forms that differ from

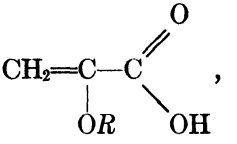


in both vinyl and hydroxyl groups, but in these the bonds or charge distribution of the carbonyl group is also changed, for instance in the form

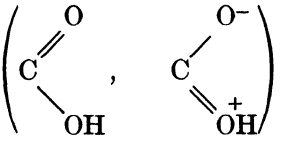


The proof of this theorem may be stated as follows: Owing to the resonance between groups B and C, the group B is for part of the time in the phase B', which does not resonate with A. The resonance between A and B is therefore reduced and, consequently, effects due to this resonance are diminished but are not reversed.

Considering the cross-conjugation as a resonance effect, it is possible to have a cross-conjugation effect on a cross-conjugation. The second cross-conjugation decreases the effect of the first. Thus in



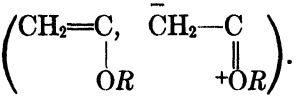
the effect of the resonance



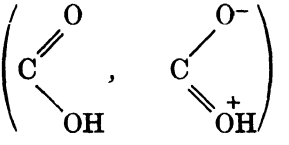
is diminished by the resonance



This effect is diminished in turn by the resonance



This last resonance tends to bring the resonance effect of



back to its normal value. Each degree of cross-conjugation has a diminishing effect, and in general we need only consider the first degree of cross-conjugation.

The magnitude of the cross-conjugation term in log K of an acrylic acid is the difference between the observed value and that calculated by equation 13 from the inductive constant assigned the vinyl or derived vinyl group.

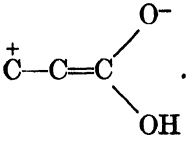
The change from CH_3COOH to $CH_2{=}CH{-}COOH$ is the replacement of the methyl group ($I_C = -0.4$) by the group $CH_2{=}CH$ ($I_{CH_2CH} = 1.4$) occurring one atom nearer the carboxyl group than a substitution on the alpha atom of a fatty acid. The polar effect of this change is equivalent to that for the replacement of an alpha hydrogen by a group with $I = (1.4 + 0.4)\ 2.8 = 5.04$. Such a change gives an acid with $K = 10^{-3.44}$ if calculated by equation 13. The observed value of the dissociation constant of acrylic acid is $10^{-4.25}$. This difference is attributable to the acid-weakening effect of the cross-conjugation in



The resonance term for the cross-conjugation is -0.8. This is equivalent to 1.10 kcal./mole.

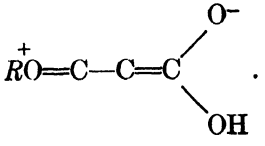
In a similar manner the change from CH_3COOH to $R{CH}{=}{CH}{-}COOH$ involves a polar term equivalent to the introduction of a group for which $I = 3.35$ at the alpha position in a fatty acid. Log K calculated for such an acid by equation 13 is -3.84. The observed values for β-monoalkylacrylic acids are about -4.7. The resonance term for the cross-conjugation of these acids is -0.86, which is equivalent to 1.2 kcals./mole.

Alkyl groups in β-alkylacrylic acids should have unusually large acid-weakening effects because the negative polarity of the groups is easily transmitted through the double bond, and it favors the acid-weakening cross-conjugation arising from the contribution of the structure

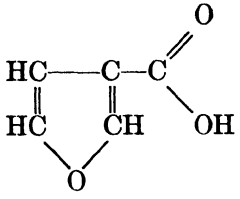


These large acid-weakening effects of the alkyl groups are found. The values differ little for the various alkyl groups and are doubled in β-dialkylacrylic acids. With acrylic acid as the reference acid, Δ log K for methyl = 0.44, for ethyl = 0.44, for n-propyl = 0.45, for dimethyl = 0.86, for ethyl methyl = 0.9 (*cis*) and 0.88 (*trans*).

An oxygen atom in an acrylic acid is acid-weakening, owing to the enhancement of the cross-conjugation from the contribution of forms of the type

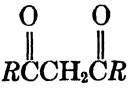


Thus furoic acid

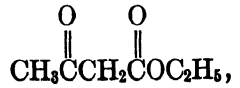


is much weaker than acrylic acid; in fact it is weaker even than acetic. Log $K_{(\text{furoic acid})} = -7.52$.

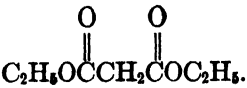
As the carbonyl group can resonate with an attached group with unshared electrons, a resonance effect of the carbonyl group is lowered by cross-conjugation when an alkoxyl group is attached to it. The resonance effect of the carbonyl group is very great on the C—H bond of an alpha carbon atom. Thus the acidity of



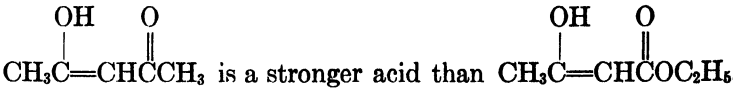
is enormously greater than that of CH_4. This effect of the carbonyl group is greatly decreased by replacing an alkyl group by an alkoxyl one. Thus $CH_3COCH_2COCH_3$ is a stronger acid than



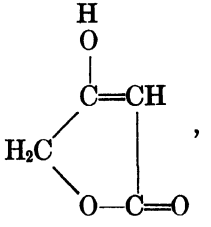
which in turn is stronger than



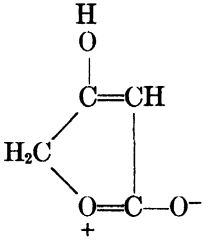
A large cross-conjugation effect is also present in the enols. Thus



Kumler has pointed out that in cyclic compounds of the type

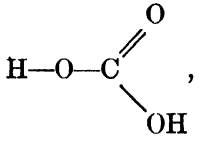


the acid-weakening effect of the unshared electrons of the lactone oxygen atom is not present. He has explained this on the assumption that the form



is depressed by the unfavorable angles, and that the acid-weakening effect of this form is reduced by the polar effect of the positively charged oxygen atom in the ring.[17]

Similarly there is an acid-weakening cross-conjugation effect in carbonic acid. The strength of the acid whose structure is



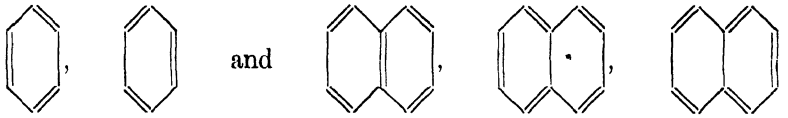
is difficult to measure directly, as in water solution it is in equilibrium with a preponderance of its anhydride, CO_2. However, as this equilibrium is not instantaneous, it can be measured and the value of $K_{H_2CO_3}$ obtained. The experimental values vary considerably, but a value of $10^{-3.5}$ can be taken as a fair approximation. If we

[17] Private communication.

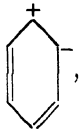
consider the change from CH_3COOH to HOCOOH as equivalent to the replacement of an α-hydrogen by a group whose inductive constant is $2.8\ (-I_C + I_O) = 2.8\ (+0.4 + 4) = 12.3$, the value calculated by equation 13 is $\log K = -1.8$, keeping in mind that there are now two dissociable protons. The cross-conjugation effect is 1.7, which is equivalent to 1.5 kcals.

27. THE AROMATIC ACIDS

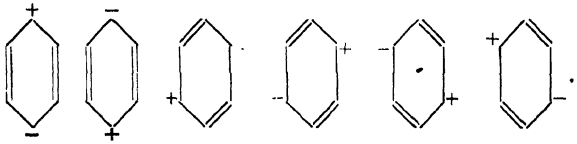
27a. Resonance of aromatic nuclei. Aromatic nuclei are strongly resonating groups on account of the multiplicity of equally stable arrangements of the bonds. Thus for benzene and naphthalene the chief resonances are, respectively:



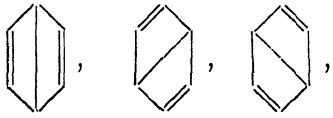
There are also ionic states beyond those that are implied by the bonds. For instance, in benzene, besides states such as



which is merely an explicit expression of the ionic component of one of the double bonds, there are also the electron arrangements



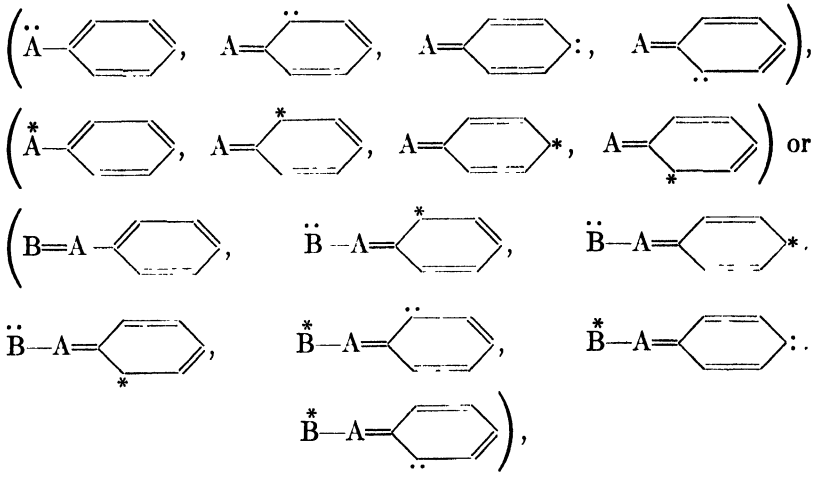
These states may also be expressed by the formulas



in which the para bond includes the ionic forms shown in the other formulas as well as the small homopolar component of the bonding of para atoms. The contribution of ionic forms to the structure of aromatic compounds gives an aryl group a high polarizability, but no polarizing power, as the polarity of each ionic form is compensated by an equal but opposite polarity of an equivalent form. In spite

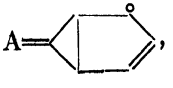
of this an aryl group appears to have an intrinsic polarity which, when combined with the effect of the polarizability of the group, gives an effective polarity. In this way the aryl group is analogous to the vinyl group.

When an aryl nucleus is bonded to an atom that has an unshared pair of electrons, a lack of electrons, or is doubly bonded to yet another atom, one of the following resonances exists:



in which an asterisk indicates less than eight valence electrons. The first of these resonances charges the para and ortho carbon atoms negatively, and the second type charges them positively. The third type may charge these atoms positively or negatively; positively if *B* is more readily charged negatively than an aromatic carbon atom, and vice versa. All of these resonances may be classed together as the resonance between the benzenoidal and quinoidal forms of the substituted aryl nucleus. In the formal representations we have shown only one of the benzenoidal forms and only one of the types of aryl nuclei, the benzene nucleus.

The benzenoidal-quinoidal resonance chiefly affects the charge on ortho and para positions, but it is not quite without action on the meta position. A charge on the ortho or para position induces a similar but smaller charge on the meta position. Also, there are small contributions from meta quinoidal forms. A meta quinoidal form has the general structure



in which the circle represents any type of unsaturation and the line joining the meta atoms represents the combined ionic and homopolar components of a meta bond. Owing to the distance between the atoms the homopolar component and the strength of a meta bond is small, and the contribution of a meta quinoidal form is very small. As a first approximation benzenoidal-quinoidal resonance may be assumed to act primarily on the ortho and para carbon atoms, and only by induction from these atoms on the meta position.

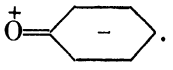
27b. Classification of aromatic acids. The ionizable proton of an acid is connected to the aryl nucleus by either a single atom or a chain of atoms. Aromatic acids may be classified according to the lack or extension along this chain of benzenoidal-quinoidal resonance. To describe this classification we shall call the ionizable proton and the atom to which it is attached the acidic group, e.g. the hydroxyl group is the acidic group of a carboxylic acid. We shall call the group on whose resonance with the acidic group the acidity of the substance largely depends an acidic resonator; e.g., the carbonyl group is an acidic resonator in a carboxylic acid. The aromatic acids may be divided into the following classes:

(1) Acids in which the aromatic nucleus resonates with neither the acidic resonator nor the acidic group. Examples are $C_6H_5CH_2COOH$, $C_6H_5OCH_2COOH$, and $C_6H_5CH_2\overset{+}{N}H_3$. (2) Acids in which the aromatic nucleus resonates with the acidic resonator but not with the acidic group. Examples are C_6H_5COOH, $C_6H_5CH{=}CHCOOH$, and $C_6H_5B(OH)_2$. (3) Acids in which the aromatic nucleus resonates with the acidic group, that is, the aromatic nucleus is the acidic resonator. The most important acids of this type are the phenols and the positive ions of the anilines.

In acids of the first type the aromatic nucleus is insulated from the acidic portion of the molecule. The aromatic nucleus, together with its substituent groups other than the connecting chain, and any part of this chain that is conjugated to the aryl group can be taken as a unit to which an inductive constant can be assigned. This unit then has the polar effect appropriate to its inductive constant, and its position in the reference acid. Thus in Table 24 the value 1.5 was assigned to the phenyl group. Using this value, the strengths of many phenyl fatty acids were calculated, and given in Table 25. The agreement between calculated and observed values is quite good.

When, in this type of acid, a substituent group resonates with the aromatic nucleus, the effect of this resonance on the dissociation of the acid depends on the position of the substituent group with respect

to the acidic group, not only in magnitude but also in sign. The sign of the effect can be predicted from the formula of the quinoidal form, which shows the location of the positive and negative charges with respect to the dissociating proton. Thus the isomeric groups p-HOC_6H_4 and C_6H_5O have the same resonance, in which the quinoidal phase is



In the quinoidal phase of p-$HOC_6H_4CH_2COOH$, the dissociating proton is nearer to the negative than to the positive charge, but in the quinoidal phase of $C_6H_5OCH_2COOH$ the reverse is true. Hence the resonance decreases the inductive constant of p-HOC_6H_4 and increases that of C_6H_5O. In this example the inductive constant for C_6H_5O is greater than the sum $I_{C_6H_5} + I_O$, while that of p-HOC_6H_4 is less than either $I_{C_6H_5}$ or I_O.

In acids of the second type the resonance between the aromatic nucleus and the acidic resonator is a cross-conjugation decreasing the acid-strengthening resonance between the acidic group and its resonator. For instance, the polar term in $\Delta \log K_\sigma$ for the change from acetic to benzoic acid is:

$$\frac{A(-I_C + I_{C_6H_5})\,2.8}{1 + B(-I_C + I_{C_6H_5})\,2.8} = \frac{0.3(0.4 + 1.5)\,2.8}{1 + 0.03(0.4 + 1.5)\,2.8} = 1.38.$$

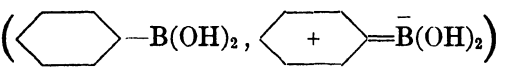
The actual value of $\Delta \log K_\sigma$ for this change is 0.55, and hence $\mathbf{R}_\sigma$, which is due to cross-conjugation, is -0.83, equivalent to 1.1 kcals./mole. The cross-conjugation effect in benzoic acid is very nearly the same as that in acrylic acid.

If one assumes that the polar term in $\Delta \log K_\sigma$ for the change from $C_6H_5CH_2B(OH)_2$ to $C_6H_5B(OH)_2$ is 2.8 times the polar term in $\Delta \log K_\sigma$ for the change from $C_6H_5CH_2CH_2B(OH)_2$ to $C_6H_5CH_2B(OH)_2$, and that in the latter change only the polar term in $\Delta \log K$ is significant, then

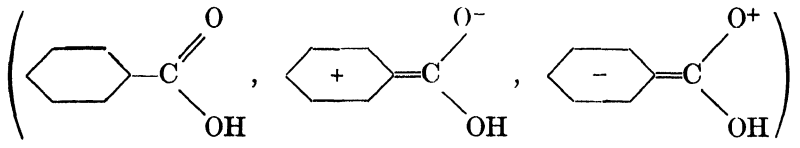
$$\log K_{C_6H_5B(OH)_2} = \log K_{C_6H_5CH_2B(OH)_2} + 2.8\,(\log K_{C_6H_5CH_2B(OH)_2} - \log K_{C_6H_5CH_2CH_2B(OH)_2}) + \Delta\mathbf{C},$$

in which $\Delta\mathbf{C}$ is a cross-conjugation resonance term. The three dissociation constants measured in water are $K_{C_6H_5B(OH)_2} = 13.7 \times 10^{-10}$, $K_{C_6H_5CH_2B(OH)_2} = 7.55 \times 10^{-10}$ and $K_{C_6H_5CH_2CH_2B(OH)_2} =$

1×10^{-10}, and hence $\Delta C = -2.19$. This is equivalent to 3 kcals./mole. That the resonance



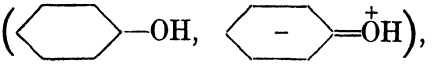
has a greater acid-weakening effect than the resonance



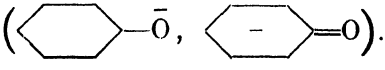
is to be expected.

Substitution of groups in the aromatic nucleus of acids of the second type produce changes in acidic strength not only by changing the inductive constant of the aryl group, as in acids of the first type, but also by changing the cross-conjugation. However, in both ways the group affects the dissociation constant in the same direction and, consequently, though the effects will be very different in the individual acids, their relative effects will be very similar, as they vary only in the proportions of the effects that are assigned to induction and cross-conjugation. These variations are of secondary importance, and as a first approximation one can assume that the relative effects of substituents are the same in acids of the first and second types. We shall see later that this assumption does not hold for ortho substituents.

In aromatic acids of the third type, the aryl group resonates more strongly with the acidic group after it has lost a proton than before, and the resonance is acid-strengthening. For instance, in phenol the resonance in the acid is

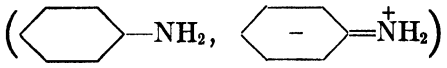


while that in the ion is



It is obvious that in the ion the energies of the quinoidal forms are much nearer to those of the benzenoidal than in the acid, and the resonance decreases the free energy of the ion more than it does that of the acid. The resonance is therefore acid-strengthening. In

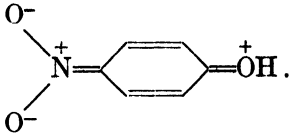
anilinium ion there is no resonance in the acid but there is the resonance



in the conjugate base, and again the resonance is acid-strengthening.

When one uses the value of the inductive constant for the phenyl group obtained from the fatty acids, $\Delta \log K_\sigma$ for the change from water to phenol is equal to $1.5 + \mathbf{R}_\sigma$, and with an observed value for $\Delta \log K_\sigma$ of 6, $\mathbf{R}_\sigma = 4.5$. Similarly, $\Delta \log K_\sigma$ for the change from NH_4^+ to $C_6H_5\overset{+}{N}H_3$ can be put equal to $1.5 + \mathbf{R}_\sigma$, with an observed value of 4.5, so that $\mathbf{R}_\sigma = 3$. These calculations must be very rough approximations, as the inductive constant assigned to the phenyl group includes a polarizability term. The value 1.5 is certainly too high in the case of anilinium ion, and the resonance term is greater than 3. As $C_6H_5CH_2NH_2$ is a weaker base than ammonia, the polar term for the phenyl group is positive in ammonium ion derivatives, so that an upper limit of 4.5 can be set for the resonance effect in the dissociation of anilinium ion.

Substitution of groups in the aromatic acids of the third type can affect the dissociation by changing the inductive constant of the aryl group, by introducing a cross-conjugation or by introducing a resonance beween the acidic group and the substitutent. An example of the last effect is *p*-nitrophenol, in which the hydroxyl and nitro groups allow the extra quinoidal form



Although this extra resonance effect is in the same direction as the effect of the nitro group on the other types of acids, it is too large not to perturb the relative effect of the group as found in the other types of acids.

27c. Meta groups. A substituent group affects the polarity of the atoms of a benzene ring through its polar and resonance effects. The polar effect is greatest on atom 1, next on atoms 2 and 6, next on atoms 3 and 5, and least on atom 4. The resonance effect is large on atoms 2, 4, and 6, but a smaller polarity of the same sign is induced on atoms 1, 3, and 5 by the polarity of atoms 2, 4, and 6.

The actual polarity induced by the group on any atom in the ring is the sum of the polar and resonance effects of the group.

Although the resonance effect at the meta position is at a minimum, it is still large enough to make the relative effects of groups on the polarity of the meta position not the same as the relative inductive constants of the groups. Thus if we take $\Delta \log K_\sigma$ for meta substitutions in phenylboric acid as a measure of the polarity induced on the meta position and divide by the inductive constant of the group, the quotient is in no sense a constant, even though the two quantities usually have the same sign. The values for $\Delta \log K_\sigma$ for meta substitution in phenylboric acid are 0.06, 0.24, 0.74, 0.88, and 1.55 for NH_2, OH, F, Cl, and NO_2 respectively. The corresponding inductive constants are 1.3, 4, 9, 8.5, and 12. The quotients are 0.05, 0.06, 0.08, 0.10, and 0.13. Small values are characteristic of atoms of the second period of elements with at least one pair of unshared electrons. For these atoms the polar and resonance effects are opposed.

A meta substituent cannot produce much effect either by interaction with the acidic group or by cross-conjugation. Direct conjugation results only from meta bonded forms, and must be small. The effect of a meta substitution can then be taken as that of an electric charge imposed on the atom to which the side chain is connected, and transmitted from this point by induction to the seat of the reaction. It is therefore to be expected that the relative values of $\Delta \log K_\sigma$ should be approximately independent of the reference acid when the structural change is restricted to a substitution of an electrically neutral group for a meta hydrogen atom in all types of aromatic acids. This is equivalent to saying that Hixon-Johns' method could be applied to these reactions, and further that if $\log K$ or $\Delta \log K$ is plotted and an arbitrarily chosen straight line is used for one of the reference acids, straight lines will be obtained for the others. How good an approximation this is can be seen by inspection of Figure 36. In this figure $\Delta \log K_\sigma$ for phenylboric acid has been arbitrarily taken as a straight line at a 45° angle.

In a study of the relative rate and equilibrium constants of reactions of meta and para substituted benzene derivatives, Hammett[18] made the observation that the relative effects of the substitutions are the same in all cases. The equation for this rule is $\log K_\sigma = \log K_u + \sigma\rho$, where σ is a constant for the substitution, that is, for

[18] Hammett, L. P., *J. Am. Chem. Soc.*, **59**, 96 (1937).

the group and the position of substitution, and ρ is a constant for the particular type of reaction studied. The equation applies to rate constants as well as equilibrium constants. It is natural to take σ

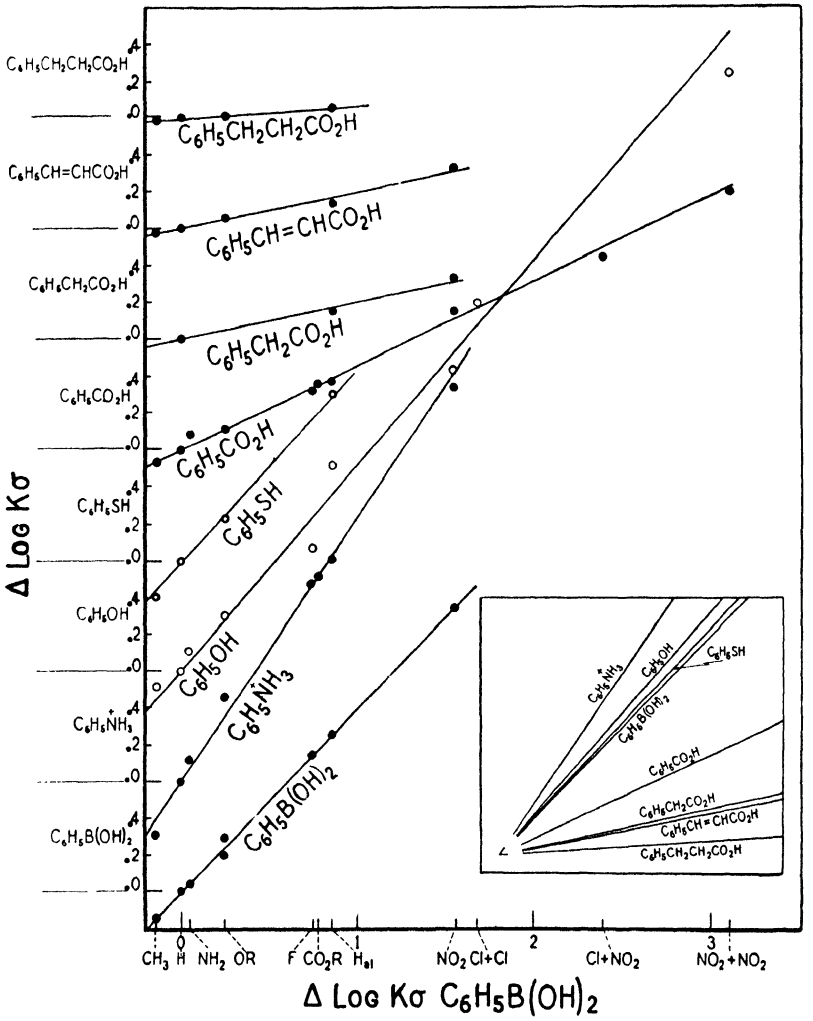


Figure 36. The effects of meta substituents on the strengths of certain aromatic acids.

for hydrogen as zero. The values of σ for other groups are then either positive or negative, but their magnitudes still depend on an arbitrary choice of a value of ρ for some reaction. The slopes of the lines in Figure 36 are the ρ values for the dissociation constants of

the types of acid, if ρ for phenylboric acid is arbitrarily taken as unity. Hammett chose ρ for the dissociation constants of benzoic acid as unity. Hammett's equation can be taken as a first approximation to the effects of meta and para substitutions in the benzene ring. The agreement between the points and the straight lines in Figure 36 shows that for the dissociation constants of meta derivatives of benzene the equation is a fairly close approximation.

The approximation is not sufficiently close to warrant a separation of certain groups. Thus, in the halogens Cl, Br, and I, there is a compensation between polarity and resonance, and their σ values are so close that we have not considered it necessary to separate them, so the mean values have been used, under the caption Hal. The σ value of F is sufficiently different to warrant a separate point. Again we have not distinguished between OH, OCH_3, and OC_2H_5, or between COOH, $COOCH_3$, and $COOC_2H_5$. These two sets of groups have been designated as OR and CO_2R, respectively. The points for *m*-hydroxy and *m*-ethoxy are both shown in the line for phenylboric acid. The abscissa value is the mean.

The values shown are taken from the various collections of acid strengths. The values differ somewhat, especially for phenols and anilines. Where possible, some preference has been given to the measurements in a single investigation, where the reference acid has also been measured. For example, we have used the $\Delta \log K_\sigma$ values found by Bennett, Brooks, and Glasstone[19] for halogenated phenols and anilines, and the curve for thiophenol is from the work of Schwarzenbach and Egli.[20]

Similarly, most of the values for phenylboric acids are taken from the single series of investigations by Branch, Yabroff, and Bettman.[20a] Water has not always been the solvent. Thus the above-quoted investigations are for 30, 48, and 25 per cent alcohol, respectively. However, when electrically neutral substituents are used, $\Delta \log K_\sigma$ values are practically constant for changes of solvent between water and 50 per cent alcohol, although the actual values of the dissociation constants are markedly affected by the addition of alcohol. Not all the dissociation constants have been measured at 25°C. Here

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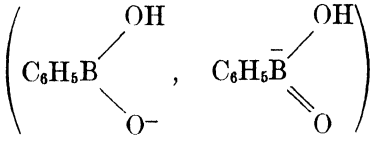
[19] Bennett, G. M., Brooks, G. L., and Glasstone, S., *J. Chem. Soc.*, 1821 (1935).

[20] Schwarzenbach, G., and Egli, H., *Helv. Chim. Acta*, **17**, 1183 (1934).

[20a] Branch, G. E. K., Yabroff, D. L., and Bettman, B., *J. Am. Chem. Soc.*, **56**, 937, 1850, 1865 (1934); Clear, C. G., and Branch, G. E. K., *J. Org. Chem.*, **2**, 522 (1938).

again $\Delta \log K_\sigma$ does not change appreciably between room temperature and 25°C., when both the acid and the reference acid are measured at the same temperature.

The slopes of the lines in Figure 36 are 0.075 for $C_6H_5CH_2CH_2COOH$, 0.21 for $C_6H_5CH_2COOH$, 0.20 for $C_6H_5CH{=}CHCOOH$, 0.46 for C_6H_5COOH, 1.0 for $C_6H_5B(OH)_2$, 1.12 for C_6H_5SH, and 1.44 for $C_6H_5\overset{+}{N}H_3$. These values correspond to Hammett's ρ value except for the difference in choice of an arbitrary standard. Hammett's value for phenol is 20 per cent lower than ours. There are marked differences in the slopes of the lines for acids with the same number of atoms between the phenyl group and the dissociating proton. For instance, the values for $C_6H_5CH_2CH_2COOH$ and $C_6H_5CH{=}CHCOOH$ are 0.075 and 0.20, respectively; those for C_6H_5COOH and $C_6H_5B(OH)_2$ are 0.46 and 1, respectively, and those for C_6H_5OH and $C_6H_5\overset{+}{N}H_3$ are 1.18 and 1.44, respectively. The effect of the group is transmitted more readily through the doubly than through the singly bonded pair of atoms, and is consequently greater in $C_6H_5CH{=}CHCOOH$ than in $C_6H_5CH_2CH_2COOH$. The resonance in phenylborate ion

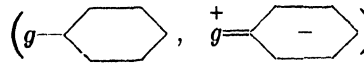


brings the charge effectively nearer to the phenyl group than the resonance in benzoate ion does. The difference in the last pair, phenol and anilinium ion, is not readily explained.

The points for some disubstituted acids are shown in the figure. These points fit the lines when the abscissa is the sum of the values of $\Delta \log K_\sigma$ ($C_6H_5B(OH)_2$) for each group; i.e., the effects of the groups are additive. It appears to be more difficult to reach a saturation polarization of the benzene ring than of a saturated hydrocarbon chain. This is in accord with the higher polarizability of the aromatic nucleus than of the saturated chain.

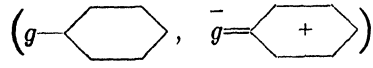
27d. Para groups. The value of $\Delta \log K_\sigma$ for a group in the para position may be greater or less than that of $\Delta \log K_\sigma$ for the same group in the meta position. In some instances $\Delta \log K_\sigma$ for a group has a different sign for meta and para substitution. For example, a meta alkoxyl group always increases the acidic strength, but a para

alkoxyl group always decreases it. When the quinoidal resonance between the group and the benzene nucleus is



$$\Delta \log K_{m\text{-}\sigma} > \Delta \log K_{p\text{-}\sigma},$$

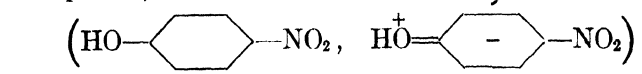
and when the resonance is



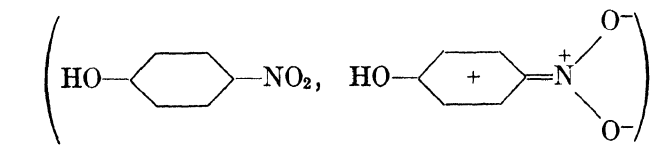
$$\Delta \log K_{p\text{-}\sigma} > \Delta \log K_{m\text{-}\sigma}.$$

The resonance of a para group can induce a charge nearer to the acidic group than the resonance of a meta group can, and the effect of the resonance of a group is greater when the group is para than when it is meta. For the groups NH_2, OR, OH, F, and to a lesser extent the other halogens, $\Delta \log K_{m\text{-}\sigma} > \Delta \log K_{p\text{-}\sigma}$; while for the groups NO_2, $COOR$, COOH, CN, and $B(OH)_2$, $\Delta \log K_{p\text{-}\sigma} > \Delta \log K_{m\text{-}\sigma}$. For the methyl group, $\Delta \log K_{m\text{-}\sigma} > \Delta \log K_{p\text{-}\sigma}$. In general, groups for which $\Delta \log K_{m\text{-}\sigma} > \Delta \log K_{p\text{-}\sigma}$ are ortho-para orienting, and those for which $\Delta \log K_{p\text{-}\sigma} > \Delta \log K_{m\text{-}\sigma}$ are meta orienting. (See section 52b.)

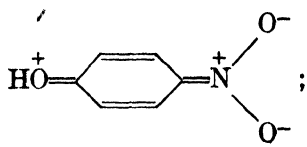
The effect of a para group on the strength of an acidic derivative of benzene is not restricted to its polarity and its quinoidal resonance with the ring. When two groups are para to each other and each has a quinoidal resonance with the benzene nucleus, there is an interaction between the two groups through the benzene ring which may be either an enhancement or an interference between the resonances of the two groups with the ring. The former occurs when the resonances of the groups induce opposite charges in the ring, and the latter when the resonances induce similar charges in the ring. Thus in *p*-nitrophenol, besides the resonances



and



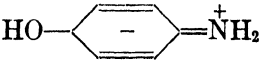
further resonance results from the possibility of the important structure



while in

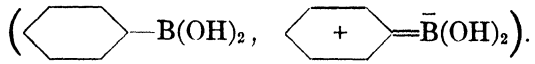


the state

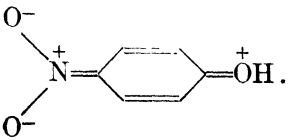


leaves no double bond next to the hydroxyl group, and so interferes with the resonance between the hydroxyl group and the benzene ring. Thus the amino group produces a cross-conjugation, which decreases the resonance effect of the phenyl group on any reaction of the hydroxyl group.

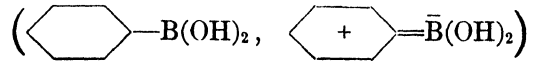
Whether a given para group capable of a quinoidal resonance will produce no further resonance effect, a resonance with the acidic portion of the molecule, or an interference with resonance between the acidic portion of the molecule and the benzene ring, depends on the reference acid into which the group is introduced; consequently, the relative values of $\Delta \log K_{p-\sigma}$ vary with the reference acid when the group is capable of quinoidal resonance. For instance, the resonance effect of a *p*-nitro group in $C_6H_5CH_2COOH$ is restricted to its quinoidal resonance with the benzene ring. In $C_6H_5B(OH)_2$ it interferes with the resonance



In C_6H_5OH it has an additional resonance due to the structure

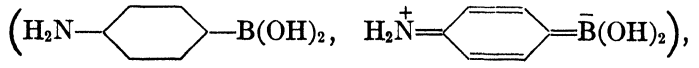


In this example the interference with the acid-weakening cross-conjugation due to the resonance

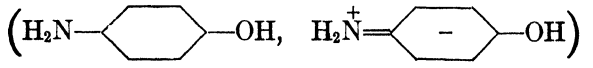


increases the acidic strength, but the effect is small, being a cross-conjugation of a cross-conjugation, so that the resonance effect of the nitro group on the strength of phenol is relatively much greater than it is on the other two acids. On the other hand, if we choose a group whose quinoidal resonance induces a negative charge in the

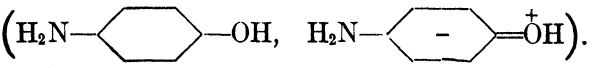
ring, in phenylboric acid it would produce an extra acid-weakening resonance by interaction with the boron atom,



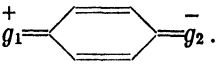
and in phenol it would have an acid-weakening cross-conjugation, since the resonance



interferes with the resonance



In this case the interference is a first-order cross-conjugation, and it is not possible to predict whether the acid-weakening effect of the amino group would be more marked in phenylboric acid or in phenol. It may be noted that, whether the normal resonance effect of a group is acid-strengthening or acid-weakening, it is enhanced in the para position either by cross-conjugation or by the existence of an additional important structure of the type



Owing to the foregoing additional resonance effects, the relative values of $\Delta \log K_\sigma$ for para groups are not independent of the reference acid, and we cannot put $\Delta \log K_{p\text{-}\sigma} = \sigma\rho$, where ρ is determined by the reference acid and σ by the para group.

However, if we choose reference acids of the same class, we may put $\Delta \log K_\sigma$ for both meta and para groups approximately equal to $\sigma\rho$, where ρ is determined by the reference acid and σ by the group and its position. That is, for every group two values of σ are needed; one for the meta, the other for the para position. Two examples of such sets of reference acids are (1) benzoic and phenylboric acids, and (2) phenol, thiophenol, and anilinium ion.

The relationship between $\Delta \log K_\sigma$ for benzoic and phenylboric acids are shown in Figure 37, in which the points are for $\Delta \log K_{p\text{-}\sigma(C_6H_5COOH)}$ against $\Delta \log K_{p\text{-}\sigma(C_6H_5B(OH)_2)}$, and the line is for $\Delta \log K_{m\text{-}\sigma(C_6H_5COOH)}$ against $\Delta \log K_{m\text{-}\sigma(C_6H_5B(OH)_2)}$. A few 3,4 disubstituted benzoic acids are included, the groups being chosen so that no great resonance or chelation between them is likely. The points for para substituted and 3,4 disubstituted acids fall close to the line (meta substituents).

The relationship between $\Delta \log K_{p\text{-}\sigma}$ values for phenol, thiophenol, and anilinium ion are shown in Figure 38. In this figure, curve I is a plot of $\Delta \log K_{\sigma(C_6H_5SH)}$ against $\Delta \log K_{\sigma(C_6H_5OH)}$ for meta and para groups. The data is taken from the work of Schwarzenbach and Egli, using their measurements for both the phenols and the thiophenols. The experiments were done in 48 per cent alcohol, and at 20°C. Curve II shows the points $\Delta \log K_{p\text{-}\sigma(C_6H_5OH)}$ against $\Delta \log K_{p\text{-}\sigma(C_6H_5\dot{N}H_3)}$.

In Figures 37 and 38 the points for meta substitution are not shown. Instead, the straight lines are those drawn for meta groups alone and shown in Figure 36. The line in Figure 37 is that for

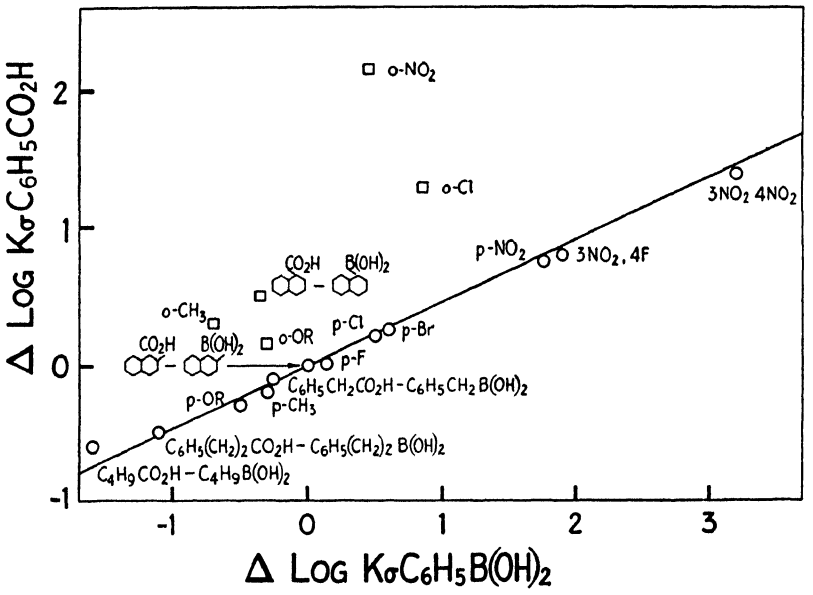


Figure 37. A comparison of the effects of substitution on the strengths of phenylboric and benzoic acids.

benzoic acid in Figure 36. The lines in Figure 38 are those shown for thiophenol and phenol in Figure 36, with the correction for the change of abscissa from $\Delta \log K_{\sigma(C_6H_5B(OH)_2)}$ to $\Delta \log K_{\sigma(C_6H_5OH)}$ for curve I and to $\Delta \log K_{\sigma(C_6H_5\dot{N}H_3)}$ for curve II.

The points for para substituents fall fairly well on the meta line in the three cases shown in Figures 37 and 38. The agreement is very good when $\Delta \log K_{\sigma(C_6H_5COOH)}$ is plotted against $\Delta \log K_{\sigma(C_6H_5B(OH)_2)}$, but not so good when $\Delta \log K_{\sigma(C_6H_5OH)}$ is plotted against $\Delta \log K_{\sigma(C_6H_5\dot{N}H_3)}$.

The accuracy of measurements of the strengths of phenols and

anilinium ions is not as great as that of benzoic and phenylboric acids. Many investigators have mentioned the difficulty of obtaining good measurements of the strengths of phenols and anilines, and the data in the literature are not very consistent. However, the points that vary most from the line are those for the groups NO_2, F, and NH_2. The first of these has a very strong resonance when para to hydroxyl or amino groups, and the other two introduce a strong cross-conjugation. There is no consistency between the last two groups, as the point for fluorine falls below the line, while that for the amino group is above the line. The average deviation

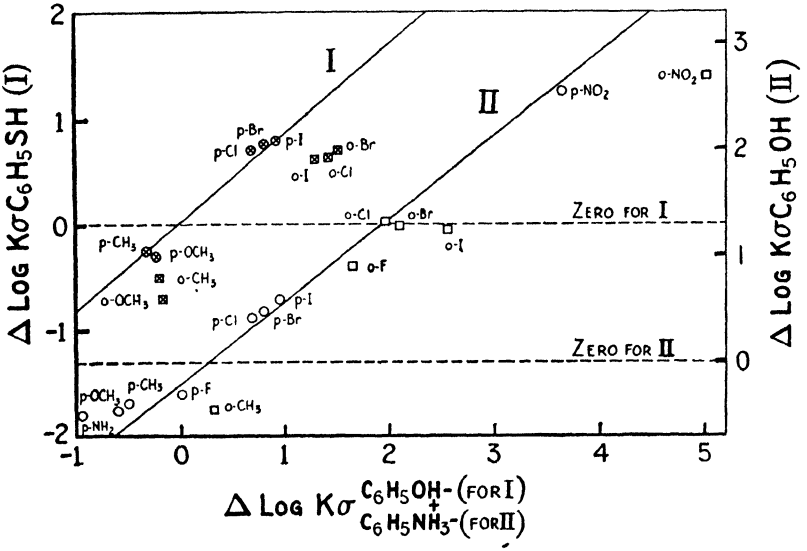


Figure 38. Comparison of the effects of substitution on the strengths of related aromatic acids. Curve I, phenol and thiophenol; curve II, anilinium ion and phenol.

for para groups in the benzoic-phenylboric curve is 0.03 units; that in the phenol-anilinium ion curve is 0.17. The discrepancy for the amino group is very large, amounting to 0.5 units. This discrepancy could be considerably reduced by using other values given in the literature for the acid and base strengths of *p*-aminophenol and *p*-phenylenediamine, respectively, but the values used appear to be the best choice. It would seem advisable to postpone judgment on the relative effects of the strong cross-conjugations that occur in amino-, alkoxy- and fluoro-substituted phenols and anilines until one is sure of the reliability of the measurements.

From Figures 37 and 38 it appears that the Hammett equation,

$\log K_\sigma = \log K_u + \sigma\rho$, is a close approximation for both meta and para substitutions when acids of similar type are compared. It also holds for some other structural changes. In Figure 37 we have included points for the introduction of methylene groups between the phenyl and the carboxyl or boric acid groups, and for the substitution of an alkyl group for the aromatic nucleus. Even though these structural changes alter the type of acid, the points fall fairly well on the line. We have also introduced the points for the substitution of naphthyl groups for the phenyl group. In this case the point for the β-naphthyl substitution is close to the line, but that for α-naphthyl substitution is not. The substitution of α-naphthyl is an ortho substitution, and as such a single value of σ for the substitution cannot be used for both benzoic and phenylboric acids. That Hammett's equation is a very poor approximation for ortho substitutions can be seen in Figures 37 and 38, where the ortho points have been plotted as squares. These points do not fall on the meta lines.

We have already explained that the equation $\Delta \log K_\sigma = \sigma\rho$ cannot hold for para groups that resonate strongly with the benzene ring when aromatic acids of different classes are compared. However, when the resonance is small this equation can be applied to acids of different classes, each reference acid having a single ρ value, and each group two σ values, one for meta and the other for para substitution.

In Figure 39 we have plotted a mean $\Delta \log K_\sigma$ for phenol and anilinium ion against a mean value of $\Delta \log K_\sigma$ for benzoic and phenylboric acids. The mean value of $\Delta \log K_\sigma$ used for phenol and anilinium ion is not the simple average. The observed $\Delta \log K_{\sigma(C_6H_5OH)}$ is first changed to a "corresponding" $\Delta \log K_{\sigma(C_6H_5\dot{N}H_3)}$, and this value is averaged with the observed value of $\Delta \log K_{\sigma(C_6H_5\dot{N}H_3)}$. This "corresponding" $\Delta \log K_{\sigma(C_6H_5\dot{N}H_3)}$ is obtained from the graph of $\Delta \log K_{\sigma(C_6H_5OH)}$ against $\Delta \log K_{\sigma(C_6H_5\dot{N}H_3)}$ (curve II, Figure 38) by taking the value of the abscissa of a point on the curve whose ordinate is the observed value of $\Delta \log K_{\sigma(C_6H_5OH)}$. In the same way the mean $\Delta \log K_\sigma$ for benzoic and phenylboric acids is the average of the observed value of $\Delta \log K_{\sigma(C_6H_5COOH)}$, and the abscissa of a point on the graph of $\Delta \log K_{\sigma(C_6H_5COOH)}$ against $\Delta \log K_{\sigma(C_6H_5B(OH)_2)}$ (Figure 36), whose ordinate equals $\Delta \log K_{\sigma(C_6H_5COOH)}$. The two sets of mean values are therefore expressed as $\Delta \log K_{\sigma(C_6H_5\dot{N}H_3)}$ and $\Delta \log K_{\sigma(C_6H_5B(OH)_2)}$ values, respectively. The theoretical curve for the graph of $\Delta \log K_{\sigma(C_6H_5OH-C_6H_5\dot{N}H_3)}$ against $\Delta \log K_{\sigma(C_6H_5COOH-C_6H_5B(OH)_2)}$ is the curve for $\Delta \log K_{m\text{-}\sigma(C_6H_5\dot{N}H_3)}$ against

$\Delta \log K_{m\text{-}\sigma(C_6H_5B(OH)_2)}$ (see Figure 36). This is a straight line whose slope is 1.44, and which passes through the origin.

The points for meta groups and those para groups that do not resonate very strongly with the benzene ring fall as close to the line as might be expected from the accuracy of the data. Points that do not fall near the line show resonance effects that are specific to

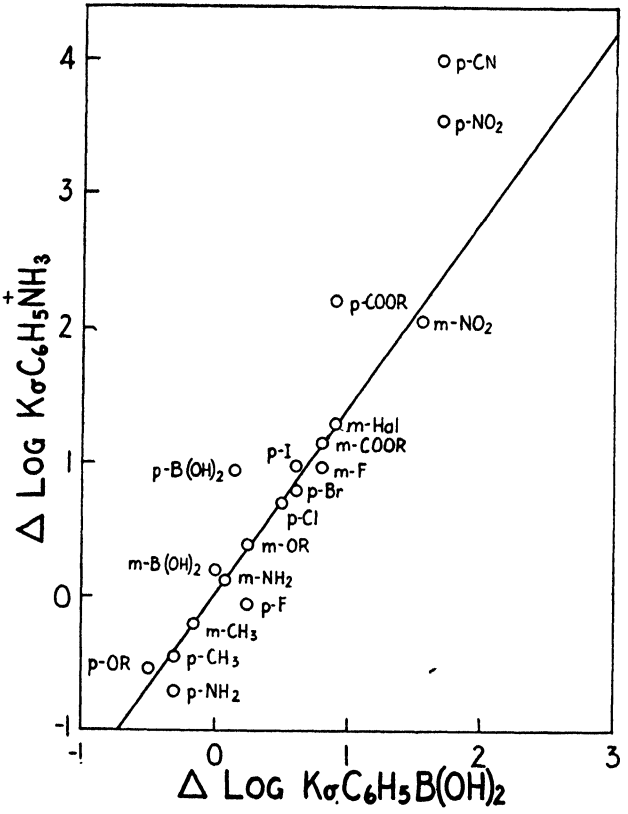
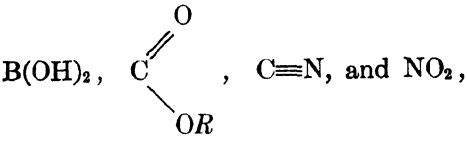


Figure 39. Comparison of the effects of meta and para substitution on the strengths of aromatic acids of different type.

one or the other of the two classes of acids. Only points for electrically neutral meta and para groups are given.

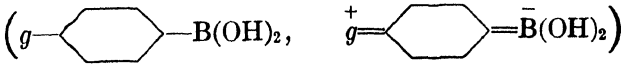
Figure 39 shows very clearly the much greater effect of a para group, whose resonance with the benzene ring induces a positive charge in the ring, on an aromatic acid in which the aromatic nucleus resonates with the acidic group itself (C_6H_5OH and $C_6H_5\overset{+}{N}H_3$), than

on an acid in which the aromatic nucleus resonates with the acidic resonator (C_6H_5COOH and $C_6H_5B(OH)_2$). The points for such para groups,

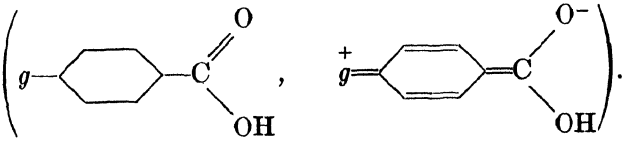


average 1.1 units above the line, while the average deviation of the points for meta and poorly resonating para groups is 0.07.

The points for the para groups that resonate strongly with the benzene ring, inducing a negative charge on the ring (NH_2, OR, and F) are, on an average, 0.16 units below the line. It would appear that the deviation from the simple equation $\Delta \log K_\sigma = \sigma\rho$ for para groups of this type indicates that the cross-conjugations in anilines and phenols are more important perturbing factors than the resonances



and



But again judgment should be reserved on this point, for in this type of phenol and aniline, experimental error is apt to be great. To sum up, one can state that Hammett's equation $\log K_\sigma = \log K_u + \sigma\rho$ is a fairly close approximation for meta and para substitution, except when a para-substituted group resonates so as to put a positive charge in the ring. In such cases it is necessary to use two values of σ for the group in the para position; one when the atom from which the proton dissociates resonates directly with the aromatic nucleus, and the other for acids in which the benzene resonances are less directly concerned with the dissociation. Hammett recognized this limitation and assigned two σ values to the para nitro group, a benzoic and a phenolic value.

27e. Ortho groups. The quinoidal resonance of a group in the ortho position is very similar to that of the same group in the para position. On the other hand, the ortho position is closer to the

ionizable proton than the meta position is, and it would be expected that the inductively transmitted polar effect of a group should be greater from the ortho than from the meta or para position, while its resonance effects should be very similar in the ortho and para positions. Many examples may be quoted that support these ideas. Thus the chlorine atom, whose resonance effect is small in comparison with its polar effect, generally increases the strength of aromatic acids much more from the ortho than from the meta or para position. Or again, though the polar effect of the alkoxyl group tends to strengthen an acid, the ortho alkoxyl aromatic acids are generally weaker than their meta isomers, the strong acid-weakening resonance of the alkoxyl group being much more effective from the ortho than from the meta position. Were the effects of an ortho group restricted to its quinoidal resonance and its inductively transmitted polarity, $\Delta \log K_{o\text{-}\sigma}$ for one reference acid plotted against $\Delta \log K_{o\text{-}\sigma}$ for another but closely related reference acid would give the same curve as the corresponding plot for meta or para groups; and, were one to use only poorly resonating groups, the curve for ortho groups would be the same as that for meta groups even if the reference acids chosen did not belong to the same class. That this is not so can be seen by inspection of Figures 37 and 38, in which the points for ortho groups do not coincide in any way with the curves that fit the meta and para groups.

The anomalies of ortho compounds are not restricted to their acidic strengths, but are found in all kinds of comparisons of the properties of related compounds. One of the first anomalies to be observed was the slower esterification of ortho substituted benzoic acids than of the corresponding meta and para acids. This was attributed to the possibility of the physical interference of ortho groups, and was called steric hindrance. Flürscheim,[21] who early noted the anomalous strengths of ortho substituted aromatic acids, attributed the phenomenon to steric hindrance. He supposed that the ortho group hindered the return of the proton more than it did its escape. The effect was therefore supposed to make ortho acids anomalously strong.

The effects of ortho substituents are often very complex. Sometimes they appear to decrease the strength of an acid, or to increase the rate of a reaction. The modern trend has been to be less explicit as to their nature and to call them ortho effects rather than steric

[21] Flürscheim, B., *J. Chem. Soc.*, 725 (1909).

hindrances. However, there seems little doubt that they are due to the proximity in space of ortho groups, and in many cases to be due to an actual spatial interference of the groups with each other.

Although the existence of an ortho effect can be observed in graphs like those shown in Figures 37 and 38, this method only indicates that an ortho effect exists in one of two acids, but not in which acid it exists, or whether it is acid strengthening or acid weakening. For instance, $\Delta \log K_{o\text{-Cl}(C_6H_5COOH)}$[21a] is much greater than 0.46 times $\Delta \log K_{o\text{-Cl}(C_6H_5B(OH)_2)}$; there is, therefore, either an acid-strengthening ortho effect in $o\text{-ClC}_6H_4CO_2H$ or an acid-weakening ortho effect in $o\text{-ClC}_6H_4B(OH)_2$. However, we can observe the existence of an ortho effect and its sign by comparing the effect of a group in the ortho position with its effects in the meta and para positions. For instance, all meta- and para-methyl aromatic acids are weaker than the reference acid, but many ortho-methyl acids are stronger; e.g., $o\text{-CH}_3C_6H_4COOH$, and $o\text{-CH}_3C_6H_4\overset{+}{N}H_3$. In these cases we can assume that there is an acid-strengthening ortho effect. The accuracy with which we can observe ortho effects in this way depends on how accurately we can judge what would be the strength of the ortho acids if there were no ortho effects. At present this cannot be done quantitatively, and so no quantitative measure can be given for ortho effects.

Any comparisons of the strengths of ortho substituted aromatic acids show an almost haphazard array of values such as those shown in Figures 37 and 38. The only regularity observable for the ortho groups in these figures is that for any pair of reference acids, A_1 and A_2, for which a plot of $\Delta \log K_{\sigma(A_1)}$ against $\Delta \log K_{\sigma(A_2)}$ is made, the points for ortho groups generally fall all above or all below the line on which the meta and para groups fall. Thus for $\Delta \log K_{\sigma(C_6H_5COOH)}$ against $\Delta \log K_{\sigma(C_6H_5B(OH)_2)}$ the ortho points are all above the line, and for $\Delta \log K_{\sigma(C_6H_5OH)}$ against $\Delta \log K_{\sigma(C_6H_5\overset{+}{N}H_3)}$ the ortho points are either below or near the line.

One may readily imagine ways in which the proximity of ortho groups may affect the strength of an acid:

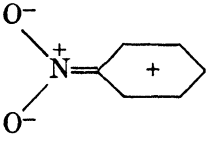
(1) In an ortho-substituted group, the direction of the group dipole is different from that which it would have in the meta or para group, and so its directly transmitted effect may have the reverse sign. It

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[21a] The notation $\Delta \log K_{o\text{-Cl}\,(C_6H_5COOH)}$ is used to indicate the change in $\log K$ for an o-Cl substitution in benzoic acid. Other subscripts have the corresponding significance.

is rather difficult to cite examples of such cases. Apparently the polarizability of the benzene ring is such that direct effects of electrically neutral groups are not great compared with induced effects. Theoretically the difference in the direction of the dipoles must contribute to the anomalies of the strengths of ortho-substituted aromatic acids, but by itself it is insufficient to account for the irregularities.

(2) A quinoidal resonance involves the contribution of a structure in which the group is doubly bonded to the benzene ring. The structures are favored by atomic arrangements in which the group is so rotated that it is coplanar with the benzene ring and its substituent groups. Thus in $C_6H_5NO_2$ the contribution of



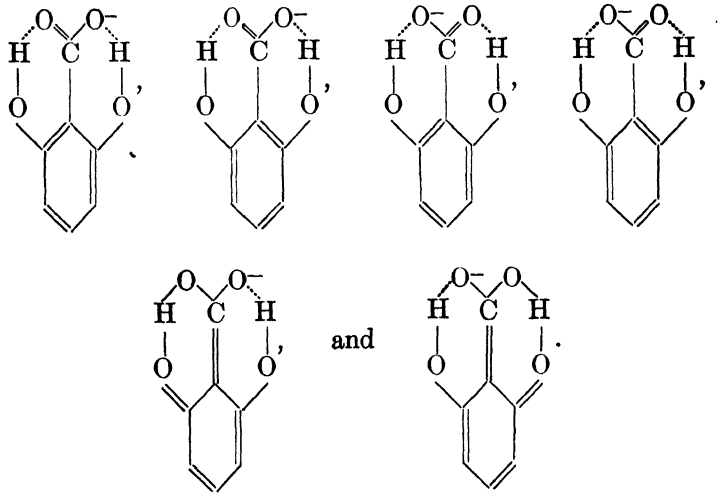
is greatest when the atoms of the nitro group are in the plane of the ring. This type of arrangement may bring atoms of ortho groups so close together that they repel one another and this interferes with the resonances, and decreases the effect that the resonance has on the strength of the acid. Examples can be cited that are apparently due to this factor in ortho effects. For instance, in 2,5-dinitro-, 2-nitro-5-chloro-, and 2-nitro-5-bromobenzoic acids there is less steric hindrance to the resonance of the 2-nitro group than in the corresponding 2,3 isomers; consequently, the 2,5 acids are stronger than the 2,3 acids. The dissociation constants are 2.4×10^{-2}, 1.35×10^{-2}, 1.3×10^{-2} for the 2,5 acids against 1.3×10^{-2}, 4×10^{-3} and 3.2×10^{-3} for the 2,3 acids, respectively. However, exceptions may readily be found; e.g., 2,3-dinitrophenol is stronger than the 2,5 isomer, and it is not possible to attribute all ortho effects to this cause. We have already discussed the ortho effect due to the steric hindrance of resonance in considering the dipole moments of aromatic compounds. There we found that the steric hindrance to aminobenzene resonance could be accentuated by substituting methyl groups for the hydrogen atoms of the amino group. A similar phenomenon has been observed in the strengths of ortho substituted anilinium ions by Davies and Addis.[22] The acid $o\text{-}CH_3C_6H_4\overset{+}{N}H_3$ is stronger than $p\text{-}CH_3C_6H_4\overset{+}{N}H_3$. This shows

[22] Davies, W. C., and Addis, H. W., *J. Chem. Soc.*, 1622 (1937).

that there is some other type of ortho effect that more than compensates for the steric hindrance to the resonance. But the steric hindrance to the resonance can be increased by putting methyl groups on the nitrogen atom, and o-$CH_3C_6H_4\overset{+}{N}H(CH_3)_2$ is a weaker acid than its para isomer.

(3) Groups in the ortho position may have an atom of one group so near to one of the other group that the resonance resulting from the alternative bonding of this atom may be energetic enough to overcome the repulsion of the groups, and result in the formation of a chelate ring. When the energy of the chelation is greater in the acid than in its ion, the acid is weakened; and when the opposite is the case, the acid is strengthened. The formation of a ring may also be the result of a pair of unshared electrons of one group being accepted by another group ortho to it.

Salicylic acid is an example of an ortho effect due to chelation.[23] This acid is as strong as o-chlorobenzoic acid, in spite of the acid-weakening resonance of the hydroxyl group. Baker[24] has pointed out that in the still more anomalously strong acid, 2,6-dihydroxybenzoic acid ($K_a = 10^{-1.3}$), the chelation in the ion is greatly assisted by the resonance between the almost equivalent structures:



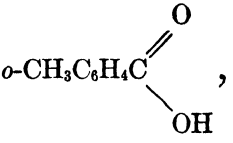
(4) The fourth factor in ortho effects is that groups in the ortho position are so close together that they repel one another, and this

[23] Branch, G. E. K., and Yabroff, D. L., *J. Am. Chem. Soc.*, **56**, 2568 (1934).
[24] Baker, W., *Nature*, **137**, 236 (1936).

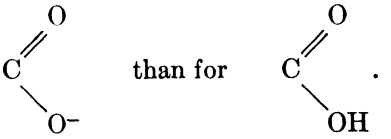
repulsion increases the potential energy of the molecule. This repulsion is affected by ionization; when it is decreased by ionization the acid is strengthened, and when it is increased it is weakened. The factors that govern the increase or decrease of the repulsive energy or ionization are very similar to those that decrease or increase the energy of ring formation, so that the third and fourth factors in the ortho effect behave in very similar ways. The criterion that separates them is whether the groups have a net repulsion or attraction, and this criterion often is impossible to apply and is really immaterial. Let us consider two molecules being forced together. Because of the repulsive forces, the potential energy of the system increases as the molecules approach. However, as they approach there is a resonance due to the alternative bonding of some atom or atoms to one or another of the molecules, or there is a tendency to share electrons between the molecules. These processes reduce the potential energy. If this reduction is greater than the potential energy of repulsion, the molecules attract each other and form a compound, but even if it is not, the reduction in potential energy still depends on these bond-forming forces. In the same way the bond-forming forces between two ortho groups may overcome the repulsive forces and give a ring closure, or merely reduce the potential energy arising from the close proximity of the groups. But in both cases the bond-forming forces are altered by the loss of a proton from one of the groups, and in analogous ways. If the ionization makes the repulsion less, or the ring closure stronger, the effect is acid-strengthening, and the reverse is true if the ionization increases the repulsion or makes the ring closure weaker. Consequently, we are often able to reason correctly about an ortho effect without knowing whether a ring is actually formed or not.

As we have already mentioned, the methyl group definitely shows a positive ortho effect in $o\text{-}CH_3C_6H_4\overset{+}{N}H_3$ and $o\text{-}CH_3C_6H_4COOH$. In the former, and in its conjugate base, the methyl and amino groups are brought so close together that they repel one another. The resulting potential energy is decreased by the energy of the resonance resulting from the transfer of protons from one group to the other. In $o\text{-}CH_3C_6H_4\overset{+}{N}H_3$, this can only be an exchange of protons, but in $o\text{-}CH_3C_6H_4NH_2$ the proton from the methyl group may go to the unshared pair of electrons of the amino group. This should result in a greater decrease of the energy of repulsion in $o\text{-}CH_3C_6H_4NH_2$ than in $o\text{-}CH_3C_6H_4\overset{+}{N}H_3$, and the ortho effect should therefore increase

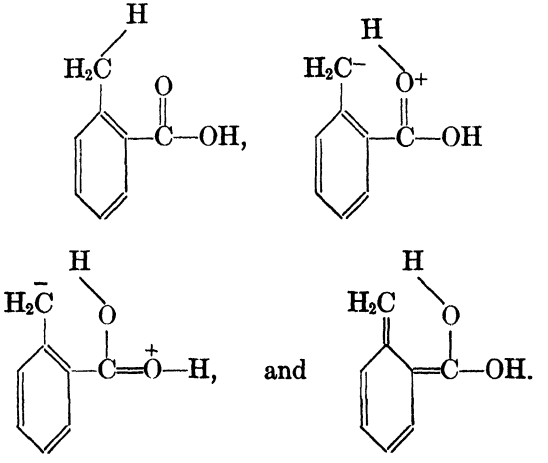
the acid strength. It is unlikely that a chelate ring is formed, as the bond angles for a chelate ring containing four atoms other than the proton link are unfavorable. In ortho benzene derivatives we find that five atoms other than the proton link seem to be the most favorable number for chelate hydrogen-bridged rings. Further, a hydrogen atom attached to carbon does not have the same facility for forming another bond as protons attached to other atoms. In *o*-toluic acid,



the tendency for bond formation through a hydrogen bridge between the methyl group and the oxygen atom of the carboxyl exists, and should be stronger for



The ortho effect should be positive. It is possible that in this case a chelate ring does exist, as the chelation involves a resonance between several forms:



The last form does not directly increase the strength of the acid, but indirectly it assists ionization by holding the carboxyl group in a

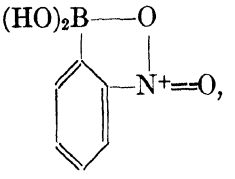
position favorable to the second and third forms, whose contributions increase the acidic strength.

In o-$CH_3C_6H_4OH$ we have the same case as in o-$CH_3C_6H_4\overset{+}{N}H_3$ except that the methyl proton can be transferred to the oxygen atom in both the acid and its ion. But this tendency should be greater in the ion than in the acid. We should therefore expect a positive ortho effect, but we cannot predict whether it is greater or less than the corresponding effect in o-$CH_3C_6H_4\overset{+}{N}H_3$. There seems little doubt that there is a positive ortho effect in o-$CH_3C_6H_4OH$, as this acid is stronger than its para isomer. Further, $\Delta \log K_{o\text{-}CH_3(C_6H_5SH)}$ is much more negative than $\Delta \log K_{o\text{-}CH_3(C_6H_5OH)}$, and it is difficult to account for a negative ortho effect in o-$CH_3C_6H_4SH$. However, the ortho effect of the methyl group is less marked in o-cresol than in o-toluidine.

The lack of electrons on the boron atom of o-$RC_6H_4B(OH)_2$ results in some compensating force of attraction between the boric acid group and any group ortho to it. This may result in chelation or in a reduction of the normal repulsion between ortho groups. In the ion the boron atom is almost saturated by the negatively charged oxygen atom. Consequently, the stabilizing interaction between the boron atom and the ortho group tends to decrease the strength of the acid. The change in the saturation of the carbon atom of a carboxyl group on ionization is less than that of the boron atom of a boric acid group, and the acid-weakening effect of the interaction of the boron atom of the boric acid group with an ortho group is greater than that of the carbon atom of the carboxyl with an ortho group. The ortho effect is therefore more negative or less positive in an ortho derivative of phenylboric acid than in the corresponding derivative of benzoic acid, and points for ortho groups in a plot of $\Delta \log K_{\sigma(C_6H_5COOH)}$ against $\Delta \log K_{\sigma(C_6H_5B(OH)_2)}$ should fall above the line determined by meta and para substitutions. This effect is shown in Figure 37.

In o-nitrophenylboric acid, the effect of the interaction between the boron atom and the ortho group is present in an exaggerated form. This acid is weaker than its meta isomer. If we assume no ortho effect in o-nitrobenzoic acid, the ortho effect in o-nitrophenylboric acid is -4.0. If we assume zero for the ortho effect in o-nitrophenylboric acid, that in o-nitrobenzoic acid is 1.8. It seems probable that there is a negative ortho effect in o-nitrophenylboric acid and a positive one in o-nitrobenzoic acid, but that the former is

greater in magnitude than the latter. A large negative ortho effect in *o*-nitrophenylboric acid is readily understood. The negatively charged oxygen atom of the nitro group is correctly situated for combination with the boron atom. The resulting compound,



has both six- and five-membered rings.[25]

28. MISCELLANEOUS ACIDS

In the preceding four sections (24 to 27) we considered in some detail the correlations between the structure of a molecule and its acidity when this acidity is due to the ionic dissociation of an O—H bond or, in a few special cases, of S—H or $\overset{+}{N}$—H bonds. These are not the only bonds which can be made to dissociate to give hydrogen ion, although for polyvalent atoms they are the easiest. By a suitable choice of structure it is possible to make N—H an acid group and even C—H; the order of the acidity of these bonds being $\overset{+}{N}$—H > O—H > N—H > C—H. The reason for the acidity of $\overset{+}{N}$—H is obviously the excess positive charge. The order of the others is that of decreasing nuclear charge, the octet being complete in each case. From the examination of the O—H acids, it was found that the groups whose introduction into the molecule produced the greatest acid-strengthening effects were those groups which had high polarities or introduced important new resonances. These groups, in an order of decreasing effectiveness as resonance-inducing groups when attached directly to the oxygen atom, or attached indirectly through a conjugated system, were

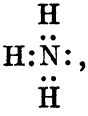
$$NO_2 > C{\equiv}N > CH_3{-}\overset{\overset{O}{\|}}{C} > C{=}C.$$

These same groups are the most effective acid-strengthening substituents for the ammonia and methane acids as well, with the added

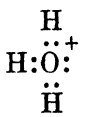
[25] Bettman, B., Branch, G. E. K., and Yabroff, D. L., *J. Am. Chem. Soc.*, **56**, 1865 (1934).

possibilities in these cases of having two and three such groups, respectively, attached directly to the atom from which proton dissociates (N or C).

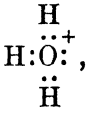
28a. Ammonia acids. In order to judge the acid-strengthening effect of a group, one must have some estimate of the strength of the unsubstituted acid. In the case of



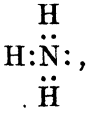
such an estimate can be made from a comparison with the structure



whose acid strength in water is the molarity of water, 55. The only difference between ammonia and hydronium ion is the unit positive nuclear charge on the oxygen. If the inductive constant for a unit positive charge, $I_c = +12.3$, is assumed and account is taken of the fact that this constant is valid for unit positive charge on the atom next to the oxygen by multiplying it by 2.8, one obtains its effect if it were directly on the oxygen, which is a value of $\Delta \log K$ of about 34.5. This is equivalent to saying that if the positive charge were removed from the structure



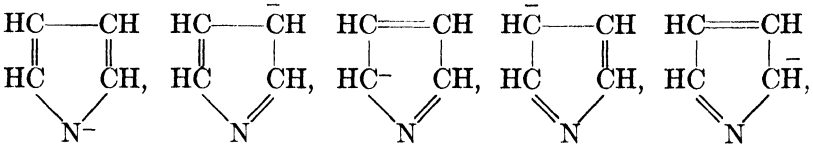
giving the structure



the strength of the acid would change from 55 to 10^{-33}. We thus have an estimate of the acid strength of unsubstituted ammonia.

When two of the feebly acid-strengthening group C=C are substituted into ammonia to give the ring structure pyrrole, the result is a compound which will form a potassium salt quite readily when treated with the metal, but which is still too weak an acid to have

any real quantitative measure of its strength (circa 10^{-15}). This acidity is due to the resonance in the ion,

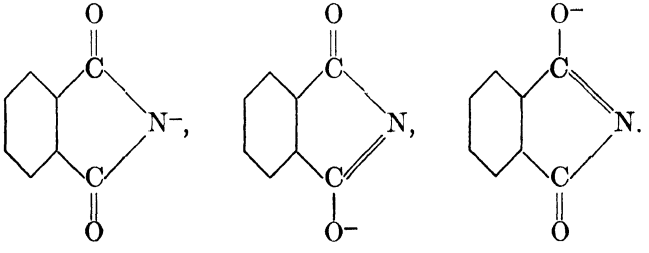


which in the undissociated acid is much less important because of the separation of charge which is required there. In the pyrrole ion the form with the charge on N is more stable than the other four. Replacing CH by N makes it possible to produce a structure in which there are more nitrogen atoms to carry the charge. If three CH groups are replaced by N, the resulting ion is that of tetrazole, which also has five forms, but the situation is reversed: four of the forms are equivalent low-energy forms (charge on N) and one is a high-energy form (charge on C). Tetrazole is therefore a much stronger acid than pyrrole, having a dissociation constant of the order of 10^{-5}.

The next acid-strengthening group, the acyl group,



is more effective, a single substitution being sufficient to produce an acid with a dissociation constant of about 10^{-15}, while two acyl groups produce a fairly strong acid; e.g., phthalimide, $K_a = 4 \times 10^{-8}$. Here again the important resonance in the ion is responsible, since in the undissociated imide it involves a separation of charge:



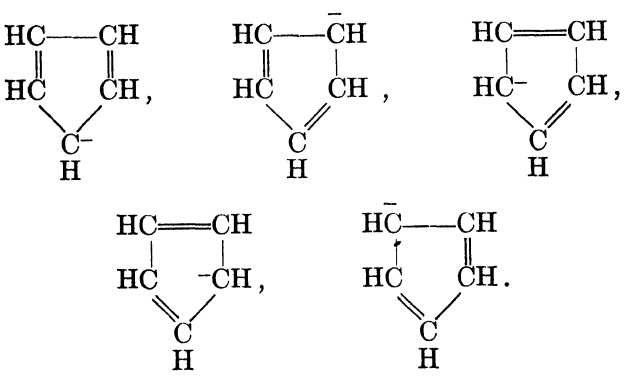
Still more effective is the CN group, cyanamide having a dissociation constant of about 4×10^{-11} while dicyanamide is a strong acid, $K \simeq 10^{-1}$. And here again the same principles apply, the new resonance forms being less important in the undissociated acid because of the separation of charge necessary there which is not neces-

sary in the ions whose contributing forms are, for cyanamide ion, $H—\bar{N}—C\equiv N$, $H—N=C=\bar{N}$, and for dicyanamide ion, $N\equiv C—\bar{N}—C\equiv N$, $\bar{N}=C=N—C\equiv N$, $N\equiv C—N=C=\bar{N}$. An interesting intermediate case is that of N-cyanoacetamide whose dissociation constant (10^{-4}) lies between that of a diacyl amide (10^{-8}) and dicyanamide (10^{-1}).

Finally, a single NO_2 group in ammonia is sufficient to produce a very appreciable acid strength, nitramide having a dissociation constant of about 2×10^{-7}.

28b. Methane acids. In a manner exactly analogous to the one which was used in estimating an acid dissociation constant for NH_3, it is possible from a comparison with $\overset{+}{N}H_4$ to obtain a value of approximately 10^{-43} as a formal representation of an acid strength for CH_4. In a similar manner the effect of the various groups on the acid strength of methane may be traced.

Two vinyl groups, producing the ring structure cyclopentadiene, have in this case an exceptionally powerful effect because of the exact equivalence of all five resonance forms of the ion:[26]

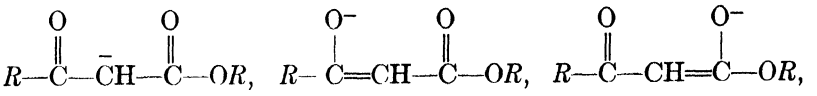


Alkali metal salts of cyclopentadiene are known.

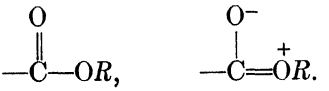
A single acyl group produces a substance which will react with sodium (acetone), whereas two acyl groups produce a substance with a measurable acidity ($K_{(\text{acetylacetone})} \simeq 10^{-8}$). There is an interesting effect of cross-conjugation to be observed in this case. (See also section 26a.) If one of the acyl groups is part of an ester, as in acetoacetic ester, the acidity of the methane is greatly reduced, becoming $\simeq 10^{-11}$. This reduction is due to the non-equivalence of

[26] Wheland, G. W., *J. Chem. Phys.*, **2**, 480 (1934).

the resonance forms of the ion and to the condition that the ester carbonyl contribution to the methane acid-strengthening resonance is reduced by an amount corresponding to the degree to which it contributes to the ester resonance. The three methane acid-strengthening resonance forms are



the last of which is mutually exclusive with the ester resonance forms



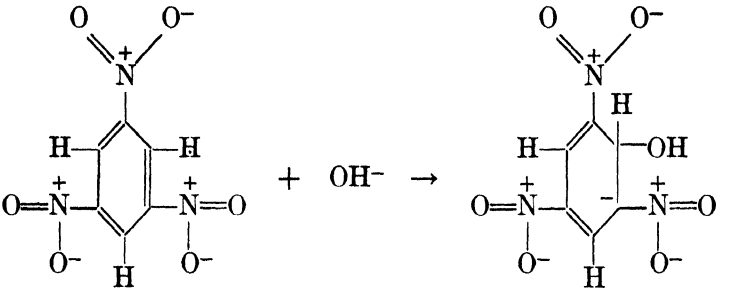
The effect of the CN group is quite readily observable even in CH_3CN, which reacts quite rapidly with sodium, while the acid strength of malononitrile, $CH_2(CN)_2$, is given as about 10^{-11} and cyanoform, $HC(CN)_3$, is a strong acid ($K \simeq 10^{-1}$).

Similarly, the series nitromethane, dinitromethane, and nitroform have been assigned the constants 10^{-11}, 10^{-4}, and 10^{-1}, respectively. It is interesting to note the reduction of the effectiveness of the NO_2 group when it is separated from the methane carbon atom by a conjugated system such as the phenyl group. The dissociation constant of trinitrotriphenylmethane[27] can be estimated to be about 10^{-13}.

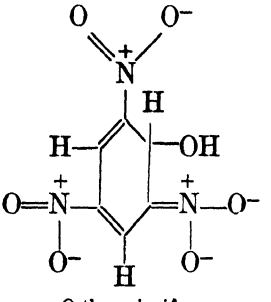
28c. Generalized acids. In section 22 it was pointed out that in order that a substance be an acid it is not necessary that it be capable of dissociating to give a hydrogen ion. There are many such substances among inorganic compounds[28]—e.g., BCl_3, SO_3—but among organic compounds, aside from boric acid derivatives and similar substances, there are relatively few whose acidity is unequivocally not due to a dissociable proton. One of the best examples of such an acid is trinitrobenzene. In this case one cannot use the ordinary dissociation constant to describe its strength as an acid, unless one formally describes it as the dissociation of a hydrate, which it clearly is not. It is, however, used as an indicator, and the change to a deeply colored substance occurs in the pH range 14–14.3.[29] The

[27] Lewis, G. N., and Seaborg, G. T., *J. Am. Chem. Soc.*, **61**, 1894 (1939).
[28] Lewis, G. N., *J. Frank. Inst.*, **226**, 293 (1938).
[29] Calculated as the dissociation of a hydrate, this would correspond to an acid-dissociation constant of about 10^{-14}.

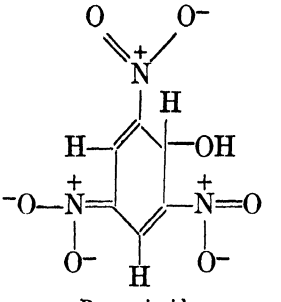
acidity is due to the ability to combine with base. For the base OH^-, the reaction may be written



with relatively stable resonance forms in the ion of the type:



Ortho-quinoid



Para-quinoid

Chapter VII

ENERGY RELATIONSHIPS IN SOME OTHER REACTIONS

29. IONIC RESONANCE AND THE HEAT OF FORMATION

In the discussion of the hydrogen molecule in Chapter III, it was shown that a better approximation to the experimental value for the heat of the reaction $2H \rightarrow H_2$, was obtained when a small contribution of the ionic states $H^+ :H^-$ and $H^- :H^+$ was included in the ground state of the hydrogen molecule. When the two atoms in the bond are unlike, the contribution of the ionic forms will be expected to be greater, and the two forms will not contribute equally. This condition was held mainly responsible for the appearance of dipole moments in single bonds between unlike atoms, and for the inductive effect of Chapter VI. In this section we will examine its effect on the bond energy of single bonds between unlike atoms: for example, the hydrogen halides and the halogen halides.

Since the experimentally measured value for the dissociation energies of these diatomic molecules (bond energies in these cases) include the effects of whatever ionic resonance there might be, it is necessary to have some estimate of what the energy would be if the bond were purely homopolar or, to be more precise, had only the ionic resonance which will always be associated with a homopolar bond between like atoms. Pauling[1] has done this by two methods: (1) by assuming that the energy of the homopolar bond $A—B$ would be given by the arithmetic mean between the energies of $A—A$ and $B—B$, i.e., $E_h(A—B) = \frac{1}{2}[E(A—A) + E(B—B)]$, or (2) by assuming that $E_h(A—B)$ is the geometric mean of $E(A—A)$ and $E(B—B)$; i.e., $E_h(A—B) = [E(A—A) \times E(B—B)]^{\frac{1}{2}}$. Since the postulate of the arithmetic mean fails in a number of cases (alkali hydrides), we will concern ourselves here only with the results of the second assumption. In Table 27 are given the bond energies (dissociation energies) of hydrogen, the halogens, the hydrogen halides, and some halogen halides, together with the values for the purely homopolar bonds calculated by use of the assumption of the geometric mean. The

[1] Pauling, L., *The Nature of the Chemical Bond.* Cornell University Press, 1939.

experimental values are the heats of dissociation determined either spectroscopically or from thermal measurements. The values in the fourth column for the difference $\Delta = E(A{-}B) - E_h(A{-}B)$ are all positive; i.e., the experimental value of the bond energy between these unlike atoms is always greater than that calculated from the geometric mean. In columns five and six are given the energies required to form A^+ and B^- from A and B and to form A^- and B^+ from A and B, in the gas phase, obtained from the ionization potentials and electron affinities of the respective atoms. Furthermore, it may be seen that, in each series of related compounds, the hydrogen halides and the halogen halides, Δ increases with the difference between the energies of A^+, B^- and A^-, B^+. From these data, then,

TABLE 27

BOND ENERGIES (KCALS./MOLE) OF CERTAIN HALIDES

Molecule	$E(A{-}B)$ Bond Energy (Exper.)	$E_h(A{-}B) = [E(A{-}A) \times E(B{-}B)]^{1/2}$	$\Delta = E(A{-}B) - E_h(A{-}B)$	$E(A^+, B^-) - E(A, B)$	$E(A^-, B^+) - E(A, B)$
H—H	103.4			296	296
F—F	63.5			330	330
Cl—Cl	57.8			206	206
Br—Br	46.1			191	191
I—I	36.2			162	162
H—F	147.5	81.0	66.5	213	413
H—Cl	102.7	77.3	25.4	220	283
H—Br	87.3	69.0	18.3	225	256
H—I	71.4	61.2	10.2	233	224
Cl—F	86.4	60.6	25.8	200	337
Br—Cl	52.7	51.6	1.1	180	211
I—Br	42.9	40.9	2.0	154	193
I—Cl	51.0	45.7	5.3	148	220

we can conclude that the geometric mean does give a fair approximation to the energy of the homopolar bond which, however, includes the ionic resonances $A^+ : B^-$ and $A^- : B^+$ when they are of the same energy as they are in homonuclear diatomic molecules. When, however, one form has a very much lower energy than the other, as must be the case in HF, the energy of the bond is much greater than that calculated by the geometric mean, because of the large contribution to resonance of the ionic form $H^+ : F^-$.

30. VALENCE BOND RESONANCE AND HEAT OF FORMATION

In order to estimate quantitatively the amounts of stabilization produced in a compound by the possibility of writing more than one valence bond structure—e.g., as in benzene (see Chapter IV)—it is

necessary to have some estimate of the energy of the molecule if that resonance were not present. This Pauling has done by means of a set of bond energies obtained primarily from the data on heats of combustion, or heats of formation of the compounds, together with the heats of formation of the products of combustion, CO_2 and H_2O, and the heats of formation of the atoms from the elements in their standard states. Only compounds for which it is not possible to write more than one valence bond structure can be used, and it is found that the values so derived for the bond energies are additive and give a fairly good approximation to the heat of formation, from the atoms, of a large number of non-resonating molecules. It should be borne in mind, however, that these values do not necessarily represent the energy required to break only the bond in question in a polyatomic molecule. They represent only averages whose sums are a fairly accurate representation of the total energy of the molecule. The state of affairs may be better illustrated by a few examples of the method. The heat of formation of methane from hydrogen gas and graphite is given as -18.1 kcals./mole by Parks and Huffman.[2] In addition, we must have the heat of sublimation of graphite, 124.3 kcals., and the heat of dissociation of hydrogen, 103.4 kcals. These three reactions can be combined so as to give a value for the heat of formation of methane from atoms, 349.2 kcals.

$$\begin{aligned} \text{C(graph.)} + 2\text{H}_2 &= \text{CH}_4\text{(g)} & \Delta H &= -18.1 \text{ kcals.} \\ \text{C(g)} &= \text{C(graph.)} & \Delta H &= -124.3 \text{ kcals.} \\ 4\text{H(g)} &= 2\text{H}_2\text{(g)} & \Delta H &= -206.8 \text{ kcals.} \\ \hline \text{C(g)} + 4\text{H(g)} &= \text{CH}_4\text{(g)} & \Delta H &= -349.2 \text{ kcals.} \end{aligned}$$

One fourth of this value, namely 87.3, is taken as the energy of the C—H bond. This is clearly not the energy required for the reaction $CH_4 \rightarrow CH_3 + H$, but is the average of the energies required for the reactions $CH_4 \rightarrow CH_3 + H$, $CH_3 \rightarrow CH_2 + H$, $CH_2 \rightarrow CH + H$, and $CH \rightarrow C + H$. From the heat of formation of ethane from the elements in their standard states, -23.5 kcals., the heat of formation from the atoms is found to be 582.3 kcals., from which is subtracted the energy of 6 C—H bonds to give the value 58.5 kcals. as the energy of the C—C bond. Here again this need not be the heat of the reaction $C_2H_6 \rightarrow 2CH_3$.

[2] Parks, G. S., and Huffman, H. M., *The Free Energies of Some Organic Compounds*. Chemical Catalog Co., New York, 1932.

In this manner Pauling has compiled a table (28) of single and multiple bond energies which reproduce the heats of formation, from atoms, of the large class of compounds for which not more than one covalent-bond structure may be written.

The least accurate quantity used in the calculation is the heat of sublimation of graphite. Any individual bond-energy value which has been derived from a carbon compound is dependent upon the value taken for the heat of sublimation of graphite. However, differences and deviations from the additivity rule are independent of what value is taken.

TABLE 28
BOND ENERGIES (PAULING)

Bond	Bond Energy kcals./mole	Bond	Bond Energy kcals./mole	Bond	Bond Energy kcals./mole
H—H	103.4	C—N	48.6	C=C	100
C—C	58.6	C—O	70.0	C≡C	123
N—N	23.6	C—S	54.5	C=O (ald.)	149
P—P	18.9	C—F	107.0	C=O (ket.)	152
O—O	34.9	C—Cl	66.5	C=N	94
S—S	63.8	C—Br	54.0	C≡N (HCN)	144
Cl—Cl	57.8	C—I	45.0	C≡N (cyanide)	150
Br—Br	46.1	N—F	68.8	C=S	103
I—I	36.2	N—Cl	38.4	O=O (^1D state of O_2)	96
C—H	87.3	P—Cl	62.8	N≡N (N_2)	170
N—H	83.7	P—Br	49.2	N=O (see Table 33)	113
P—H	63.0	P—I	35.2		
O—H	110.2	O—F	58.6		
S—H	87.5	O—Cl	49.3		
H—F	147.5	S—Cl	66.1		
H—Cl	102.7	S—Br	57.2		
H—Br	87.3	N—O (see Table 33)	57.0		
H—I	71.4				

30a. The branched-chain effect. There is, however, at least one group of such apparently single-structure compounds for which this simple rule of the additivity of bond energies fails; namely, the branched-chain hydrocarbons. If the additivity rule were true, all saturated hydrocarbons having the same number of carbon and hydrogen atoms would have the same heat of formation, and this is certainly not true. Generally the branched chain has a smaller heat content than the straight chain by several kcals. It should be remembered that most of these heats of formation are for 298°K and therefore include some contribution depending on the symmetry of the molecule and the character of its vibrations. In a few cases the ΔH_0° has been determined[3]: *n*-butane $\Delta H_0^\circ = -23.90$ and iso-

[3] Pitzer, K. S., *J. Chem. Phys.*, **5**, 473 (1937).

TABLE 29

HEATS OF HYDROGENATION OF SOME UNSATURATED SUBSTANCES

(ΔH at 355°K. unless otherwise stated.)

Hydrocarbon	$-\Delta H$
Addition of 1 H_2	
Ethylene	32.58
Propylene	30.12
Butene-1	30.34
Heptene-1	30.14
Butene-2 (*trans*, low boiling)	27.62
Butene-2 (*cis*, high boiling)	28.57
Pentene-2 (*cis-trans* mixture)	27.95
Isobutene	28.39
Isopropylethylene	30.33
tert.-Butylethylene	30.34
4,4-Dimethylpentene-1	29.53
1-Methyl-1-ethylethylene	28.49
1-Methyl-1-isopropylethylene	28.00
2,4,4-Trimethylpentene-1	27.24
Trimethylethylene	26.92
Tetramethylethylene	26.63
Cyclohexene	28.59
Cyclopentene	26.92
Cycloheptene	26.52
Cyclooctene	23.52
Allene	41.16
1,3-Butadiene	26.72
1,4-Pentadiene	30.66
1,5-Hexadiene	30.40
1,3-Cyclohexadiene	26.70
1,3-Cyclopentadiene	23.95
Benzene	−5.57
Addition of 2 H_2	
Allene	71.28
1,3-Butadiene	57.07
Addition of 2 H_2	
1,3-Pentadiene	54.11
2,3-Dimethylbutadiene	53.87
1,4-Pentadiene	60.79
1,5-Hexadiene	60.52
1,3-Cyclohexadiene	55.37
1,3-Cyclopentadiene	50.87
Acetylene	75.06
Methylacetylene	69.70
Dimethylacetylene	65.58
1,3-Cycloheptadiene	51.26
Addition of 3 H_2	
Benzene	49.80
Ethylbenzene	48.92
o-Xylene	47.25
Mesitylene	47.62
Hydrindene	45.80
Cycloheptatriene	72.85
Addition of 4 H_2	
Styrene	77.48
Indene	69.91
Hydrocarbon Derivatives	
Vinyl acetate	31.1
Crotonic aldehyde	25.2
2-Ethoxypropene	25.1
Acetone	13.4
Methylethylketone	13.2
Cyclopentanone	12.50
Cyclohexanone	15.42

butane $\Delta H_0^\circ = -25.45$; butene-1 $\Delta H_0^\circ = +4.72$ and isobutene $\Delta H_0^\circ = +0.85$. These values measure only the electronic or binding energies, and the difference between the isomers is maintained.

Such effects appear also in the energy of the ethylenic double bond as evidenced by the heats of hydrogenation. Here the values are more significant, since they are directly measurable and are not small effects to be deduced from measurements of such relatively large effects as the heats of combustion. Kistiakowsky[4] and his collaborators have measured directly the heats of hydrogenation of a number of unsaturated compounds by carrying out the hydrogenation catalytically in a calorimeter. The results are given in Table 29.

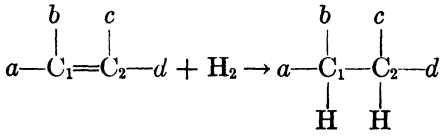
TABLE 30

HEATS OF HYDROGENATION AND DEGREE OF BRANCHING

ΔH_{355} for Eq. *A*			ΔH_{298} for Eq. *B*		
R_1	R_2	$-\Delta H$	R_1	R_2	$-\Delta H$
0	0	32.6	0	0	15.5
1	0	30.2	1	0	13.2
2	0	28.3	2	0	11.3
2	1	26.9	3	0	9.6
2	2	26.6	1	1	10.6
1	1 (*cis*)	28.6	3	3	7.2
1	1 (*trans*)	27.6			

R_1 and R_2 represent the number of carbon atoms attached to atoms 1 and 2, respectively.

The variation in the monoolefines is 6 kcals. (32.6 for ethylene to 26.6 for tetramethylethylene). The values fall into groups depending upon the number of carbon atoms (or hydrogen atoms) attached to the atoms involved in the double bond. In Table 30 are collected the values classified in this way for the reaction

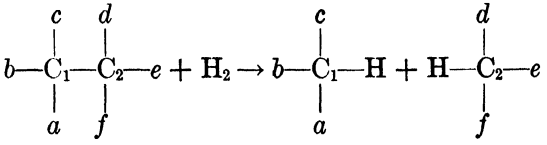


(A)

[4] Kistiakowsky, G. B., Romeyn, H. Jr., Ruhoff, J. R., Smith, H. A., and Vaughan, W. E., *J. Am. Chem. Soc.*, **57**, 65 (1935); Kistiakowsky, G. B., Ruhoff, J. R., Smith, H. A., and Vaughan, W. E., *J. Am. Chem. Soc.*, **57**, 876 (1935); Kistiakowsky, G. B., Ruhoff, J. R., Smith, H. A., and Vaughan, W. E., *J. Am. Chem. Soc.*, **58**, 137 (1936); Kistiakowsky, G. B., Ruhoff, J. R., Smith, H. A., and Vaughan, W. E., *J. Am. Chem. Soc.*, **58**, 146 (1936); Dolliver, M. A., Gresham, T. L., Kistiakowsky, G. B., and Vaughan, W. E., *J. Am. Chem. Soc.*, **59**, 831 (1937); Dolliver, M. A., Gresham, T. L., Kistiakowsky, G. B., Smith, E. A., and Vaughan, W. E., *J. Am. Chem. Soc.*, **60**, 440 (1938); Conn, J. B., Kistiakowsky, G. B., and Smith, E. A., *J. Am. Chem. Soc.*, **61**, 1868 (1939). For bromination of some olefines, see Conn, J. B., Kistiakowsky, G. B., and Smith, E. A., *J. Am. Chem. Soc.*, **60**, 2764 (1938).

where a, b, c, and d may be hydrogen atoms or carbon atoms of other alkyl groups.

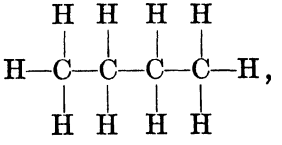
In Table 30 are also given the values of ΔH for the reaction



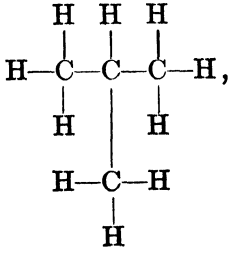
(B)

calculated from the available thermodynamic data for the gaseous substances at 298°K.

All these variations may be understood on the assumption that the energy of a single or double bond between a pair of carbon atoms is the smaller, the more carbon atoms there are attached to the ones concerned in the bond. If this were attributed to resonance, one must assume contributions from forms in which there are bonds between atoms that are not bonded to each other in the classical formulas. This is equivalent to saying that the exchange integrals between electrons on non-adjacent atoms are not negligible. Presumably, however, one need consider only the interactions of atoms separated by not more than one atom. Although branching of the chain does not increase the total number of such atoms, it does increase the number of such pairs of identical atoms. For example, in *n*-butane,



there are 8 pairs of hydrogen atoms whose electron interactions are not represented by the formula and which are separated by only one atom. There are two such pairs of carbon atoms and 14 such carbon-hydrogen couples, making a total of 24 non-adjacent interactions. In isobutane,



the corresponding numbers are 9 for hydrogen, 3 for carbon, and 12 for carbon-hydrogen, making again a total of 24. If this is the explanation of the branching effect, then the exchange in what we have called the carbon-hydrogen couple must be less important than the others. This assumption is not unreasonable, as this interaction involves an exchange of electrons in different kinds of bonds and hence of different energies. Thus, in Figure 40, electron pairs 1 and 2 are in similar states and will have an appreciable exchange integral, as will also electron pairs 3 and 4. However, pairs 2 and 3 will be in quite different energy states and hence their exchange (or resonance) will be small by comparison. Since similar energy effects are found among the isomeric alcohols and alkyl halides, it must be assumed, if this same explanation is to be valid, that it is the C—H electron pair which is unique.

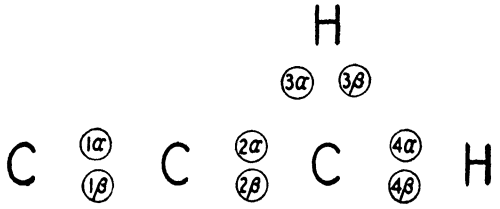


Figure 40. The electronic structure of branching chains.

30b. Ring strain. Another case for which the normal additivity of bond energies must fail, but for which the reason is somewhat more apparent, is that of the cycloparaffins. It has long been known that cyclopropane and cyclobutane exhibit an instability compared with the *n*-paraffins, and Baeyer proposed his strain theory to account for it. He suggested that the instability increased as the carbon bond angles were forced to depart from the tetrahedral angle (109° 28′) in order to form the ring. Thus in cyclopropane, in which the three carbon atoms are coplanar, the angle between C—C bonds is 60°. The total distortion for a pair of bonds is then 109° 28′ − 60° = 49° 28′, and each carbon bond must be strained by half that amount, or 24° 44′. On constructing models, it may be seen that the cyclobutane and cyclopentane rings having the least departure from the tetrahedral angle for the C—C bonds are the coplanar ones. For cyclohexane and all higher-membered rings, on the other hand, strainless rings can be constructed in which the carbon atoms are not coplanar but are buckled or puckered, as shown in Figure 41 for

cyclohexane. Although the *cis* form cannot be transformed into the *trans* form by simple rotation about single bonds, the deformation of bonds required to make the transformation is small, so that the activation energy for the conversion is less than 5 kcals. and the two forms would be very rapidly interconverted, so that their isolation as independent isomers would be extremely difficult if not impossible.

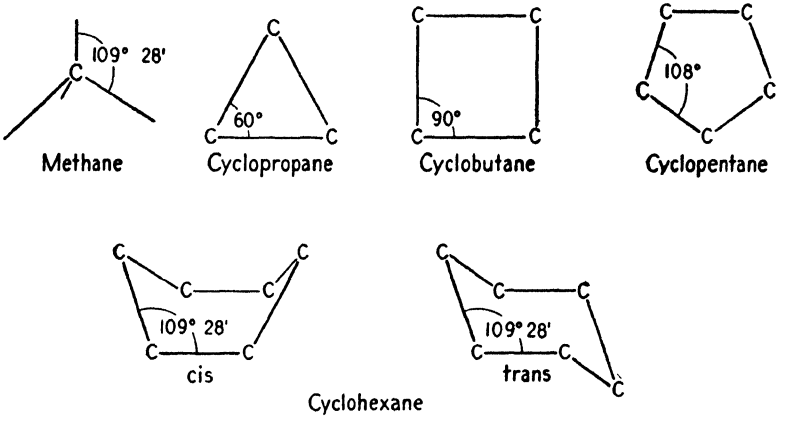


Figure 41. The configuration of cycloparaffins.

TABLE 31
HEAT OF COMBUSTION OF GASEOUS CYCLOPARAFFINS

No. of C Atoms in the Ring	ΔH Comb. kcals./CH_2	Angle of Strain for the Least Strained Structure
2	170	+54° 44′
3	168	+24° 44′
4	162[a]	+9° 44′
5	159	+0° 44′
6	158	0
7	158	0
8, 15, 17	157–158	0
n-paraffins	157	0

[a] Calculated from cyclobutane derivatives.

This ring strain makes itself apparent in physical properties such as absorption spectra, parachor, molar refraction, heat of combustion, etc., as well as in chemical instability. Probably the most readily interpreted physical property, and the one with which we are concerned here in the assignment of bond energies, is the heat of combustion. Since straining the ring involves an increase in the heat content, the heat of combustion per methylene group should increase as the strain

increases. This is actually observed (Table 31) insofar as the data go. There is no direct measurement of the heat of combustion of cyclobutane, and the value given in the table is a mean of several values derived from cyclobutane derivatives. Although the position of cyclobutane is still uncertain, it is evident that the three- and four-membered rings are certainly unstable, whereas all of the higher ones show very little strain.

From the foregoing discussion it is evident that the selection of certain fixed values for the bond energies of carbon bonds, even in compounds for which only one valence formula can be written, cannot be made to within a few kcals., and that the conclusions with respect to valence-bond resonance energies which follow are uncertain to the same extent.

30c. Resonance energies. If, now, the attempt is made to use the values given in Table 28 for the calculation of the heats of formation of compounds for which more than one covalent-bond structure may be written, i.e. compounds having more than one valence-bond formula contributing to resonance, it is found that they are always more stable than the calculation would lead one to believe. For example, the heat of formation of gaseous benzene from its atoms should be 3(C=C) + 3(C—C) + 6(C—H) = 999.6 kcals. Experimentally this value is about 1037 kcals. The difference, about 37 kcals., called the resonance energy, is the degree to which benzene has been stabilized by the various contributing resonance structures, of which the two Kekulé structures are the most important. Another estimate of the resonance energy of benzene, and probably a much better one, may be obtained from the difference between the heat of hydrogenation of benzene to cyclohexane and three times the heat of hydrogenation of cyclohexene (3 × 28.59). This gives the value 36.0 kcals.

It will be recalled that the theoretical calculation for the resonance energy of benzene carried out in Chapter IV gave the value 1.105 α, where α was an exchange integral that could not be directly evaluated. Using the empirically determined resonance energy of benzene as 36 kcals., α becomes about 33 kcals. Approximate calculations similar to that for benzene have been carried out for a number of other molecules.[5] For naphthalene the result is 2.04 α. Using the value of α obtained from benzene, the calculated resonance energy of

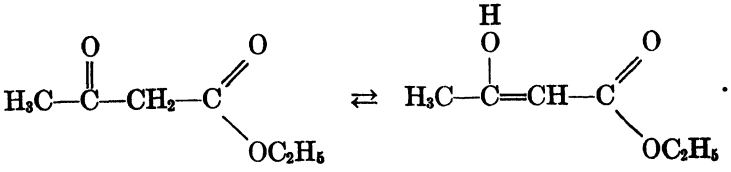
[5] Hückel, E., Grundzüge der Theorie ungesättigter und aromatischer Verbindungen, *Z. Elektrochem.*, **43**, 752, 827 (1937); Pauling, L., and Wheland, G. W., *J. Chem. Phys.*, **1**, 362 (1933); **2**, 482 (1934); Sherman, J., *J. Chem. Phys.*, **2**, 488 (1934); Penney, W. G., *Proc. Roy. Soc.*, **146**, 223 (1934).

naphthalene is 67 kcals., as compared with the value 75 kcals. obtained from the bond energy table and the heat of combustion. Similarly, anthracene gives 3.09 α or 101 kcals., compared with the empirical value of 105, and phenanthrene is 3.15 α or 104 kcals. as compared with the empirical value of 110 from heat of combustion. The calculation for these aromatics is thus fair, but when it is tried on butadiene the discrepancy is very great. The heat of hydrogenation of butadiene to butane is 57.07 kcals.; that of butene-1 to butane is 30.3 kcals. If there were no interaction between the two double bonds in butadiene, its heat of hydrogenation should be twice that of butene-1, since both double bonds in the diene are of the same type as that in butene. The difference, 3.6 kcals., represents the resonance energy of butadiene. The calculation for butadiene gives 0.23 α, or 7.5 kcals.[6] This is not surprising in view of the approximations involved, and the value of α is probably quite different for unsaturated aliphatic compounds.

In spite of the uncertainties involved in the assignment of bond energies, and the relatively large errors which must obtain in the small difference between two large quantities (heats of combustion), it is very instructive to examine the empirical resonance energies which are so calculated. In Table 32 (*A* and *B*) are given some of the values calculated by Pauling and Sherman, together with the structure for which the energy of formation from the atoms is calculated, and some of the more important resonance forms to whose contribution to the state of the molecule the resonance energy can be attributed.

31. TAUTOMERISM

Another phenomenon in which qualitative, if not quantitative, correlation of equilibrium and constitution has become possible is that of tautomerism. Our primary concern here will be the relative stability of the isomers made possible by the shifting of a hydrogen atom and a rearrangement of the double bonds of the system, of which the well-known case of acetoacetic ester is an example:

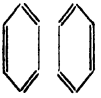
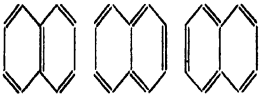
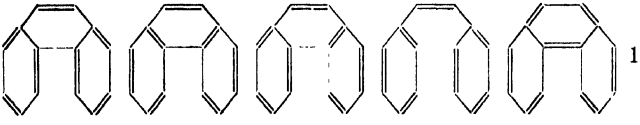
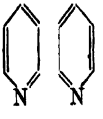
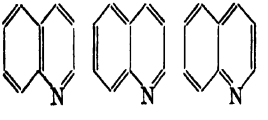
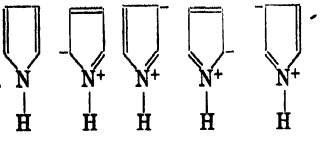
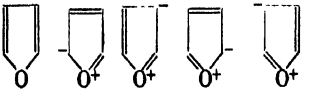
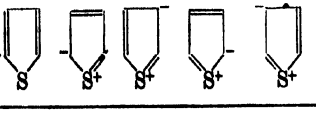


Keto form Enol form

[6] Pauling, L., and Sherman, J., *J. Chem. Phys.*, **1**, 679 (1933).

TABLE 32-A

PRINCIPAL RESONANCE FORMS AND RESONANCE ENERGIES OF SOME COMMON SUBSTANCES

Substance	Principal Resonance Forms*	Resonance Energy (kcals.)
Benzene.....		37
Naphthalene . .		75
Anthracene ...		105
Phenanthrene ..		110
Pyridine		43
Quinoline		69
Pyrrole		31
Furan		23
Thiophene		31

* The first form is the structure to which the resonance energy is referred.

TABLE 32-A—*Continued*

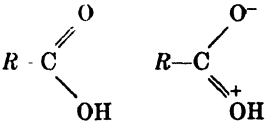
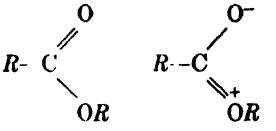
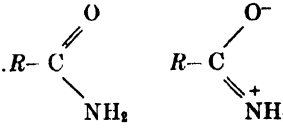
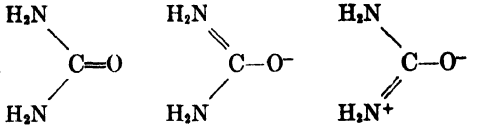
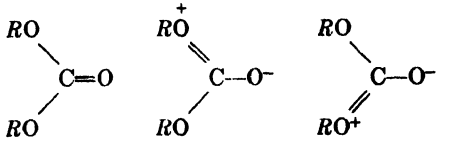
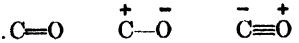
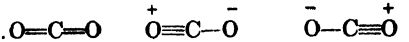
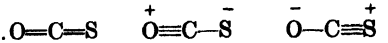
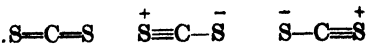
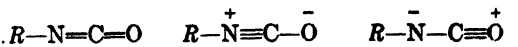
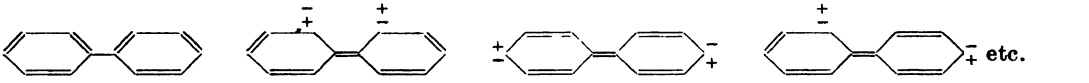
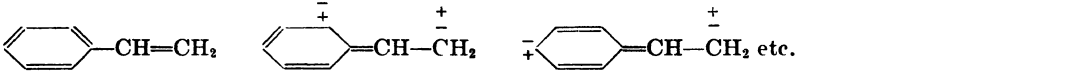
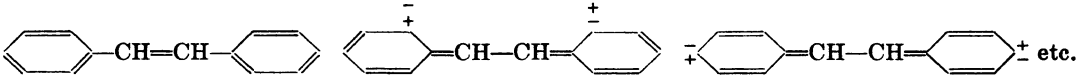
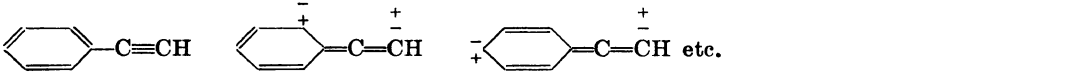
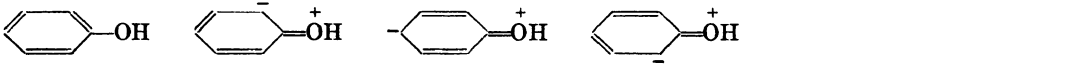
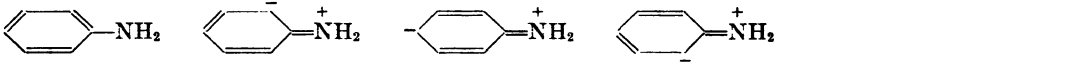
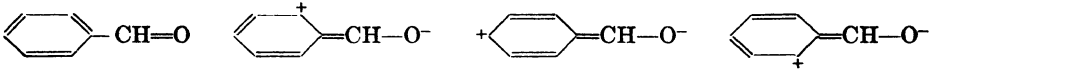
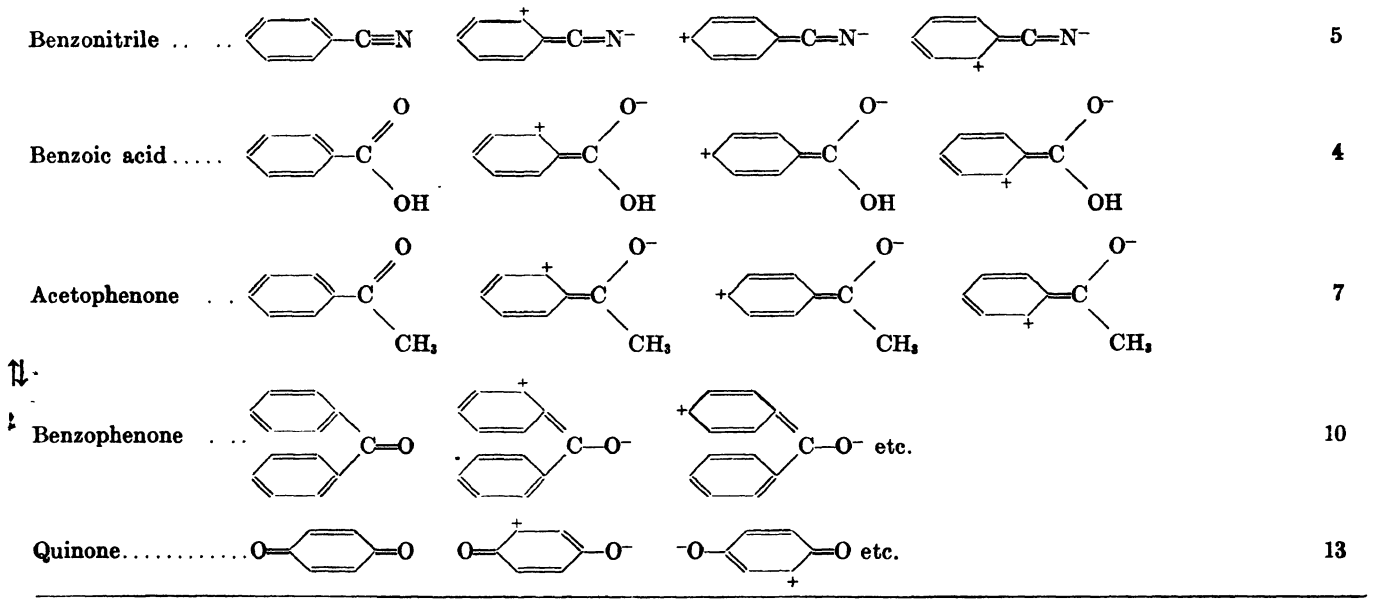
Substance	Principal Resonance Forms	Res. Energy
Acids		28
Esters		24
Amides		21
Urea.		37
Dialkyl carbonates		42
Carbon monoxide.		58
Carbon dioxide. . . .		33
Carbonyl sulfide. . . .		20
Carbon disulfide.		11
Alkyl isocyanate. .		7

TABLE 32-B

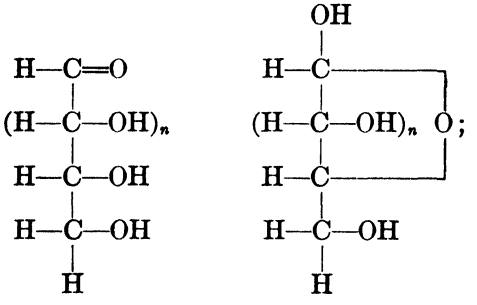
The resonance energies for the following structures are those in excess of what results from the benzene resonance within the ring, and, in the case of benzoic acid, of what is in the carboxyl group itself (as in alkyl carboxylic acids).

Substance	Principal Resonance Forms	Res. Energy
Biphenyl		8
Styrene		7
Stilbene		15
Phenylacetylene		10
Phenol		7
Aniline		6
Benzaldehyde		4

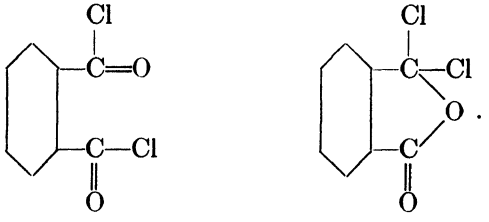


Benzonitrile	5
Benzoic acid	4
Acetophenone	7
Benzophenone	10
Quinone	13

There are cases of other types of tautomerism, such as the ring-chain tautomerism in aldehyde and ketone alcohols (especially the sugars),



or tautomerism involving the displacement of atoms or groups other than hydrogen, as in phthaloyl chloride:



But in general, very little has been done on these equilibria in the way of determining the effects of substituents or changes in structure on the position of the equilibrium. Furthermore, it seems that many of these cases could be more aptly classified under a more general grouping of molecular rearrangements.

It should be mentioned at the outset that in an equilibrium in which both tautomers are present in measurable quantities—e.g., as in ethyl acetoacetate—the difference in energy between them must be very small. Thus if, for the keto $\rightleftarrows$ enol equilibrium at room temperature, there is present 1 per cent enol,

$$\Delta F = -RT \ln K = -RT \ln \frac{[\text{enol}]}{[\text{keto}]} = -1.38 \log \frac{[\text{enol}]}{[\text{keto}]}$$

$$= -1.38 \log 1/99 = 2.76 \text{ kcals./mole.}$$

If on the other hand there is 99 per cent enol,

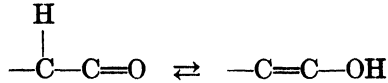
$$\Delta F = -1.38 \log 99 = -2.76 \text{ kcals./mole.}$$

A difference, therefore, of only 5.52 kcals./mole in the free energy (or in the heat content, since entropies of the two tautomers

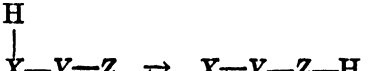
cannot be very different) will shift the equilibrium from what is directly experimentally measurable as all keto to all enol. This does not mean, however, that a compound whose keto form, let us say, is something more than 5 or 6 kcals. more stable than its enol form will not show reactions characteristic of, or which may be attributed to, its enol form, for it may happen, as in the bromination of acetone, that the keto form is very unreactive in comparison with the enol form, and that the reaction goes by way of the very minute amount of enol form which is present. Or, in other cases, derivatives of the enol form may be obtained although no directly measurable amount of enol may be present.

The relative energy of the two tautomers can be divided into at least three well-recognizable categories: (1) the bond energies, (2) the resonance energies (and inductive effects), and (3) the electrostatic energies. Of these the one concerning which we have the best information is the first, the bond energies; and these are not known any better than to within one or two kcals. even insofar as their relative values only are concerned. The resonance energies are known with an even smaller degree of certainty and the coulombic interactions of the various distributions of charge or dipoles are not known at all. This last, however, is probably smaller than the first two, and the difference between a pair of tautomers in this part of the energy is probably still less. The resonance energies, on the other hand, may be very different in the two tautomers; in fact, in many cases these are the determining factors. So it is evident that any calculation of the actual position of an equilibrium within the measurable range of 5 kcals. is almost hopeless. It is possible, however, by use of the bond and resonance energies given in the previous section, to state in a general way which form will tend to be the more stable. Further, by keeping in mind the characteristics of groups and configurations especially with respect to their quantitative tendencies to take part in resonance systems, it is possible to understand the variations of equilibrium within a given series of compounds of one type.

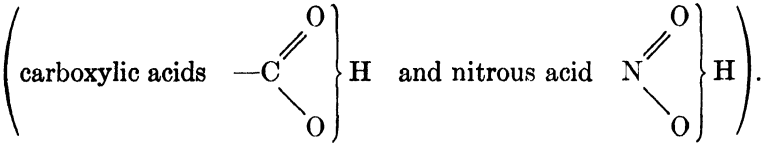
The keto-enol tautomerism represented by



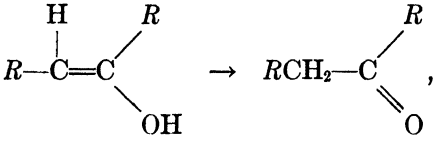
may be generalized into a three-atom tautomerism,



in which the atoms X, Y, and Z are such as can exist in the required valence states. For the three atoms C, N, and O, there are ten such tautomeric systems, excluding those in which oxygen is the central atom for reasons of valence and those in which both terminal atoms are oxygen, since these tautomers cannot be made distinguishable:



In Table 33 are given the values of ΔH for the tautomeric change calculated from the differences in bond energies only. It is gratifying to find that these values correspond with the generally accepted opinions that, in simple cases, (1) the ketones and aldehydes are stable with respect to the vinyl alcohols, (2) the amides are stable with respect to the imidols, (3) the aldimines are stable with respect to the vinylamines, (4) the oximes are stable with respect to nitroso compounds, (5) diazohydroxy compounds are stable with respect to nitrosamines, (6) hydrazones are stable with respect to azo compounds. Opinions 1, 4, and 6 are correct beyond any reasonable doubt. The reactions

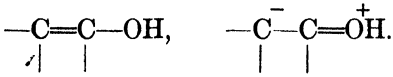


$$R\text{CH}_2\text{—NO} \rightarrow R\text{CH=NOH},$$

and

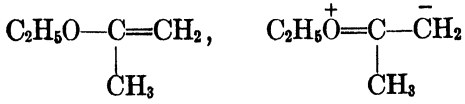
$$R\text{CH}_2\text{—N=N}R \rightarrow R\text{CH=N—NH}R$$

are practically complete unless the R groups introduce extraneous resonance. Even the simple reactions are not free of resonance, which may act in the same direction as, or in an opposite direction from, the bond energy. In the keto-enol case, there is a resonance in the enol which would diminish the ΔH given in Table 33:



We may form an estimate of the amount of the resonance energy from the heat of hydrogenation of 2-ethoxypropene, which is 25.1

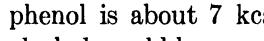
kcals. Since the heat of hydrogenation of a corresponding hydrocarbon, isobutene, is 28.3 kcals., the resonance



contributes an energy of about 3.2 kcals. The resonance energy of phenol is about 7 kcals., so that the resonance energy of a vinyl alcohol would be expected to be somewhere between 3.2 and 7 kcals. It is apparent that this value is still far too small to have much of

TABLE 33

ΔH FOR THE REACTION OF THE THREE-ATOM TAUTOMERISM



Involving C, N, and O, Calculated from the Assigned Bond Energies*

X	*Y*	*Z*	ΔH (kcals./mole)
C	C	O (aldehydes)	+15
C	C	O (ketones)	+18
N	C	O	+10
C	C	N	+8
C	C	C	0
N	C	N	0
C	N	O	−12
N	N	O	−8
C	N	C	0
C	N	N	−9
N	N	N	0

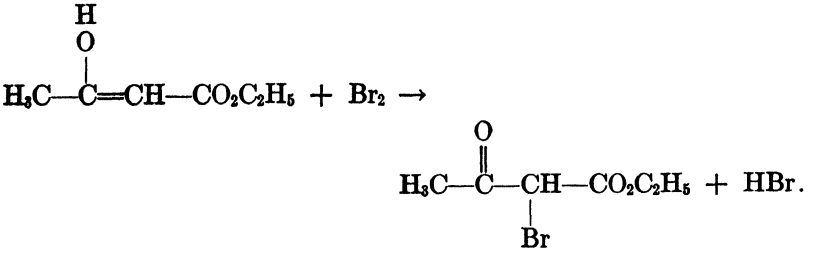
* The values for N—O and N=O used in this calculation are 57 and 113 kcals., respectively. These were obtained from the heats of combustion of ethyl nitrate, dimethylnitrosamine, acetoxime, and nitrosobenzene by making them consistent within themselves and with suitable resonance energies.

The value 57 kcals. for N—O includes the energy of the resonance (A=N—OH, $\bar{A}$—N=$\overset{+}{\text{O}}$H), so this type of resonance cannot be introduced as a factor favoring the A=N—OH tautomer, when 57 kcals. is used for the N—O bond energy.

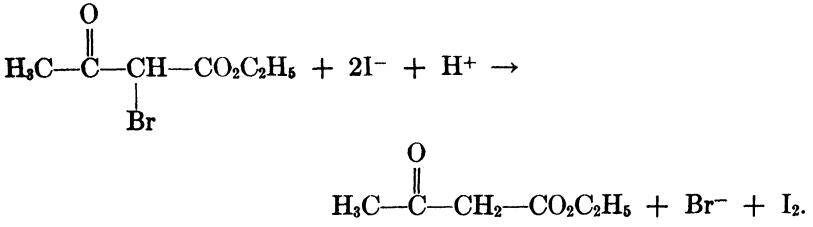
an effect on the prediction made on the basis of bond energies alone. However, when other resonance (or inductive) effects are introduced by changes in structure, the relationships may be greatly altered, even to the extent of being reversed.

31a. Keto-enol equilibria. The C—C—O system has been very extensively investigated. It is the tautomeric equilibrium about which most information is available. These investigations were made possible by the discovery of a chemical method of analysis of keto-enol mixtures by K. Meyer. It depends upon the fact that

the enol form, containing an ethylenic double bond, reacts immediately with bromine, whereas the keto form does not:

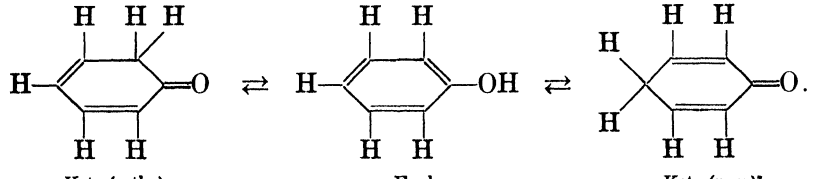


The excess bromine is removed by the immediately successive addition of a phenol. Finally the iodine liberated from a solution of iodide ion (KI) by the ethyl α-bromoacetoacetate is titrated:



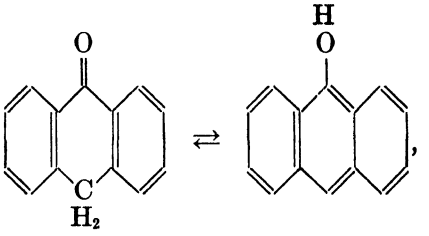
Other methods, mainly physical, such as the refractive index or the absorption spectrum, have been used, but in general it is not very easy to obtain an unequivocal quantitative estimate of the amounts of the two tautomers present by these methods. They are, however, very useful in establishing qualitative relationships, especially in other tautomeric systems for which no other very suitable method of analysis exists.

As we have already seen, the simple aldehydes and ketones are well over on the keto side. A relatively simple case in which the equilibrium is practically completely on the enol side is that of phenol:



[7] The para-keto form is included here, since the bond energy differences are the same as for the ortho-keto form, and the resonance energies not very different. These results are thus comparable to those on anthranol, of which the para-keto form has been isolated.

This is readily understood, since the large resonance energy of the benzene ring will stabilize the enol. A quantitative estimate can be made by adding, to the ΔH from bond energies, +18 kcals., a value corresponding to the change in the resonance energies. For the keto form, a maximum value for the resonance in the conjugated system C=C—C=C—C=O is estimated at about 10 kcals.[8] For the enol form, the total resonance energy is 44 kcals. (37 for the benzene ring and 7 for the interaction of the OH with the ring). The net change in resonance energy for the keto-enol change is thus about −34 kcals., which gives + 18 − 34 = −16 kcals. as ΔH for the reaction Cyclohexadienone → Phenol, indicating an equilibrium far over on the enol side. On the other hand, a similar calculation for anthranol-9 (9-hydroxyanthracene),



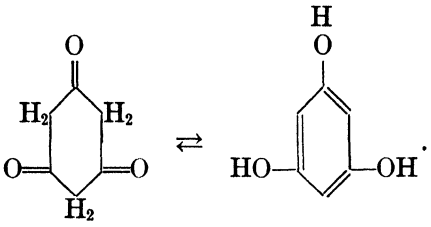
Anthrone Anthranol

gives a value for ΔH of about −5 kcals. This is within the range in which the other effects may bring about an appreciable quantity of both forms in the equilibrium mixture, either as solids or in solution. For instance, the −5 kcals. are calculated from Pauling's resonance values of anthracene without correction for the lack of hydrogens on four carbon atoms. These carbons are not changed in the tautomerism, and so the error in the resonance energy alone may more than account for the −5 kcals. Actually both forms have been isolated as crystalline solids; anthrone melting at 150–155°, anthranol at 120°. The fact that the melting point of the anthrone is higher than that of the anthranol indicates that its crystal lattice energy is greater than that of the anthranol, and it is not surprising that the solid anthranol is very easily converted into solid anthrone.

When three hydroxy groups are symmetrically placed on the benzene ring to form phloroglucinol, the compound shows the reactions

[8] This value is considerably greater than the sum of the resonance energies of C=C—C=C, 3.6 kcals., from the heat of hydrogenation of butadiene, and of C=C—C=O, 2.4 kcals., from the heat of hydrogenation of crotonaldehyde.

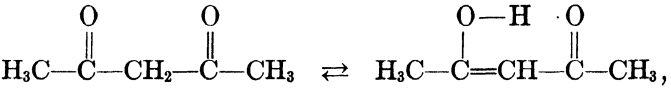
of both forms quite readily, the enolization energy of three keto groups just about balancing the resonance energy of one benzene ring:



In this case ΔH (including the resonance energies) is about -4 kcals. and is thus within the range of the accuracy of the estimated energy values and the influence of the other effects.

Another case in which the resonance (and other) effects in the enol form just about balance the extra stability of the keto form (due to bond energies) is that of the β-diketones and β-ketonic esters. For this reason it is here also that the effect of substituents and solvent has been most thoroughly investigated. Unfortunately, for these systems the quantitative estimates of resonance energies (and other effects) are too crude to be of much use. The observed trends, however, are found to conform very well with expectations based upon the tenets we have just outlined.

The equilibrium for acetylacetone,

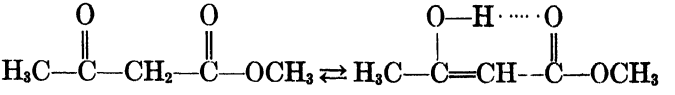


has been measured in the vapor phase and found to be 92 per cent enol, which corresponds to $\Delta H = -1.5$ kcals. (assuming no entropy difference). This would require that the extra stability of this enol be about 19.5 kcals. This is not unreasonable when one considers the high degree of symmetry of this form. From other sources a very crude estimate of this effect may be made by adding the several partial effects; 8 kcals. for the hydrogen bond, 7 kcals. for the vinyl alcohol (phenolic), and 3 kcals. for the C=C—C=O system, making a total of about 18 kcals. Actually the resonance of the system of "complementary resonators" HO—C=C—C=O must be greater than the simple sum of the two independent resonances

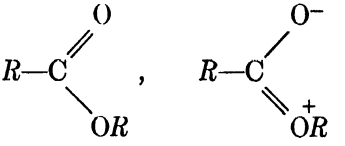
$$(\mathrm{HO{-}C{=}C},\ \mathrm{H\overset{+}{O}{=}C{-}C^{-}})\ \text{and}\ (\mathrm{C{=}C{-}C{=}O},\ \mathrm{C^{+}{-}C{=}C{-}O^{-}}),$$

just as the dipole moment of *p*-nitraniline is greater than the sum of the moments of aniline and nitrobenzene.

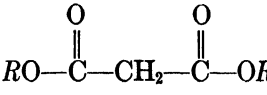
If one of the methyl groups of acetylacetone is replaced by a methoxyl group to give methyl acetoacetate, the vapor-phase equilibrium



is found to be 54 per cent enol. Here, in addition to having destroyed the identity of the two carbonyl groups and thus reducing any resonance energies involving an interchange between them, one of them now partakes of the very strong ester resonance

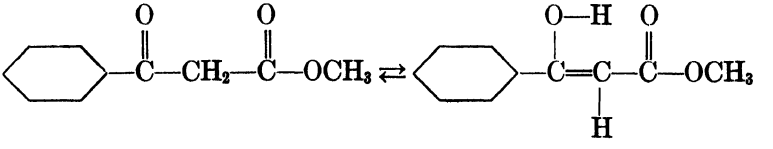


and in so doing is prevented from full participation in the other resonances of the enol. Since this ester resonance is present in both keto and enol forms, the stability of the enol is reduced, with the result already mentioned. It is the latter effect which is the more important one, since even when symmetry is again restored as in the malonic esters



there is no appreciable amount of enol. Here both carbonyls are occupied by the ester resonance.

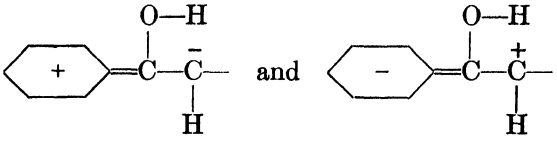
Another case in which the symmetry effect is outweighed by a further resonance contribution is that of methyl benzoylacetate, for which the equilibrium



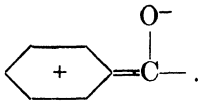
in hexane[9] is found to be 69 per cent enol. This is somewhat greater than the value 54 per cent for methyl acetoacetate and is to be at-

[9] This is in all probability very close to the value in the vapor phase. See Table 34.

tributed to the greater contribution to the resonance energy of the enol of the forms



than the contribution to the keto resonance of the form

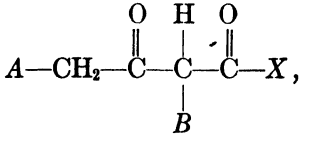


Compare the value 7 kcals. for the excess resonance energy of styrene with 4 kcals. for benzaldehyde (see Table 32-B). If the phenyl group is substituted for a methyl group of acetylacetone to give benzoylacetone, the equilibrium is displaced toward the enol so that even the pure liquid substance is 98–99 per cent enol as compared with 80 per cent enol for pure liquid acetylacetone.

In recent years a large number of β-keto esters and some β-diketones have been investigated in an attempt to discover some of the smaller effects of the substituents, especially alkyl groups on the keto-enol equilibrium. In Table 34 are given the values for the equilibrium constant

$$K = \frac{[\text{enol}]}{[\text{keto}]}$$

for a series of compounds of the type



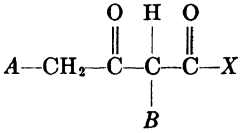
measured in hexane solution together with some values in the vapor phase.

Strictly speaking, any comparisons with the theory above outlined should be made only with the vapor-phase equilibrium, but, as may be seen from the table, the equilibrium in hexane is not very different from that in the vapor for those cases in which both have been measured. In most other solvents, however, the differences are quite appreciable and the solvent effect in general will be considered in the next section. The last column of the table, headed K (corr.

hexane), is an equilibrium constant corrected for the fact that when a substituent other than H is introduced into the position *B* of the

TABLE 34

KETO-ENOL EQUILIBRIA IN 1,3 DIKETONES OF THE STRUCTURE



AT 25°C. AS DETERMINED BY BROMINE TITRATION

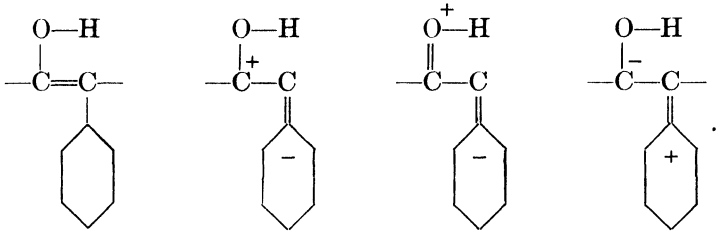
A	*B*	*X*	$K = \frac{[\text{enol}]}{[\text{keto}]}$		
			K(gas phase)	*K*(hexane) (0.1 M)	*K*(corr.[c] hexane)
[a]H	H	OCH_3	1.2		
H	H	OC_2H_5	0.86	0.96	0.96
H	CH_3	OC_2H_5	0.16	0.13	0.26
H	C_2H_5	OC_2H_5	0.11	0.17	0.34
H	*n*-C_3H_7	OC_2H_5	0.17	0.18	0.36
H	iso-C_3H_7	OC_2H_5	0.065	0.062	0.124
H	*n*-C_4H_9	OC_2H_5	0.15	0.11	0.22
H	*sec*-C_4H_9	OC_2H_5	0.099	0.103	0.21
H	C_6H_5	OC_2H_5	4.0	2.0	4.0
H	$CH_2C_6H_5$	OC_2H_5	0.14	0.14	0.28
H	H	CH_3	11.5	11.0	11.0
H	C_2H_5	CH_3	5.50	3.62	7.24
H	$CH_2C_6H_5$	CH_3	2.33	2.0	4.0
[b]H	H	OCH_3		1.27	1.27
H	H	OC_2H_5		0.88	0.88
H	H	*n*-OC_3H_7		1.20	1.20
H	H	iso-OC_3H_7		1.18	1.18
H	H	*n*-OC_4H_9		1.23	1.23
H	H	iso-OC_4H_9		1.41	1.41
H	H	*sec*-OC_4H_9		1.28	1.28
H	*n*-C_4H_9	OC_2H_5		0.081	0.162
H	$CH_2C_6H_5$	OC_2H_5		0.079	0.158
CH_3	CH_3	OC_2H_5		0.11	0.22
C_2H_5	C_2H_5	OC_2H_5		0.085	0.17
n-C_3H_7	*n*-C_3H_7	OC_2H_5		0.064	0.128
iso-C_3H_7	iso-C_3H_7	OC_2H_5		0.025	0.05
tert-C_4H_9	*tert*-C_4H_9	OC_2H_5		0.020	0.04
n-C_5H_{11}	*n*-C_5H_{11}	OC_2H_5		0.047	0.094
n-C_7H_{15}	*n*-C_7H_{15}	OC_2H_5		0.051	0.102
n-$C_{12}H_{25}$	*n*-$C_{12}H_{25}$	OC_2H_5		0.030	0.06

[a] Conant, J. B., and Thompson, A. F., Jr., *J. Am. Chem. Soc.*, **54**, 4039 (1932).
[b] Ness, A. B., and McElvain, S. M., *J. Am. Chem. Soc.*, **60**, 2213 (1938).
[c] See the following paragraph for explanation.

type formula, the number of enolizable hydrogens is reduced to half, and thus the measured equilibrium constant would be reduced by a

probability factor of $\frac{1}{2}$ independently of any energy changes that might also appear. In order to compare the K values for such compounds (B not a hydrogen atom) with the others, the measured K values have been multiplied by 2 and are given in the last column.

In addition to the rather large effects of changing the group in the X position which we have already discussed, there is apparent a smaller but nonetheless real effect of substituting an R group for H in both the B and the A positions, the effect being considerably larger in the B than in the A position. In every case but one, such a substitution decreases the equilibrium constant; i.e., increases the stability of the keto relative to the enol form. The one case for which the reverse is true, ethyl α-phenylacetoacetate, is very readily understood, since here in the enol form the phenyl group is conjugated with a vinyl alcohol grouping and the enol is stabilized by the extra resonance forms



The general effect of the substitution of a hydrogen atom by an R group has been repeatedly observed in other cases, and an examination of Table 30 leaves it altogether possible that such a substitution might be more effective in stabilizing adjacent single bonds slightly more than adjacent double bonds. There is also undoubtedly a purely steric effect concerned here as well, but a detailed analysis is not yet possible.

31b. Solvent effect. From Table 34 it may be seen that the keto-enol equilibrium is much the same in hexane solution as it is in the vapor phase, but in general the solvent has a very marked effect on the position of the equilibrium. In Table 35 are given the values of the equilibrium constants for three different substances in a variety of solvents. In general, the effect of each solvent is about the same on each of the three substances in the table and on a number of others of the same type (β-diketones). These results can be understood when we consider how the solvent may influence the several conditions which permit the enol to exist at all in these compounds. One of the large sources of energy for stabilizing the enol is the energy of the hydrogen chelation or internal hydrogen bonding of these β-dike-

tonic compounds. Any solvent which is capable of preventing this chelation would reduce the enol stability. Hydroxylic solvents which can satisfy the requirements of C=O as a base without the necessity of internal chelation are just the ones which reduce the enolization to the greatest extent. The hydrogen of chloroform is also sufficiently acid to fulfill this function. Another way in which the solvent might affect the equilibrium is through its stabilizing effect, as a polarizable dielectric or as an aggregate of highly polar molecules, on the more polar of the two forms, which is almost certainly the ketonic form. The dipole moment of ketones is about 2.7 while that of alcohols is about 1.7, in addition to the fact that the enol is chelated into a fairly symmetrical ring structure. It is to this

TABLE 35

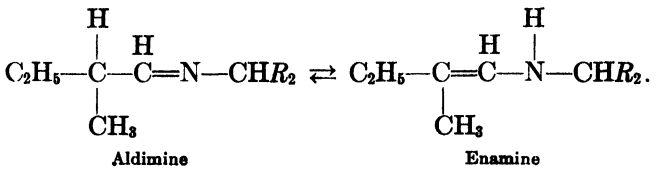
EQUILIBRIUM CONSTANT $K = \frac{[\text{enol}]}{[\text{keto}]}$ IN VARIOUS SOLVENTS*

Solvent	Ethyl Acetoacetate	Methyl Benzoylacetate	Acetyl-acetone
Water	0.004	0.008	0.24
Formic acid	.011	.028	0.9
Acetic acid	.061	.16	2.8
Methyl alcohol	.074	16	2.6
Pure liquid mixture.	.079	.20	3.2
Chloroform	.089	.19	3.8
Ethyl alcohol	.15	.35	5.3
Benzene	.22	.45	5.7
Hexane	.9	2.2	12.0
Vapor	.9		11.5

* Meyer, K. H., *Ber.*, 45, 2843 (1912); 47, 826, and with Wilson, F. G., 832, 837 (1914).

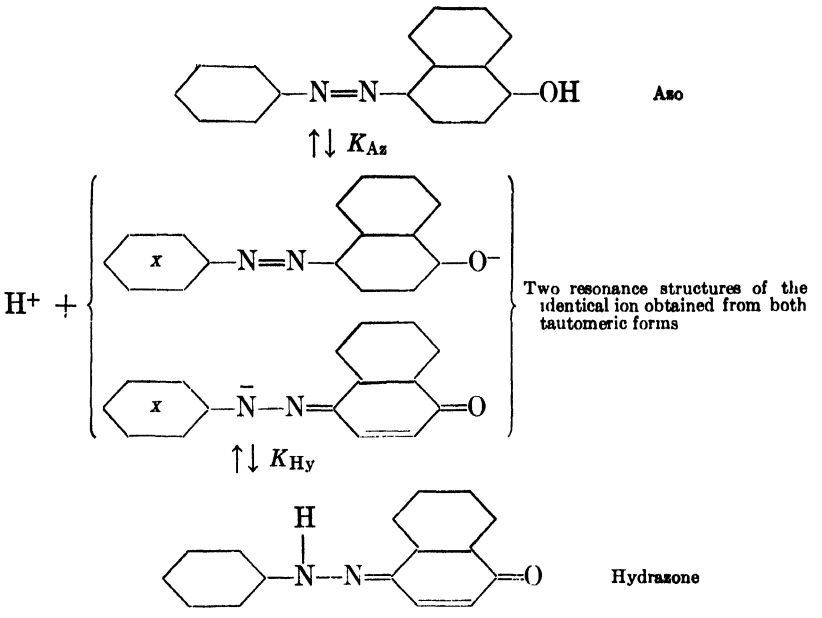
source that the ketonizing effect of such solvents as nitrobenzene (10 per cent enol of ethyl acetoacetate), benzene, or ether (27 per cent enol of ethyl acetoacetate) may be attributed.

31c. Other tautomeric systems. Although the data for systems other than keto-enol are far less complete and unequivocal, the results of Table 33 are confirmed, and the same principles of resonance and induction which were used in the interpretation of the keto-enol equilibria account quite satisfactorily for those cases which do not agree with Table 33. For example, the aldimine-enamine equilibrium is in general on the side of the aldimine:



the bond energy difference is the same for all three and is about 22 kcals. in favor of the hydrazone form. The various polar form contributions to the resonance energy of both the azo and hydrazone forms are probably much the same for all three compounds, and in any case are considerably smaller than the contribution of the strictly equivalent non-polar Kekule forms. It is, therefore, to be expected that the change in the contribution of these equivalent homopolar forms will be the controlling factor in the relative position of the equilibrium in this series of three compounds. These changes occur only in one of the two aromatic groups, that which changes from a phenolic to a quinoidal structure. The discussion that follows refers to this aromatic group alone. In the first case (I) essentially one benzene resonance is lost in going from azo to hydrazone. This (37 kcals.) is apparently quite sufficient to overbalance the bond energy stability of the hydrazone (22 kcals.), so that benzeneazophenol is essentially entirely in the azo form, as evidenced by both its physical and chemical properties. In the second case (II) a naphthalene resonance is replaced by a benzene one, while in the third case (III) an anthracene resonance is replaced by two benzene resonances. A way of estimating the quantitative degree of the change is to take the ratio of the number of equivalent resonance structures in the azo form to the number in the hydrazone form, considering only that part of the molecule which changes. These ratios are: for benzene, 2; for naphthalene, 1.5; and for anthracene, 1. In actual fact, the anthrol compound (III) is entirely in the hydrazone form, while the naphthol (II) has appreciable quantities of both forms present at equilibrium. The resonances of the condensed-ring systems will appear again in a more quantitative way when we consider the oxidation-reduction potentials of their quinones, where an experimental justification of using the ratio of the number of homopolar resonance forms to estimate the relative magnitudes of the resonance effects of condensed aromatic rings will be given.

Since, in the case of the benzeneazo-α-naphthol, both forms are present in appreciable quantities at equilibrium, it is possible to observe the effects of substituents on the position of the equilibrium. This has been done for a number of substitutions in the benzene part of the molecule of such groups as CH_3, CH_3O, NO_2, halogen, CO_2H, etc. In order to interpret the effects of these groups, we can set up the equilibria:



in which K_{Az} is the acid dissociation constant of the azo form and K_{Hy} is the acid dissociation constant of the hydrazone form into the same pair of ions. Then, since

$$K_{Az} = \frac{[\text{ion}][H^+]}{[Az]} \quad \text{and} \quad K_{Hy} = \frac{[\text{ion}][H^+]}{[Hy]},$$

and since they must be satisfied simultaneously,

$$\frac{[Hy]}{[Az]} = \frac{K_{Az}}{K_{Hy}} \quad \text{or} \quad \log \frac{[Hy]}{[Az]} = \log K_{Az} - \log K_{Hy}.$$

Now all that is necessary is to interpret the effect of the groups on the acid strengths of the azo and hydrazone forms. But the effects of groups on acid strength have been very thoroughly discussed in Chapter VI. It was there shown that both the resonance and the inductive effects of a group on the strength of an aromatic acid could be expressed by

$$\log K_\sigma = \log K_u + \sigma\rho,$$

where K is the strength of the acid with the substitution, i.e., with a group in a particular position, K_u is the strength of the unsubstituted

or reference acid, σ is the constant characteristic of the substitution, and ρ is the constant characteristic of the reference acid representing the effectiveness of groups in general on the strength of that acid. Thus the tautomeric equilibrium constant becomes:

$$\log\left(\frac{[\mathrm{Hy}]}{[\mathrm{Az}]}\right)_\sigma = \log\left(\frac{[\mathrm{Hy}]}{[\mathrm{Az}]}\right)_u - \sigma(\rho^{\mathrm{Hy}} - \rho^{\mathrm{Az}}),$$

where the subscript σ refers to a substituted compound and the subscript u refers to the unsubstituted compound. The essential condi-

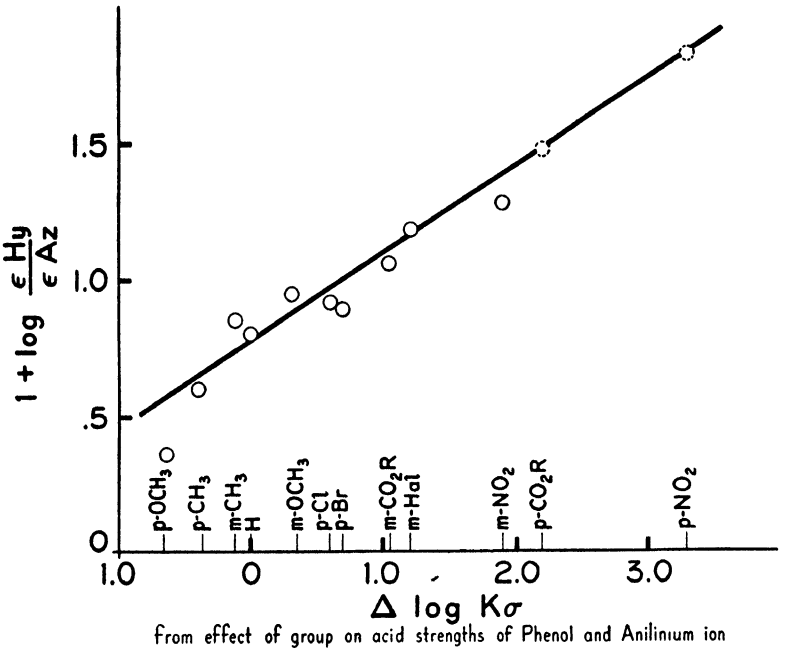


Figure 42. Comparison of the effects of meta and para substituents on the strengths of phenols with their effects on the relative stability of the hydrazone and azo forms of benzene azo-α-naphthol.

tion is the value of $(\rho^{\mathrm{Hy}} - \rho^{\mathrm{Az}})$. It has been found that the value of ρ is the larger the closer the dissociating acid group is to the seat of substitution (e.g., it is greater for phenols than for benzoic acids). It is most certainly true, then, that ρ^{Hy} is greater than ρ^{Az} for substituents in the benzene ring. Thus, acid-strengthening groups (positive σ values) increase the stability of the hydrazone over that

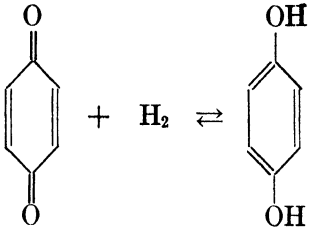
of the azo form. Furthermore, if $\log \left(\frac{[\mathrm{Hy}]}{[\mathrm{Az}]}\right)_\sigma$ is plotted against σ, something of a straight line should result whose slope is $\rho^{\mathrm{Hy}} - \rho^{\mathrm{Az}}$. Figure 42 is such a plot. The σ values are obtained from the acid strengths of phenols and anilinium ions, since for some para substituents the value of σ depends somewhat on the reference acid and the substances under consideration belong to the phenol-anilinium type of acid. The value of $\frac{(\epsilon\mathrm{Hy})}{(\epsilon\mathrm{Az})}$ is the ratio of the extinction coefficients (in alcohol) of absorption bands which are attributed to the hydrazone and azo forms, respectively.[10] In obtaining these ratios, no attempt was made to correct for the overlapping of the two bands, which are not very widely separated (400–600 Å apart). This correction would make the small values smaller and the large values larger, so that the slope of the line as drawn has very little significance. Furthermore, no attempt was made to take into account the effect of the substituents on the intensity of the color. So the agreement is well within the limits of expectation. The two dotted circles correspond to the σ values for p-NO_2 and p-CO_2H groups. The $\frac{(\epsilon\mathrm{Hy})}{(\epsilon\mathrm{Az})}$ values for these substitutions are known to be high, as shown in the figure, but their actual magnitudes could not be obtained, since there is not enough of the azo forms present for their bands to be distinguished.

32. OXIDATION-REDUCTION POTENTIALS

If an oxidizing agent and a reducing agent will react reversibly with each other to produce a new reducing agent and oxidizing agent, respectively, a noble-metal electrode immersed in such a system will come to a definite potential with respect to some standard electrode. That potential is given by the relation $E = \frac{-\Delta F}{nF_y}$, where ΔF is the free energy change for the reaction under the conditions of the experiment, n is the number of equivalents involved in the oxidation-reduction, and F_y is the Faraday constant. When the reactants and products are all at unit concentrations (or better, activities), the potential is called the normal potential, E°, which is thus a measure of the standard free energy change, ΔF°, of the reaction. One such system which is very common in organic chemistry is the reduc-

[10] Shingu, H., *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **35**, 78 (1938).

tion of a quinone to hydroquinone by hydrogen at a platinum electrode:



(1)

The potential for this type of reaction is given by

$$E = E^\circ + 0.05912 \log [H^+] + 0.02956 \log \frac{[\text{quinone}]}{[\text{hydroquinone}]},$$

so that E°, the normal potential, is the potential when the hydrogen ion concentration (activity) is unity and the concentrations (activities) of the quinone and hydroquinone are equal. These potentials are usually measured against the standard hydrogen electrode as zero. Each quinone has a characteristic oxidation-reduction potential which is a measure of its "oxidizing power"; i.e., the more positive the potential, the stronger is the quinone as an oxidizing agent. More specifically, since these potentials are measured against the hydrogen electrode, a positive potential indicates a quinone which is a stronger oxidizing agent than H^+ and a hydroquinone which is a weaker reducing agent than H_2; a negative potential indicates a quinone which is a weaker oxidizing agent than H^+ and a hydroquinone which is a stronger reducing agent than H_2. All this is expressed by the relation

$$E^\circ = \frac{-\Delta F^\circ}{nF_y}$$

for the reaction as written in equation I; i.e., the more positive is the potential, the greater is the drop in free energy in going from the quinone-hydrogen system to the hydroquinone. If we are to compare a series of quinones, the change in potential will represent the change in the relative stability of the quinone and hydroquinone in going from one compound to another, since the hydrogen remains the same for all of them. Further, it has been found that the tem-

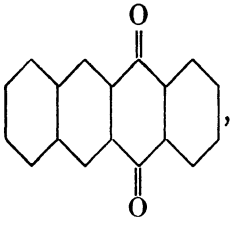
perature coefficient of the normal potential is about the same for a large number of quinones and is equal to about 0.7 mv./deg. Since

$$E^\circ = -\frac{\Delta F^\circ}{nF_v} = -\frac{\Delta H^\circ}{nF_v} + T\frac{\Delta S^\circ}{nF_v}$$

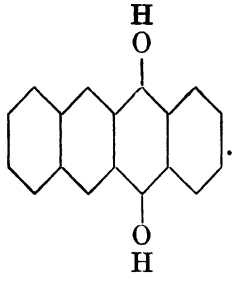
(with nF_v = 46 kcal. per volt), this temperature coefficient corresponds to an entropy change of about −32 cals./deg. for the hydrogenation of a quinone. Similar values have been found for the ΔS of a large number of other hydrogenations, and it corresponds roughly to the entropy of the mole of hydrogen which is lost in the reaction. Thus the change in potential in a series of quinones is a measure of the change in relative heat contents of the quinone and hydroquinone through the series.

32a. Homopolar valence bond resonance. The change in bond energies in the reduction represented by equation I is the same for all quinones and amounts to about 5 kcals. ($\Delta H^{\circ\prime}$ = + 5 kcals.) in favor of the quinone-hydrogen system. But for *p*-benzoquinone, experimentally, ΔH° = −42 kcals. (in alcohol solution at 25°C.), so that the benzene resonance which is gained on the hydroquinone side must be largely responsible for the observed oxidation potential of benzoquinone. Since practically all other quinones have a positive oxidation potential, it is to be expected that similar resonance effects will be the controlling factor in the magnitude of the potential. Of course other types of resonance must also play a part, such as the ionic forms in the quinone, and the phenolic resonance in the hydroquinone, as well as inductive and steric effects; but, in general, these are much smaller in magnitude than the contribution of the entirely equivalent Kekule forms. Further, in a comparison such as we are about to make of *p*-benzoquinone, 1,4-naphthoquinone, and 1,4- and 9,10-anthraquinone, the relative contributions of these secondary forms to quinone and hydroquinone can be expected to remain about the same throughout the series. We are thus left with the purely homopolar Kekule-like forms, as the controlling type of resonance in the series of quinones and the relative numbers of such equivalent forms may be used as a quantitative estimate of the relative energy of the oxidized and reduced forms. For example, in *p*-benzoquinone there is only one such form, while in hydroquinone there are the two Kekule forms. In 1,4-naphthoquinone there are two, while in the corresponding hydroquinone there are three. For 1,4-anthraquinone the change is from three to four, while in 9,10-anthraquinone the number remains constant at four. Indeed in larger linear condensed

systems the quinone can have more of these forms than the hydroquinone—six forms in

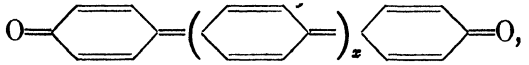


, and only five in

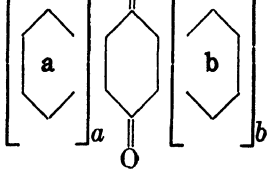


.

If we give equal weight to all of the forms of the hydroquinone, one method of expressing the change in the relative energies of the quinone and hydroquinone in a series would be the ratio of the number of forms of the quinone (n_q) to the number of forms in the hydroquinone (n_h). If, then, these be the controlling factors in the potential of the quinone-hydroquinone systems, a plot of these potentials as ordinate against the ratio n_q/n_h as abscissa should be approximately a straight line. Such is indeed the case, as is shown in Figure 43, which contains the data for the substituted para quinones together with that for diphenoquinone, stilbenequinone, and amphinaphthoquinone. A similar line is obtained for the ortho quinones, but displaced upward about 0.1 volt and parallel to the para quinone line. This would seem to indicate that there is some validity to the method of simply counting the number of forms, but there are a number of objections and refinements which should be considered. Although the simple ratio n_q/n_h gives a limiting potential for the molecule of the type



as x gets very large, since n_q remains one and n_h is equal to $2^{(x+2)}$, thus making $\frac{n_q}{n_h}$ go to zero, it has no limit for other types of molecules. Thus, in the molecule of the type



where a and b may increase indefinitely, the ratio n_q/n_h approaches no limit.[11] A function which is limited at both ends would be the

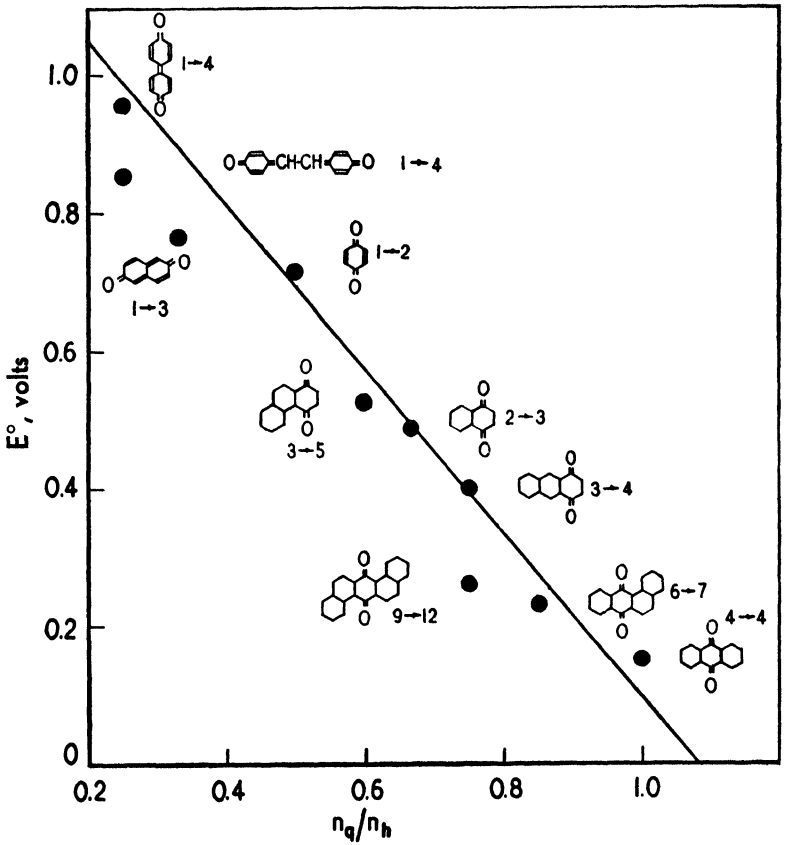
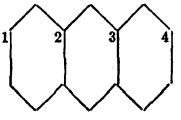


Figure 43. The oxidation-reduction potentials of certain condensed-ring-system para quinones.

[11] For the linear condensed-ring systems, the number of purely homopolar adjacent bond resonance forms, n_h, is simply equal to the number of vertical bonds when the system is written horizontally across the page; e.g., for anthracene,

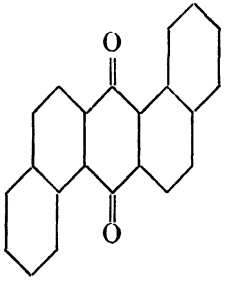


, $n_h = 4$.

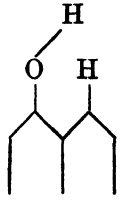
In order to obtain n_q, the system is considered simply in terms of the two independent parts on either side of the quinoidal ring and the total number of forms, n_q, is the product of the numbers possible in each part.

For the angular condensed-ring systems there is no simple rule for n_h, but n_q is still the product of the number of possible forms in each of the two parts of the molecule on either side of the quinoidal ring.

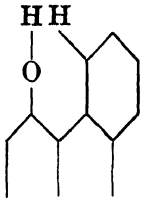
one giving the percentage change in the number of forms in the reduction process, $\frac{n_h - n_q}{n_h + n_q}$. This is limited by the values ± 1, and a plot using this function as abscissa produces about the same difficulty of fitting a straight line as the simple ratio, if all the data used in Figure 43 are included. If, however, the points for diphenoquinone, stilbenequinone, and amphi-naphthoquinone are excluded, a considerably better line is obtained through the para quinones alone. This limitation is not unreasonable, since the interactions of the quinone and hydroquinone oxygens must be quite different in the last three compounds from what they are in the para quinones. A closer examination of the para quinone points of either the n_q/n_h plot or the $\frac{n_h - n_q}{n_h + n_q}$ plot reveals that the greatest deviations are those compounds having angular arrangement of the rings, e.g.



and that these deviations are in the direction corresponding to an instability of the hydroquinone. This seems to indicate a steric repulsion between the phenolic hydrogen and the hydrogens of the ortho substituent. A small amount of inductive effect may also be included, and from the effect of a methyl group on the potential of *p*-benzoquinone (about -55 mv.) we estimate the steric repulsion correction for the system

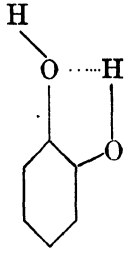


to be about 25 mv., and for the system



to be about 50 mv. These corrections are to be added to the observed potentials of the corresponding compounds in order that they may be compared with each other and with *p*-benzoquinone.

The ortho quinones can be included in the same comparison if a correction for the ortho effect in both the quinone and the hydroquinone is introduced. In the hydroquinone the source of this effect can readily be found in the hydrogen bond formation (see Chapter V) between ortho-hydroxyl groups:



The magnitude of this effect may be anywhere between 3 and 6 kcals., stabilizing the hydroquinone. The correction in the quinone is probably very small, since groups in the ortho and para positions have much the same resonance interaction, and in this case the difference in the mutual inductive effects of the pair of carbonyl oxygens in the ortho and para positions must be relatively small. So we will include all of these perturbations in a single correction of about 4.5 kcals. of extra stability of the *o*-hydroquinone. Thus, if we subtract 0.1 v., the difference between *o*- and *p*-benzoquinone, from the potential of each ortho quinone, it may be compared with the para quinones.

These corrections have been applied (column 7, Table 37) to the quinones whose experimentally determined potentials are given in column 6 of Table 37. The results have been plotted in Figure 44 with $\frac{\Delta n}{\Sigma n}$ as abscissa.[12] The linear relationship is exceptionally good,

[12] $\Delta n = n_h - n_q$ and $\Sigma n = n_h + n_q$.

especially for the para quinones, the only appreciable deviation from the straight line in this group being the most complex one measured (VII).

There is one other interesting observation in connection with this set of quinones which should be mentioned. It is possible, on the basis of bond energy calculations alone, together with a single reasonable assumption, to calculate the slope of the line of Figure 44. Using the bond energy values given in Table 28, we have seen that

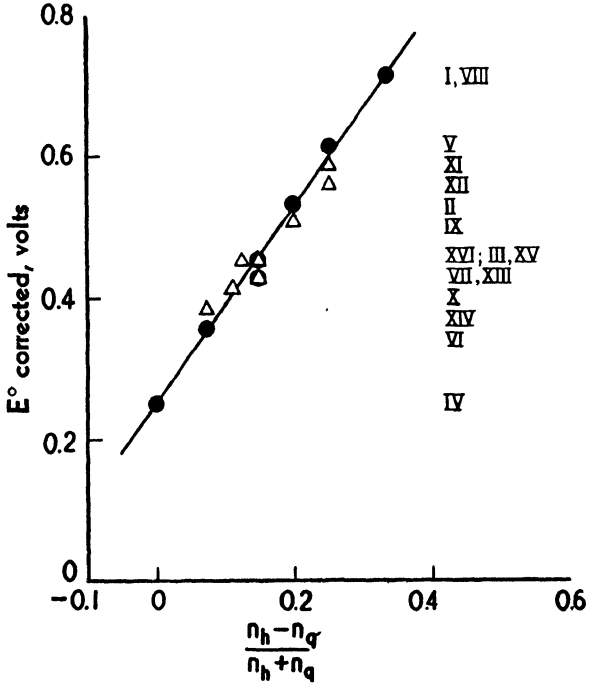


Figure 44. The adjusted oxidation-reduction potentials of certain quinones. The numbers correspond to the quinones as listed in Table 37.

the change in bond energies alone in the hydrogenation of *p*-benzoquinone to hydroquinone is about +5 kcals. This should be the ΔH for the reaction in the vapor phase when all resonance is neglected. Now, by far the most important resonance effect is the appearance of the benzene resonance in the hydroquinone. Taking this into account, we have the value $+5 - 37 = -32$ kcals. for the ΔH of the vapor phase reaction. In order to convert this into the value in solution, where the measurements are made, we must add to it the

TABLE 37

OXIDATION-REDUCTION POTENTIALS OF QUINONES

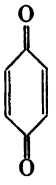
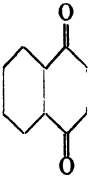
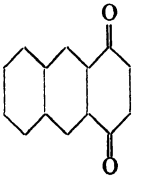
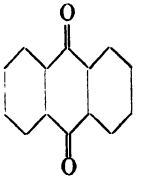
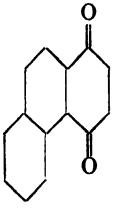
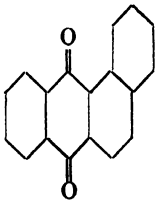
No. in Figure 44	Compound	n_h	n_q	$\frac{\Delta n}{\Sigma n}$	E° (exp.)	E° (corr.)
I		2	1	.333	.71	.71
II		3	2	.20	.48	.53
III		4	3	.143	.40	.45
IV		4	4	0	.15	.25
V		5	3	.25	.53	.61
VI		7	6	.077	.23	.36

TABLE 37—*Continued*

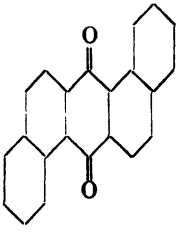
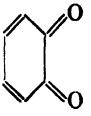
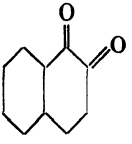
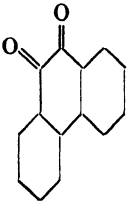
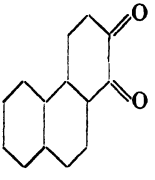
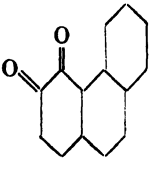
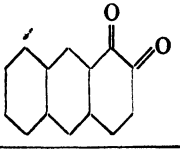
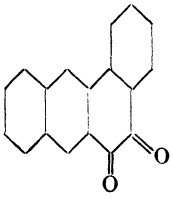
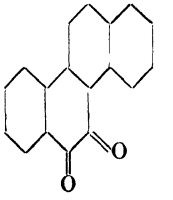
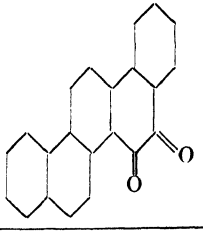
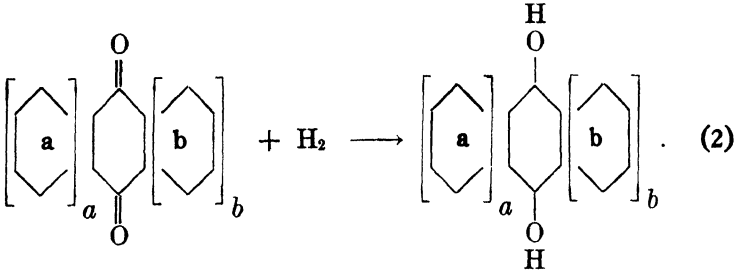
No. in Figure 44	Compound	n_h	n_q	$\frac{\Delta n}{\Sigma n}$	E° (exp.)	E° (corr.)
VII.....		12	9	.143	.27	.42
VIII.....		2	1	.333	.81	.71
IX.....		3	2	.20	.58	.51
X.....		5	4	.111	.46	.41
XI.....		5	3	.25	.66	.59
XII.....		5	3	.25	.62	.57
XIII.....		4	3	.143	.49	.42

TABLE 37—*Continued*

No. in Figure 44	Compound	n_h	n_q	$\frac{\Delta n}{\Sigma n}$	$E°$ (exp.)	$E°$ (corr.)
XIV.....		7	6	.077	.43	.38
XV.....		8	6	.143	.47	.45
XVI.....		13	10	.130	.47	.45

differences in the heats of sublimation and in the heats of solution of the quinone and hydroquinone. Actually this is about 9 kcals. in favor of the hydroquinone, so that a calculated value for ΔH (sol.) is about 41 kcals., which is not bad agreement with the experimental value of 42 kcals. It should be remembered that in this calculation no account has been taken of the ionic resonance forms in either quinone or hydroquinone. If they contribute equally to both, they will cancel out; but let us suppose that they do not contribute equally and that their difference is a constant for all of the quinone-hydroquinone systems we have considered. Furthermore, since we do not know the heats of sublimation or solution of any quinones and hydroquinones other than the one already mentioned, let us assume that the difference between them for the other quinone-hydroquinone systems is a constant. Now, lumping these two constants—the difference in ionic contribution and the difference in heat of sublimation—together, and setting the ΔH for the reaction proportional to $\frac{\Delta n}{\Sigma n}$, we have $\Delta H = A + B\frac{\Delta n}{\Sigma n}$. Inserting numerical values obtained

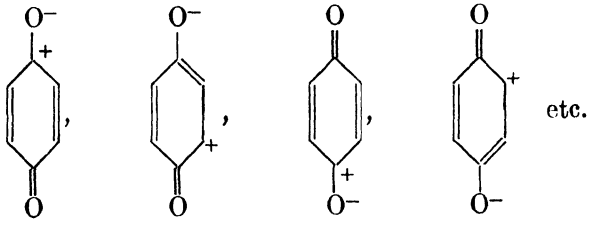
from the calculation on *p*-benzoquinone, this becomes $-32 = A + B \cdot \frac{1}{3}$. Another such relation is necessary in order to determine B, the slope of the line. In order to get this, we can use a hypothetical compound containing a large number of linearly condensed benzene rings;



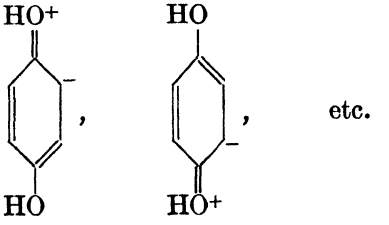
(2)

Since in the quinone the resonance in the systems **a** and **b** are independent, the total number of forms is the product of the number in **a** and the number in **b**. The total number of forms would be greatly reduced by any kind of coupling between **a** and **b**, such as is introduced when the hydroquinone is written in the ordinary form; and, since a and b are large numbers, it is reasonable to suppose that the presence of those forms will resist that coupling even in the hydroquinone. It is for a similar reason that hydrocarbons of the type of pentacene exhibit the unsaturated properties of a free radical (see section 33d). Therefore, the replacement of a single by a double carbon-carbon bond (equivalent to 42 kcals.) which would produce such a coupling will not take place, and the calculated heat of the reaction (2) will then be 42 kcals. greater than that calculated from the ordinary formulas, or +47 kcals. This gives another value to use in the equation $\Delta H = A + B\frac{\Delta n}{\Sigma n}$, and we have $47 = A + B(-1)$. Taking this, together with the expression obtained from *p*-benzoquinone, the value of B is 59.3 kcals., or about 1.3 volts. The slope of the line in Figure 44 lies between 1.3 and 1.4 volts. The actual values of the oxidation potentials for all of the quinones in the table can of course be calculated if the values of the assumed constant differences are taken as the same as those which apparently are satisfactory for *p*-benzoquinone; i.e., 9 kcals. for the difference in the heat of sublimation and heat of solution between quinone and hydroquinone, and 1 kcal. for the difference in the contribution of ionic forms, and the observed constant value of ΔS for these hydrogenations.

32b. Ionic resonance and induction. When we consider the effects of ordinary substituents in the 2 and 3 positions in a 1,4-quinone, we must be concerned with the very polar resonance and inductive effects which have been neglected or considered as constant in the preceding discussion. These are effects of a smaller order and, furthermore, there will undoubtedly be present many of the irregularities which almost always appear in ortho-substituted compounds. It is therefore not to be expected that any very good quantitative correlations will appear. Qualitatively, however, the usual order of group effects does appear, and they can be understood in terms of their relative effects on the two main ionic contributions to the resonance in the quinone and the hydroquinone, respectively. The predominating ionic resonance in quinone tends to throw a positive charge into the ring:



On the other hand, that in hydroquinone does the reverse, i.e. tends to throw a negative charge into the ring:



Hence those substituents which, through either resonance or induction, can assist the ring to accommodate the positive charge will stabilize the quinone while reducing the stability of the hydroquinone, and thus reduce the oxidation-reduction potential of the quinone. Similarly, those groups which can assist in the accommodation of negative charge will raise the potential. The former group is typified by the amino group, i.e. acid-weakening, and the latter by the nitro or sulfone groups, i.e. acid-strengthening. In Table 38 are reproduced some of the results of Fieser and Fieser on the effect of a group substituted in the 2 position in 1,4-naphthoquinone, and in the 4

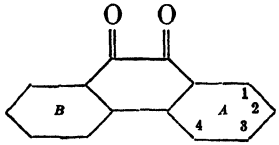
position in 1,2-naphthoquinone. It should be remembered that although 4-substituted 1,2-naphthoquinone is ostensibly free of ortho effects for the substituent, there is here the complicating ortho effect in the quinone and hydroquinone grouping itself.

TABLE 38
EFFECT OF SUBSTITUTION ON THE POTENTIAL OF NAPHTHOQUINONES*
(Alcoholic Solution)

2-Substituted 1,4-Naphthoquinone $E°$ (unsubstituted) = .48 volt		4-Substituted 1,2-Naphthoquinone $E°$ (unsubstituted) = .58 volt	
R	$\Delta E°$ (millivolts)	*R*	$\Delta E°$ (millivolts)
$NHCH_3$	−252	$NHCH_3$	−283
NH_2	−210	$NHC_4H_9(n\text{-})$	−281
NHC_6H_5	−198	NHC_2H_5	−279
$N(CH_3)_2$	−181 (aqueous)	$NHCH_2C_6H_5$	−276
$OC_4H_9(n\text{-})$	−133	NH_2	−251
OCH_3	−131	$OC_4H_9(n\text{-})$	−154
OH	−217	OCH_3	−143
CH_3	−76	CH_3	−44
$NHCOCH_3$	−67	$NHCOCH_3$	−30
$CH(C_6H_5)_2$	−51	$CH(COOR)_2$	+22
C_6H_5	−32	SO_3Na	+60
$OCOCH_3$	−9		
Cl	+24		
SO_3Na	+69		
$SO_2C_6H_4CH_3$	+121		

* Fieser, L. F., and Fieser, M., *J. Am. Chem. Soc.*, 57, 491 (1935).

All of the compounds in Table 38 are substituted in the quinoid ring. When the substituent is not in the quinoid ring its effect is much smaller and, furthermore, depends very critically upon its position with respect to the quinoid ring. For example, substituents in the 1 or 3 position in phenanthraquinone have a considerable effect on the



Phenanthraquinone

potential of phenanthraquinone, while in the 2 or 4 positions they are practically ineffective. As Fieser has pointed out, the 1 and 3 positions are, respectively, ortho and para to the quinone carbonyl (or the hydroxyl of the hydroquinone), while the 2 and 4 positions

are meta. A consideration of the possible paths by which a resonance interaction may occur between the several positions and the quinone groups will show that substituents in the 1 or 3 position may interact directly through the *A* ring with the quinoid carbonyl group, whereas any interaction between the 2 or 4 position and a carbonyl (or hydroxyl) group can occur only through both the *A* and the *B* rings and the bond connecting them. Although the magnitude of the effects of substituents not in the quinone ring is smaller than otherwise, the order is again the usual one; i.e., acid-weakening groups reduce the potential while acid-strengthening ones increase it. In Table 39 are given some of the data collected by Fieser on the effect of substituents in the 1 or 3 position on the potential of phenanthraquinone.

TABLE 39

THE EFFECT OF SUBSTITUENTS IN THE 1 OR 3 POSITION ON THE POTENTIAL OF PHENANTHRAQUINONE*

$E°$(unsubstituted) = 0.460 volt

R	$\Delta E°$ (millivolts)
NH_2	−98
CH_3	−64
OH	−50, −53
OCH_3	−39
$OCOCH_3$	+9
SO_3H	+23, +30
Br	+28
CO_2H	+49
CO_2CH_3	+58
COC_6H_5	+59
CN	+76
NO_2	+91

* Fieser, L. F., *J. Am. Chem. Soc.*, 51, 3101 (1929).

33. FREE RADICALS

In 1900 Gomberg found that solutions of hexaphenylethane in benzene exhibited the properties of a very unsaturated system. The solutions were yellow and absorbed oxygen and halogens instantly. He explained this by the assumption of the equilibrium

$$\underset{\text{Hexaphenylethane}}{(C_6H_5)_3C—C(C_6H_5)_3} \rightleftarrows 2\underset{\text{Triphenylmethyl}}{(C_6H_5)_3C—}$$

in which the reactive species is the free radical triphenylmethyl. Molecular weight determinations indicated that a 3 per cent solution of the ethane in benzene was about 2 per cent dissociated into free

radicals at about 5°C. Since that time a tremendous amount of work has been done on many substances in which a homopolar electron pair bond may be symmetrically broken, giving a structure having an odd electron. It has been found possible to prepare free radicals in which at least initially the odd electron is on N, O, S, Pb, Sn, and perhaps others, but by far the greatest number of free radicals so far prepared are those containing trivalent carbon.

The existence of the free radicals has been demonstrated by physical as well as chemical means, the most important of which is the measurement of their magnetic susceptibilities. Practically all normal organic compounds have an even number of electrons existing as pairs whose spins are opposed. Thus the net magnetic moment of the molecule, which is the resultant of the moments of all the electrons present, will be zero, since each electronic moment is balanced by the opposite one of the pair. If, however, there is an odd number of electrons in the molecule, at least one spin must be left unbalanced, thus giving the molecule a net magnetic moment and making it paramagnetic. This was first recognized by Lewis, who pointed out that NO and a few other "odd molecules" as well as the organic free radicals should be paramagnetic, as they were indeed found to be. In general the paramagnetism of a free radical containing one unpaired electron corresponds to a magnetic moment of one Bohr magneton, i.e. the moment of a single electron. A measure of the paramagnetism of a solution containing a dissociable compound can thus be used to determine the extent of the dissociation into free radicals.

In spite of the large amount of work that has been done, the quantitative prediction of the extent of dissociation of some given molecule from a primary consideration of its structure is not yet possible. One of the reasons for this is obviously the same one which was mentioned with respect to the keto-enol equilibrium. Within the measurable range of dissociation, i.e. from 1 to 99 per cent, the change in the ΔH of the reaction is relatively small, so that a great many small, perhaps secondary, effects might greatly influence the observed value of the dissociation. This can be partially overcome by extending the range of temperature over which the measurements are made, i.e. lowering the temperature for the apparently completely dissociated substances and raising the temperature for the apparently completely undissociated substances. This cannot be extended indefinitely for at least two reasons besides the purely experimental difficulties of the physical or chemical measurements at either reduced or elevated temperatures. The

temperatures cannot be raised too high, for, after all, the free radicals are essentially very reactive species and will undergo irreversible reactions with themselves or the solvent. The temperatures cannot be lowered too much, for those very substances which are most highly dissociated are usually the ones which are least soluble. Furthermore, since the extent of dissociation depends on the solvent, measurements cannot be compared indiscriminately among different solvents.

It has, however, been possible to recognize a number of conditions which, when they appear in a molecule, tend to enhance the dissociation. Since the effect of structure on the dissociation equilibrium has been studied most thoroughly among the trivalent carbon radicals, we will consider these in some detail.

33a. Trivalent carbon. The only case for which ΔH and ΔF have been directly determined for the dissociation of a C—C bond into two free radicals is that of hexaphenylethane. Using the intensity of the color of the solutions as a measure of the extent of dissociation, Ziegler[13] has determined the equilibrium constant

$$K = \frac{4C\alpha^2}{1 - \alpha},$$

where C is the concentration of the ethane in moles/l. and α is the fraction dissociated, at a number of different temperatures, obtaining the values 2.6×10^{-4} at 13°C., 7.84×10^{-4} at 30°C., and 18.8×10^{-4} at 43°C. These correspond to a value of 11.8 kcals./mole for the heat of dissociation. Similar values were obtained in other solvents. This value of 11.8 is to be compared with the heat of dissociation of the C—C bond in ethane itself, which is probably of the order of 70 to 80 kcals., the value 58.6 given in Table 28 for the C—C bond being an averaged value to be used only in calculating the heat of complete disruption of a compound into atoms. Although the heats of dissociation of most of the other ethanes into substituted methyl radicals have not been directly determined, an idea of the effectiveness of the various types of groups in promoting this dissociation may be obtained from a comparison of the amount of dissociation of the several ethanes under similar conditions. Such a comparison can be made from an examination of Table 40, in which the per cent dissociation of a number of symmetrically substituted ethanes is given, together with the name of the radical formed.

At least two determining factors are apparent upon even a

[13] Ziegler, K., *Ann.*, **473**, 163 (1929). Other methods used by Mithoff, R. C., and Branch, G. E. K., *J. Am. Chem. Soc.*, **52**, 255 (1930).

cursory examination of the table. They are (1) the size of the groups, which might give rise to purely steric effects such that the two radicals would be kept from combining, and (2) the presence of aromatic groups attached to the apparently trivalent carbon atom. Although the presence of aromatic groups must necessarily carry with it the steric condition, the reverse is not true. Furthermore, para substitution in triphenylmethyl may very markedly affect the

TABLE 40

DISSOCIATION OF ETHANES TO GIVE TRIVALENT CARBON FREE RADICALS IN BENZENE SOLUTIONS CONTAINING 2-3 PER CENT OF THE ETHANE AT 5°C.

(Unless otherwise stated.)

Radicals formed	Per Cent Dissociated[1]
Triphenylmethyl	1-3
Diphenyl-*p*-tolylmethyl[2]	5[b]
Diphenyl-*m*-xenylmethyl[3]	11-12[a]
Diphenyl-*p*-xenylmethyl[3]	15, 13-14[a]
Diphenyl-*p*-anisylmethyl	25
Diphenyl-*p*-*tert*-butylphenylmethyl[2]	8[c]
Diphenyl-*o*-tolylmethyl[2]	27[d]
Tris-(*p*-isopropylphenyl)methyl[2]	26[e]
Diphenyl-*o*-anisylmethyl	27
Diphenyl-β-naphthylmethyl	33
Diphenyl-α-naphthylmethyl	60
Tri-*m*-xenylmethyl[4]	60[f]
Phenyl-di-*p*-xenylmethyl	75
Tri-*p*-xenylmethyl	100
Tri-*o*-anisylmethyl	100
Phenyl-*p*-xenyl-α-naphthylmethyl	100
Phenylxanthylmethyl	82
Phenylxenylenemethyl	0
tert-Butyl-di-*p*-xenylmethyl[5]	70

[a] 3.6% solutions at 25°C.
[b] 4.7% solutions at 28°C.
[c] 6.1% solutions at 29°C.
[d] 5.8% solutions at 30°C.
[e] 6.8% solutions at 28°C.
[f] 2.5% solutions at 25°C.

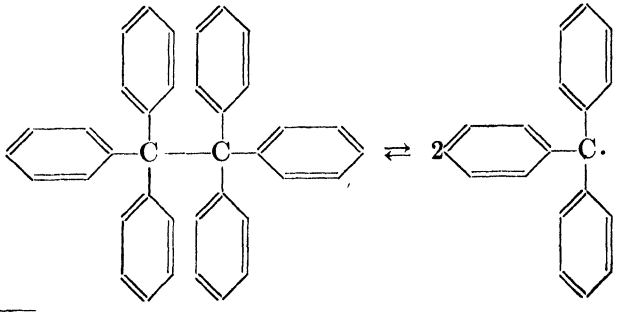
[1] From Walden, P., *Chemie der freien Radikale*, Hirzel, Leipzig, 1924, unless otherwise stated.
[2] Marvel, C. S., Mueller, M. B., Himel, C. M., and Kaplan, J. F., *J. Am. Chem. Soc.*, 61, 2771 (1939).
[3] Marvel, C. S., Mueller, M. B., and Ginsberg, E., *J. Am. Chem. Soc.*, 61, 2008 (1939).
[4] Marvel, C. S., Ginsberg, E., and Mueller, M. B., *J. Am. Chem. Soc.*, 61, 77 (1939).
[5] Conant, J. B., and Schultz, R. F., *J. Am. Chem. Soc.*, 55, 2098 (1933).

degree of dissociation without changing the steric conditions about the dissociating bond very much. Similarly, the radical diphenylcyclohexylmethyl does not exist in any appreciable amount in solutions of the corresponding ethane, although these solutions do absorb oxygen and form a peroxide. On the other hand, alkyl groups containing secondary or tertiary carbon atoms attached to the dissociating carbon atoms do have an effect toward weakening the C—C

bond in the ethane. For example, tetra-*p*-xenylethane shows no evidence of the existence of the free radical, while tetra-*p*-xenyl-di-*tert*-butylethane is about 70 per cent dissociated in dilute solution in benzene at 5°C., which is only slightly less than the dissociation of tetra-*p*-xenyldiphenylethane (75 per cent) under the same conditions. A more detailed examination of the many compounds which have a tendency to dissociate into substituted methyl free radicals fully confirms the suggestions indicated above, i.e. that the presence both of aromatic groups and of large alkyl groups containing secondary or tertiary carbon atoms tends to weaken the C—C bond in ethane, if not to actually produce an appreciable concentration of free radicals in dilute solutions at ordinary temperatures.

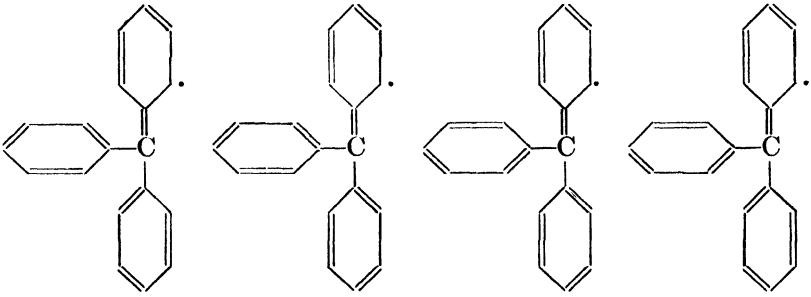
The presence of aromatic groups, however, seems to be the most important requirement for dissociation. The aromatic groups can be arranged in order of their effectiveness in promoting dissociation: α-naphthyl > *p*-benzyloxyphenyl > β-naphthyl > *o*-anisyl > *p*-anisyl > $\frac{1}{2}$ xanthyl > *p*-xenyl > *p*-tolyl > phenyl > *p*-chlorophenyl > $\frac{1}{2}$ biphenylene. A number of others could be added to the list, but this suffices to show the type of thing which is to be found. The reason for the effectiveness of the aromatic groups has been found in a consideration of the resonance which they may introduce into a molecule or radical. It has even been possible to predict an order of effectiveness among several aromatic groups.[14]

The principle of the method involves the assumption that it is not the ethane bond which is weakened (made unstable) but rather that the free radicals formed upon dissociation are stabilized by resonance to such a degree as to permit them an appreciable existence in equilibrium with the undissociated ethane, in some cases, as we have seen, to such an extent that no ethane is present. We may illustrate by considering the case of hexaphenylethane:

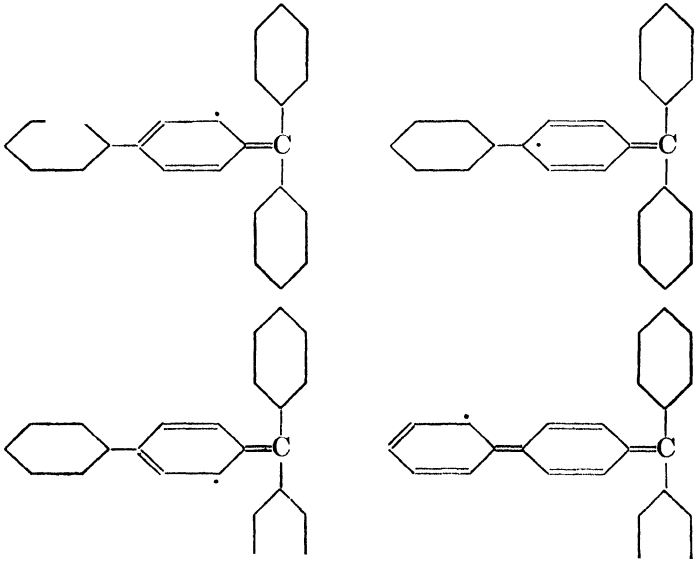


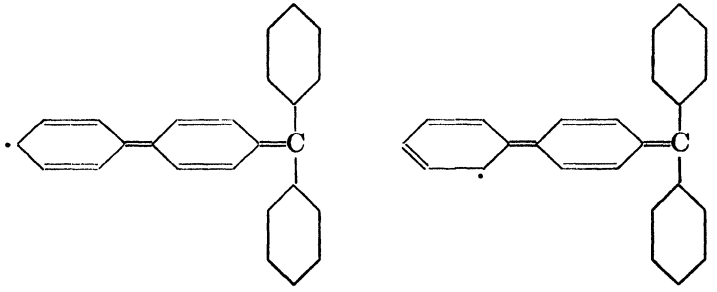
[14] Pauling, L., and Wheland, G. W., *J. Chem. Phys.*, **1**, 362 (1933); Hückel, E., *Z. Physik*, **83**, 632 (1933); *Trans. Farad. Soc.*, **30**, 41 (1934).

In each of the phenyl groups of the ethane there are all of the benzene resonances (the two chief ones being the Kekule structures) which appear again in the free radical. If these were all that were possible in the free radical, the dissociation energy would hardly differ from that of a hexaalkylethane. But in the free radical there are the additional 36 forms in which the odd electron is on an ortho or para carbon atom in one or the other of the three rings; e.g.:



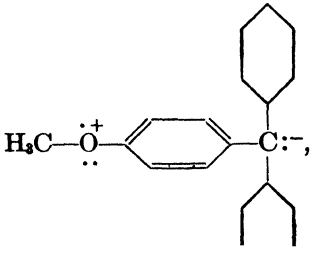
Nine such positions are possible for the odd electron, each having four forms of the rest of the molecule associated with it. It is these extra forms possible in the radical which stabilize it sufficiently to make it have an appreciable concentration in equilibrium with the ethane. If now one of the phenyls in the radical is replaced by xenyl, instead of only nine possible positions for the odd electron in the aromatic part of the molecule there will be six in the two phenyl groups and six in the xenyl group:





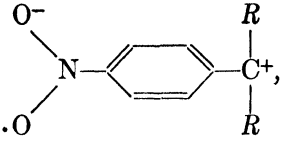
Each of the six positions in the phenyl groups and the first three in the xenyl group will have eight forms associated with it, making seventy-two forms, while each of the last three positions in the xenyl group will have four forms associated with it, making twelve more forms. These last twelve forms cannot be as important as the other seventy-two, since in them benzene resonance is destroyed. It is quite easily apparent that the greater number of forms in the diphenyl-*p*-xenylmethyl over that in triphenylmethyl should increase the amount of the former radical in equilibrium with its ethane over that of the latter, which is indeed the case experimentally. Actually, not only the number of forms, but also their relative importance must be considered in making this calculation. Carrying this out for a number of free radicals, Pauling and Wheland obtained the following order for the resonance energies of the radicals: phenylbiphenylenemethyl < triphenylmethyl < diphenyl-*p*-xenylmethyl < phenyldi-*p*-xenylmethyl < tri-*p*-xenylmethyl, etc. This corresponds very well with the experimental order. The observation of Marvel that the diphenyl-*m*-xenylmethyl exists in the free radical form to an only very slightly smaller extent than the corresponding *p*-xenyl compound may be evidence to the effect that the extra twelve forms present in the *p*-xenyl compound, which are incapable of existence in the *m*-xenyl compound, contribute very little to the stability of the radical.

The effects of substituents in the phenyl groups can in general be understood along similar lines. For example, in the *p*-anisyl group the oxygen atom offers an additional position for the odd electron,

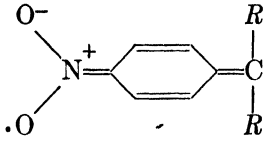


which, moreover, does not require the disappearance of a benzene resonance, although it does involve a separation of charge. Furthermore, the negative charge can now be distributed among the nine ortho and para positions in the phenyl groups; the net result is an even greater stability for the diphenyl-*p*-anisylmethyl than for diphenyl-*p*-xenylmethyl. The case of the xanthylmethyls is analogous to that of the *o*-anisylmethyls. As we shall see later, it seems that the oxygen atom may carry the odd electron much more easily than the carbon atom.

We find in the majority of cases that the effects of *p*-NO_2 and *p*-OCH_3 are in opposite directions (see Chapters VI and IX). However, they have the same effect on the stability of the triphenylmethyl radicals with respect to the ethane. The tris-(*p*-nitrophenyl)methyl is apparently completely in the free radical form in dilute solution at room temperatures, and perhaps even in the solid phase, owing to the additional forms in the free radical made possible by the presence of the nitro group. The most important of these forms are



which maintains the benzene ring (4 forms), and the quinoidal forms (2 forms).

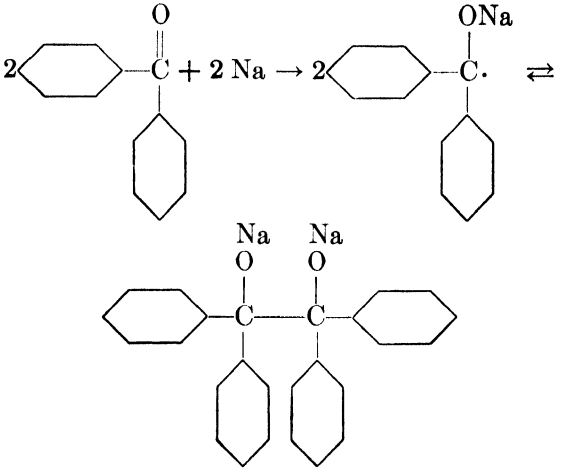


The source of the dissociating effect of secondary and tertiary carbon atoms is not so readily decided upon. It may be purely a steric effect or it may be a secondary resonance effect such as we have used to interpret the heat of hydrogenation data of section 30a. On the other hand, these may simply be two points of view for the same structural phenomenon. Compare the resonance interpretation we have given of the data of hydrogenation of hydrocarbons with the steric explanation of Conn, Kistiakowsky, and Smith.[15] The fact remains, however, that the continued substitution of

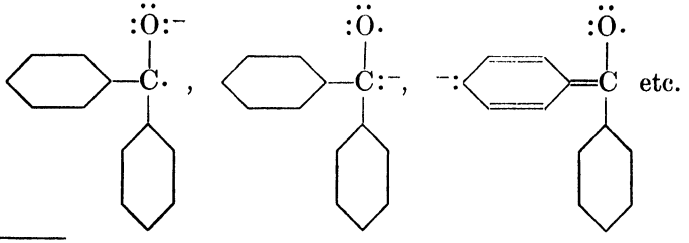
[15] Conn, J. B., Kistiakowsky, G. B., and Smith, E. A., *J. Am. Chem. Soc.*, **61**, 1868 (1939).

carbon for hydrogen in combination with carbon seems to stabilize the system in the same way as a resonance might.

Another type of free radical which may be conveniently classed as a trivalent carbon radical, although the odd electron almost certainly spends a good deal of its time on an atom other than carbon, is the group of metal ketyls. They may be obtained by various means, but most directly by the action of alkali metals on aromatic ketones containing no α-hydrogen atoms:[16]



The fact that the pinacol itself gives no evidence of dissociation into free radicals whereas the alkali metal salts may be quite highly dissociated in ionizing solvents (potassium xenyl pinacolate about 85 per cent dissociated in dioxane[17]) seems to indicate that the oxygen is much more effective in promoting dissociation when it is in the ionic state (purely coulombic repulsion of two negative groups). It may promote the dissociation in much the same way as it does in the anisyl methyls, but to an even greater extent because of its proximity to the initially trivalent carbon atom, through the resonance forms

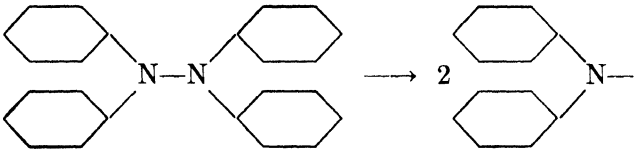


[16] Schlenk, W., and Thal, A., *Ber.*, **46**, 2840 (1913).
[17] Sugden, S., and Allen, F. L., *J. Chem. Soc.*, 440 (1936).

That the radical does not exist as the entirely free ion is evidenced by the fact that the type of metal may markedly influence the degree of dissociation into free radicals.

The existence of the equilibrium between the free radical and the pinacol salts in the solid phase has been demonstrated by the temperature coefficient of the paramagnetism of the crystals.[18] From these measurements the heat of dissociation into free radicals in the solid phase was found to be of the order of 0.3 kcal. for the potassium ketyls of benzophenone, phenyl xenyl ketone, and fluorenone. The degree of dissociation of a large number of solid metal ketyls has been measured and, although the interpretation is complicated by the necessity of considering the crystal-lattice energy effects, they can be fairly well understood in the light of the principles already discussed.

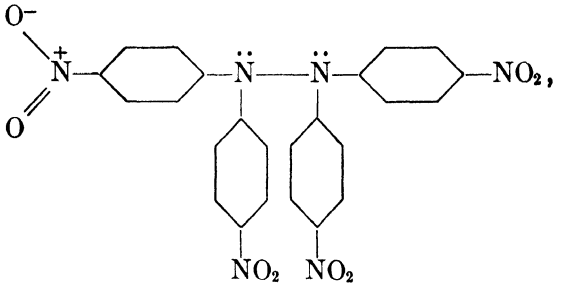
33b. Divalent nitrogen and tetravalent nitrogen. Exactly analogous to the triarylmethyl radicals are the diarylamino radicals discovered by Wieland in 1911. The tetraarylhydrazines correspond to the hexaarylethanes:

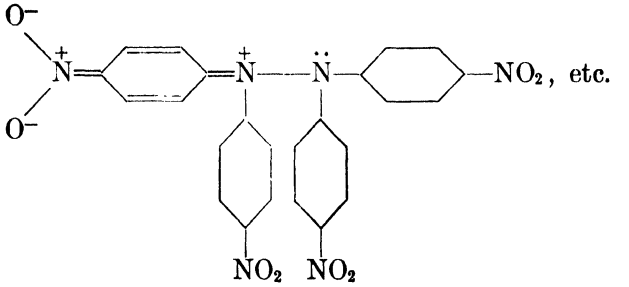


While tetraphenylhydrazine must have an elevated temperature (boiling toluene, 110°C.) to show the color of the free radical, tetra-*p*-anisylhydrazine gives a light green solution in benzene at room temperatures, and its color can be reversibly increased by warming. In contrast to the hexaphenylethanes, however, the action of the nitro group on the dissociation of the tetraphenylhydrazines is not in the same direction as that of the methoxyl or dimethylamino groups. Whereas tetra-*p*-dimethylaminophenylhydrazine is 10 per cent dissociated in dilute benzene solution at ordinary temperature, tetra-*p*-nitrophenylhydrazine seems to be even less dissociable than the unsubstituted tetraphenylhydrazine. This is readily understood when the resonance in the undissociated hydrazine as well as in the free radical is considered. In the undissociated

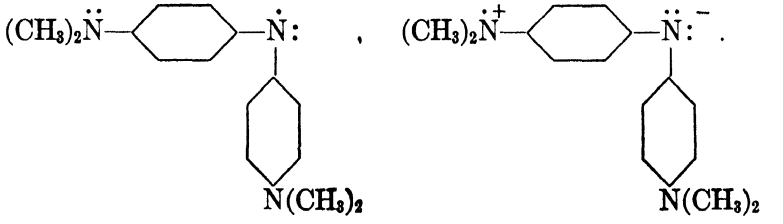
[18] Müller, E., and Janke, W., *Z. Elektrochem.*, **45**, 380 (1939).

hydrazine there is the stabilizing resonance of the electron pairs of the amino nitrogen with the nitro group:



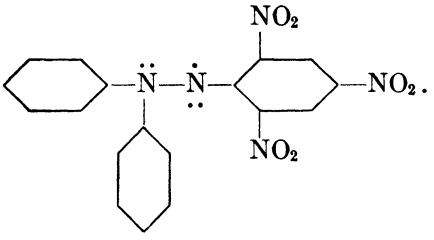


In the free radical this same resonance is possible and is mutually exclusive with the type of odd electron resonance which has been used to interpret the stability of tris-(*p*-nitrophenyl)methyl. The odd electron resonance is thus reduced in importance in aiding in the stability of the diphenylamino radical. On the other hand, a positive group containing an unshared electron pair, such as dimethylamino or methoxyl, will have a stabilizing effect on the free radical, since no resonance is possible between it and the hydrazine nitrogen in the undissociated molecule, while a very good odd electron resonance is possible in the free radical:

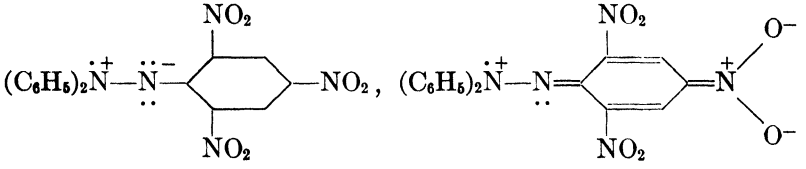


An interesting case in which a combination of these two effects (NO_2 and NH_2) produces an extremely stable free radical which does

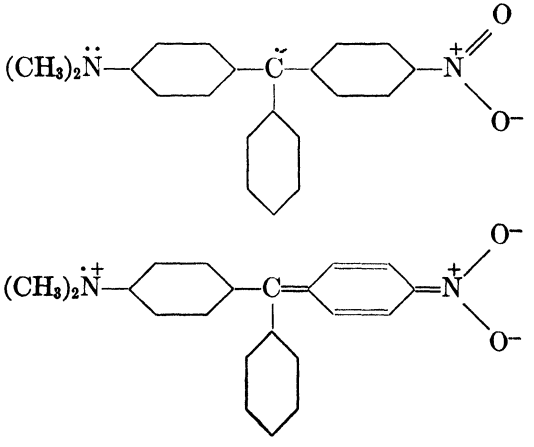
not associate even in the solid state is afforded by α,α-diphenyl-β-2,4,6-trinitrophenylhydrazyl:[19]



Here, although the nitro resonance with one electron pair of the hydrazine nitrogen is possible in the undissociated compound, it is possible with either of two electron pairs on the same nitrogen atom in the free radical after the odd electron interchange has taken place between the two hydrazine nitrogens:



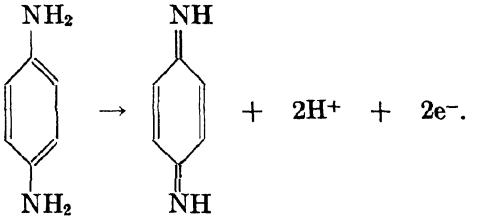
the odd electron resonance still remaining unblocked. It would be very interesting to try the effect of such a combination of groups on the triphenylmethyl radicals. For example, the conjugation between amino and nitro groups, which is impossible in the ethane, becomes possible in the free radical:



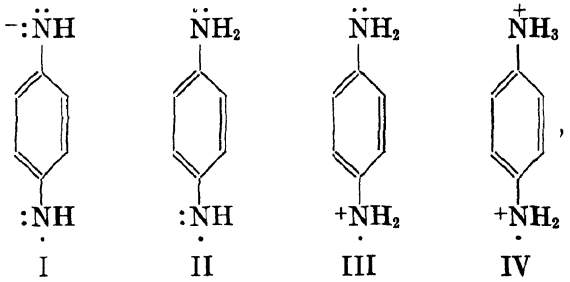
[19] Kuhn, R., *Naturwissenschaften*, **22**, 808 (1934).

Another group of free radicals which may be classed among the nitrogen free radicals are the semiquinones.[20] Although semiquinones have been observed in which atoms other than nitrogen (especially oxygen) carry the odd electron, the reasons involved are exactly analogous; and, since most of the interesting work has been done with nitrogen radicals, we will use them to illustrate the principles involved.

When a compound of the type of *p*-phenylenediamine (analogous to hydroquinone) is oxidized to quinonediimine, a two-electron change takes place:[21]



It is, however, possible under certain conditions to observe the existence of the intermediate compound from which only one electron has been removed. This observation was first made by means of an analysis of the shapes of the oxidation-reduction titration curves at various pH's, and the existence of the resulting odd molecule has since been demonstrated by magnetic measurements as well as absorption spectra. These odd molecules are free radicals and show the tendency to dimerize. The conditions under which the free radical may be expected to exist are precisely those for which an equivalent odd electron resonance may occur. For example, the semiquinone of a *p*-phenylenediamine may have any one of the four formulas, depending upon the acidity of the solution but only the ions I and III are capable of the completely equivalent



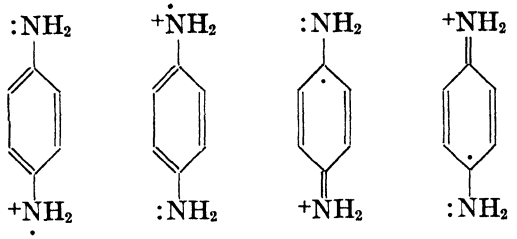
[20] Michaelis, L., *Chem. Rev.*, **16**, 243 (1935).
[21] Dilthey, W., *J. prakt. Chem.*, [2] **109**, 300 (1925).

RASPBERRY ESTER MIXTURE

Minor Components

Isopropyl alcohol
Rhodinol
Isogeraniol
Nerol
Farnesol
Cinnamyl alcohol
Methyl formate
Propyl formate
Isopropyl formate
Isobutyl formate
Hexyl formate
Decyl formate
Geranyl formate
Terpinyl formate
Benzyl formate
Rhodinyl acetate
Geranyl acetate
Neryl acetate
Guaiyl acetate
Dimethyl phenethyl carbinyl acetate
Isopropyl propionate
Isoamyl propionate
Citronellyl propionate
Benzyl propionate
Terpinyl butyrate
Isopropyl isobutyrate
Neryl isobutyrate
Terpinyl valerate
Ethyl succinate
Methyl cinnamate
Ethyl cinnamate
Isobutyl cinnamate
Ethyl salicylate
Isobutyl salicylate
Isoamyl salicylate
Benzyl salicylate
Geranyl anthranilate
Amyl heptyl acetaldehyde
Amyl methyl ketone
Methylacetophenone
Benzylacetone
Anisyl formate
Isoeugenol
Isoeugenyl methyl ether

odd-electron resonances of type *A* and of type *B* (for formula III), since only for these are both nitrogen atoms bonded to the same number of atoms:



A

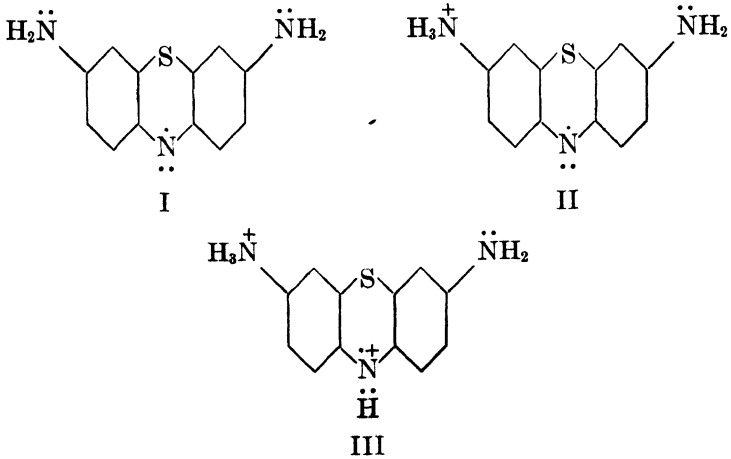
Odd electron on nitrogen (four forms)

B

Odd electron on carbon (six forms, four of them ortho quinoidal)

It is apparent that a number of minor contributing forms in which a separation of charge occurs are also possible. Accordingly it is in slightly acid solution (aqueous solutions pH 4.6; 80 per cent methanol solutions pH about 3) that the free radicals are best observed.[22] Similar considerations apply to formula I, but since this form requires extremely alkaline conditions in which the whole system is unstable, the negative ion of this free radical has not yet been obtained.

Thionine is an interesting case in which this line of reasoning was fully confirmed by experiment in an entirely different range of acidity.[23] The neutral semiquinone radical (I) of thionine

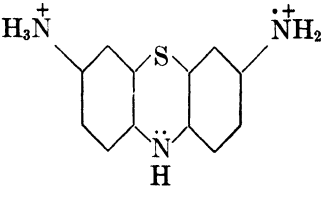


I II III

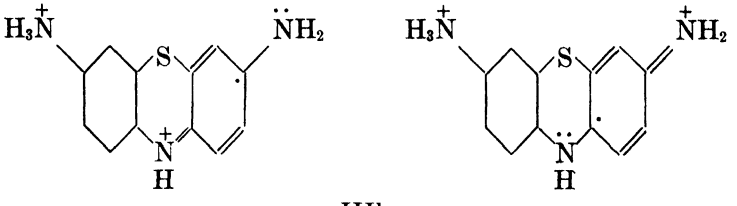
[22] Michaelis, L., Schubert, M. P., and Granick, S., *J. Am. Chem. Soc.*, **61**, 1981 (1939).

[23] Michaelis, L., Schubert, M. P., and Granick, S., *J. Am. Chem. Soc.*, **62**, 204 (1940).

has no equivalent odd electron resonance forms, but as the acidity of the solution is increased, the ions II and then III are formed. Ion II still has no equivalent resonance forms, but III has two nitrogen atoms each bonded to three other atoms, making possible the almost equivalent form IIIa as well as the pair IIIb and the four corresponding *o*-quinoidal forms.



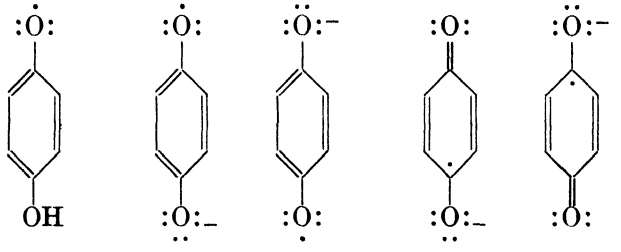
IIIa



IIIb

Thus in 25*N* sulfuric acid the semiquinone ion III is so stable that the oxidation-reduction titration curve shows a definite step at the 50 per cent point and the color of the semiquinone is quite clearly apparent throughout one half of the titration.

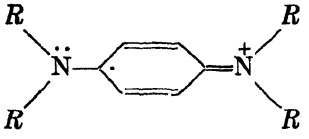
In a similar manner it may be deduced that the semiquinone of the oxygen compounds I (below) should exist to an appreciable extent only in alkaline solutions as the negative ion II.



I IIa IIb

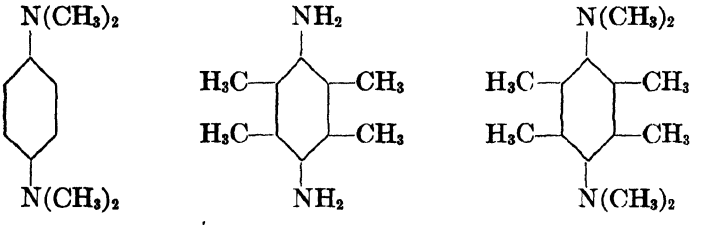
Another condition which must obtain in order that these semiquinone radicals have an appreciable stability appears from a consideration of the resonance forms of type *B* described for the *p*-phenylenediamine. When the double bond is formed between the nitrogen

atom and the ring, the other two valence bonds of the nitrogen must lie in the same plane as the ring (see section 18e on dipole moments in Chapter V):



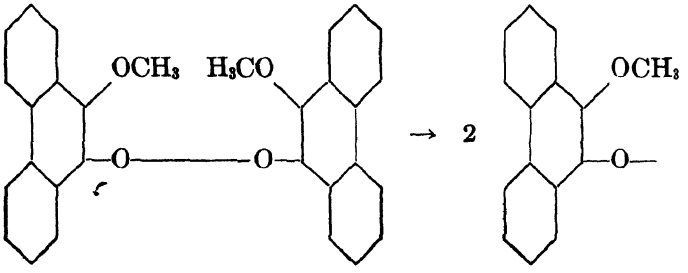
(six forms).

If the attainment of this condition is prevented by groups substituted in the positions ortho to the amino group, these forms would be eliminated, and if they are of great importance for the stability of the radical, that stability should at least be greatly reduced. Actually, when such sterically interfering groups are introduced, it is impossible to detect the radical at all. Thus,[24] of the three *p*-phenylenediamines I, II, III, (below) the first two form quite stable semiquinones, even more stable than the unsubstituted diamine, while III forms no free radical at all:



I II III

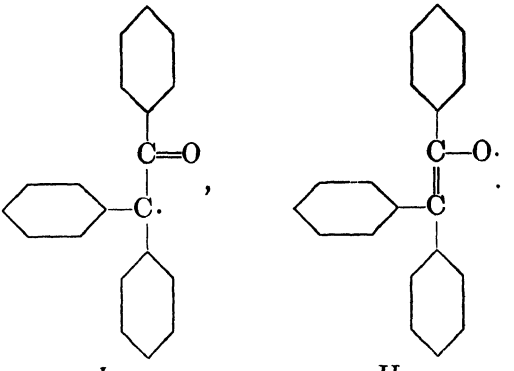
33c. Monovalent oxygen. An exactly analogous discussion applies to compounds of the type R—O—O—R which may dissociate into free radicals R—O—. Thus the 9,9′-dimethoxy-10,10′-phenanthryl peroxide[25] is about 37 per cent dissociated into free radicals in dilute solution,



[24] Michaelis, L., Schubert, M. P., and Granick, S., *J. Am. Chem. Soc.*, **61**, 1981 (1939).

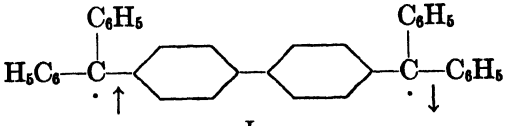
[25] Goldschmidt, S., and Schmidt, W., *Ber.*, **55**, 3197 (1922).

while the ethoxy compound is about 62 per cent dissociated under the same conditions. These radicals differ from the trivalent carbon radicals in that they do not react readily with O_2, I_2, or NO. They do, however, combine readily with other free radicals such as triphenylmethyl. It is of interest to recall in this connection the high degree of dissociation of the ethane that produces diphenylbenzoylmethyl,[26] and the fact that it does not react readily with bromine. This seems to indicate that, when it is possible for the odd electron to be on an oxygen atom, it prefers this position to a carbon atom, the forms I and II being in resonance, with II predominating:



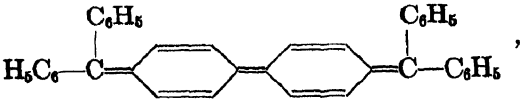
I II

33d. Diradicals. In all of the radicals so far discussed there is an odd number of electrons, and hence there must be at least one unpaired electron. Actually, the magnetic measurements have shown that there is only one unpaired electron. It is possible, however, under certain conditions to have molecules (exclusive of those containing paramagnetic metal atoms or ions) with an even number of electrons in which two of them are unpaired, thus making the molecule very reactive and presumably paramagnetic. Such molecules have been called diradicals. The simplest of these is of course the oxygen molecule. One of the first organic molecules which was believed to be a diradical[27] is the Tschitschibabin hydrocarbon (I):



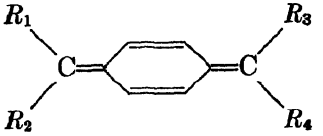
I

[26] Löwenbein, A., and Schuster, L., *Ann.*, **481**, 106 (1930).
[27] Tschitschibabin, A. E., *Ber.*, **40**, 1810 (1907).

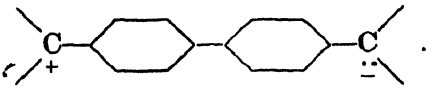


Ia

which is a violet-colored solid whose solutions absorb oxygen readily. If the two electrons were really independent of each other and could orient themselves separately in a magnetic field, the molecule would be paramagnetic. Also, if the two electrons were fixed in the molecule with parallel spins, the molecule would show paramagnetism when measured in mass. If, however, the electrons were not totally independent of each other but were required to have opposite spins in the molecule, as shown by the arrows in I, it would be diamagnetic. Finally, there might be no unpaired electrons in the ordinary sense and the structure could be written as a quinone derivative (Ia). Actually this substance is diamagnetic when measured by the ordinary methods.[28] Analogous considerations hold for hydrocarbons of the type

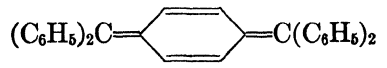


where R_1, R_2, R_3, and R_4 are aromatic groups, and they too have been found to be diamagnetic.[29] This leads to the conclusion that such molecules do not contain two entirely independent electrons and that these electrons are not fixed with their spins parallel as in oxygen. In order to understand the great reactivity of the Tschitschibabin hydrocarbon (I) without assuming the presence of an undetectably small amount of paramagnetic tautomer in equilibrium with the quinoidal form, it is necessary to assume that both forms I and Ia are resonance contributors to the ground state of the molecule. Furthermore, in form I the separated electrons may be on any of the ortho or para carbon atoms of the attached aromatic groups just as they are in triphenylmethyl. There may also be small contributions from the ionic states of the type



[28] Müller, E., and Müller-Rodloff, J., *Ann.*, **517**, 134 (1935).
[29] Müller, E., *Z. Elektrochem.*, **45**, 593 (1939).

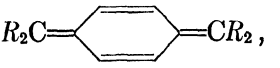
In all of these states the important condition must be satisfied that they all have the same multiplicity, i.e. that there be no change in the net spin moment of the molecule. Since the quinoidal (and the ionic forms) must have zero net spin, the other forms in which the electrons are separated must maintain this condition and the electrons must keep the antiparallel spin orientation. Thus, although the molecule be diamagnetic as a whole, the contributions from the separated-electron states (I) will give it a high reactivity and something of the character of the free radical, depending on the extent of these contributions. The fact that the hydrocarbon



absorbs oxygen only when its solutions are irradiated can be attributed to a smaller contribution of the separated-electron states to the ground state of this molecule as compared with the Tschitschibabin hydrocarbon. This enhanced contribution of the diradical states (with antiparallel spins) is due to the same principle which we have found operative in the absorption spectra of the polyphenyls (see Chapter V) and in the oxidation potentials of the diphenoquinone. In order that the two electrons of the diradical form



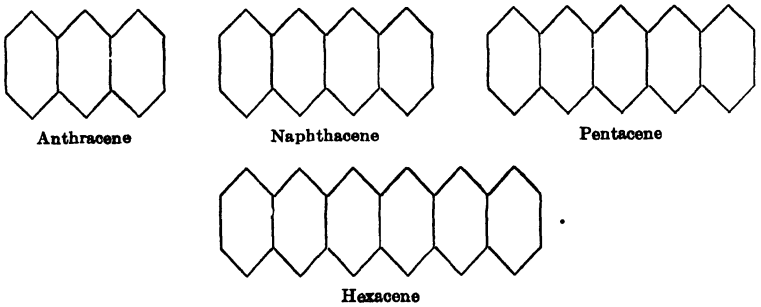
interact through the formation of a quinoidal form



a benzene resonance (Kekule form) must be destroyed. In the case of the Tschitschibabin hydrocarbon, however, two benzene resonances must be destroyed; hence the smaller contribution of the quinoidal forms in the latter case. It is to be expected that the next hydrocarbon of this series in which three benzene rings must become quinoidal for the coupling to occur will be even more reactive, and so on, until the state is reached in which the two electrons really do become independent, at which point the molecule will have mass paramagnetic susceptibility. If, however, a method is devised which could detect the paramagnetism of two widely separated unpaired electrons in the same molecule which as a whole would be diamagnetic, it should be possible to demonstrate the diradical character of the Tschitschibabin hydrocarbon by this means. Such a method is

indeed the conversion para-H_2 → ortho-H_2 in the inhomogeneous magnetic field of a paramagnetic molecule or ion.[30] Since the hydrogen molecule is so comparatively small, it can interact with only part of the large hydrocarbon molecule at a time. Thus even if the large molecule as a whole is diamagnetic, the presence of the two widely separated unpaired electrons could effect a conversion of parahydrogen. By this method the Tschitschibabin hydrocarbon has been found to be about 10 per cent diradical in a 0.016 molar solution in benzene at room temperature,[31] while the tetraphenylxylylidene is still diamagnetic even to this method of detection.

Exactly similar considerations hold for the linear condensed ring systems of anthracene, naphthacene, pentacene, and hexacene:[32]



Here again the reactivity increases as the number of rings increases. Thus, solutions of the violet-colored pentacene absorb oxygen when irradiated and solutions of the green hexacene are very sensitive to both air and light. Similarly their reactivity toward maleic anhydride increases in the same order and the condensation takes place as near the center of the chain as possible. But magnetic measurements have shown the pentacene to be diamagnetic, so that we have to apply here the same consideration of an increasing contribution of diradical forms (with antiparallel spins) as before. The reason for this increasing contribution, although the same in principle—i.e., certain resonances are prohibited by the coupling—is somewhat different in detail, being exactly analogous to the reasoning employed in the calculation of the oxidation potentials of the linear condensed-ring

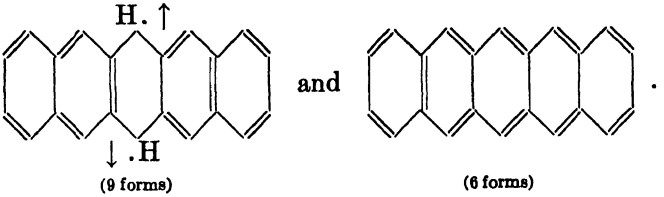
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[30] Farkas, A., *Orthohydrogen, Parahydrogen and Heavy Hydrogen.* Cambridge University Press, 1935.

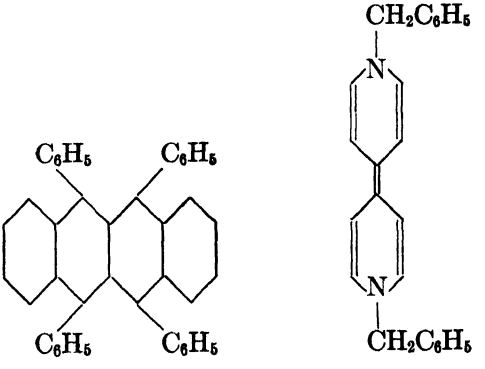
[31] Schwab, G.-M., and Agliardi, N., *Ber.*, **73**, 95 (1940).

[32] Clar, E., *Ber.*, **65**, 503 (1932); Clar, E., *Ber.*, **72**, 1817 (1939); Marschalk, C., *Bull. soc. chim. France*, **6**, 1112 (1939).

system quinones. Thus, in pentacene the two principally different resonance forms are:

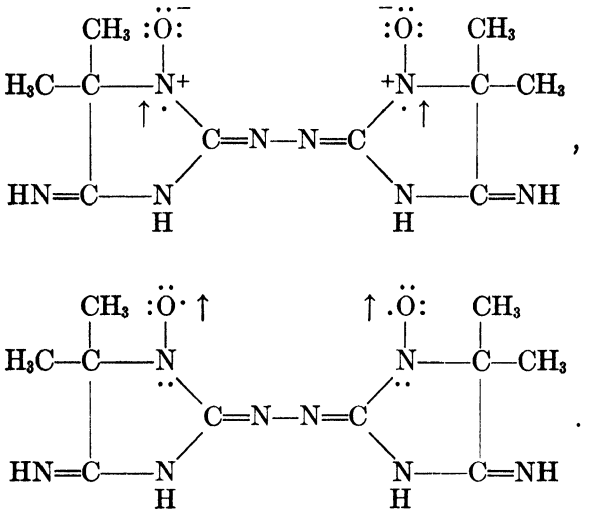


A number of other positions are possible for the separated electrons, but each of these other arrangements has fewer forms associated with it than the one shown. Thus, in the diradical form, each of the two naphthalene parts is free to take any of its three forms while, when the coupling is required, the two ends of the molecule are restricted in the number of possible configurations. A number of other molecules belonging to this class of diamagnetic reactive compounds have been found; e.g., rubrene (*A*), which forms a reversibly dissociable peroxide, and dibenzyl-γ,γ'-dipyridyl (*B*).



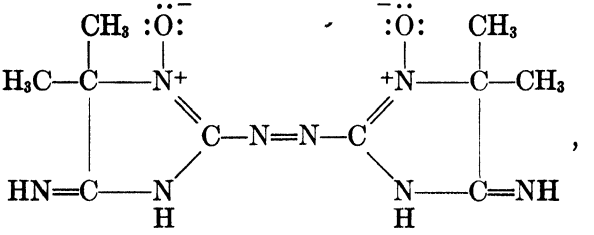
In general, then, if the attempt is made to prepare a molecule containing two unpaired electrons, and that molecule is such that these two electrons may interact with each other through the molecule merely by the shifting of double bonds, that interaction will take place and the molecule will be diamagnetic, although it may show great reactivity for the reason just outlined. It has been possible, however, to prepare a molecule which satisfies the above conditions but which shows paramagnetism in a manner very similar to that of oxygen; i.e., there are two possible distinct electronic states, one of them paramagnetic and one of them diamagnetic. They are not in

resonance with one another because of their difference in spin moment; but they are in equilibrium with each other, the position of the equilibrium depending upon the temperature because of a difference in energy of the two states. The molecule is that of porphyrindin, which may be written in the diradical form with the odd electrons on either nitrogen or oxygen in resonance:



Porphyrindin (diradical forms)

This diradical is in equilibrium with a monomeric, diamagnetic substance,

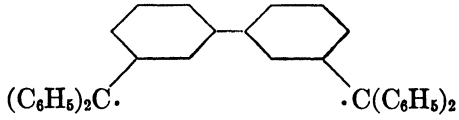


Porphyrindin (diamagnetic)

whose concentration increases as the temperature is lowered. This is a case of electronic isomerism (electromers).[29]

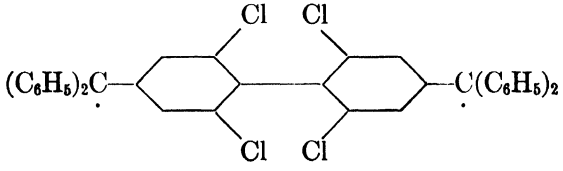
On the other hand, if the molecule containing the two unpaired electrons is such that these electrons cannot interact by simply a

shift in the double bonds, it will indeed be a paramagnetic diradical in its ground state. Such a molecule is the Schlenk hydrocarbon:[33]



which, because the two odd electrons are meta to each other, must remain in the paramagnetic condition. The diradicals will, of course, polymerize, and it has been found that an 8 per cent benzene solution of the hydrocarbon is from 6 to 8 per cent dissociated at 75°C.

Another way in which the quinoidal form may be prevented in the para compound of Tschitschibabin is the insertion of substituents in such a manner as to prevent the coplanar arrangement of the rings which is necessary in the quinoidal form. This has been done by Müller and Neuhoff,[34] who prepared the compound



and found it to be paramagnetic. The degree of dissociation in a 2.3 per cent benzene solution is given as 17 per cent at 18°C. and 28 per cent at 80°C.

34. *CIS-TRANS* ISOMERISM OF OLEFINS

The configuration of a large number of ethylenic isomers has been more or less unequivocally determined by the use of various physical methods (melting point, boiling point, acid strength, dipole moment, X-ray or electron diffraction, light absorption and Raman spectra) as well as by chemical methods (ring closures and chemical reactivity). Furthermore, in most cases it is possible to say which of the two isomers is the stable one under ordinary conditions. However, the degree of that stability, i.e. the value of ΔH or ΔF for the reaction *cis* $\rightleftarrows$ *trans*, has not been widely determined. Most of the data has been obtained from measurements of the heats of combustion of the solid compounds, and this includes the lattice energy of the crystals.

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[33] Schlenk, W., and Brauns, W., *Ber.*, **48**, 723 (1915).
[34] Müller, E., and Neuhoff, H., *Ber.*, **72**, 2063 (1939).

TABLE 41

ΔH FOR THE REACTION *cis* → *trans**

cis Compound	M. P. °C.	Heat of Combustion, kcals.	*trans* Compound	M. P. °C.	Heat of Combustion, kcals.	ΔH
Maleic acid	130	327.1	Fumaric acid	ca. 300	320.2	−6.9
Dimethyl maleate	−19	667.2	Dimethyl fumarate	101	664.1	−3.1[f]
Citraconic acid	91	478.8	Mesaconic acid	202	475.9	−2.9
Angelic acid	45	635.1	Tiglic acid	64.5	626.6	−8.5
Oleic acid	16	2682.0	Elaidic acid	51	2664.3	−17.7
Cinnamic acid	68	1048	Cinnamic acid	133	1041	−7.0
Crotonic acid	15.5	486	Crotonic acid	72	478	−8.0
p-Hydroxycinnamic acid	127	997.2	*p*-Hydroxycinnamic acid	206	992.1	−5.1
Stilbene	liquid	1769.2	Stilbene	125	1759	−10.2[f, g]
Stilbene	liquid		Stilbene	125		−3.0[a]
Butene-2	−139.3		Butene-2	−105.8		−0.95[b]
Dichloroethylene b.p.	60.2		Dichloroethylene b.p	48.0		+0.5[e]
Dibromoethylene b.p.	94.9		Dibromoethylene b.p.	85.6		+0.3[c]
Azobenzene m.p.	71.6	1555.5	Azobenzene m.p.	68.1	1545.6	−9.9[d]
Azobenzene m.p.	71.6		Azobenzene m.p.	68.1		−12.0[e]

* Taken from the compilation of A. Wassermann in Freudenberg's *Stereochemie* (F. Deuticke, Leipzig u. Wien, 1932), pp. 737, 769, unless otherwise specified.

[a] From equilibrium measurements in gas phase. Kistiakowsky, G. B., and Smith, W. R., *J. Am. Chem. Soc.*, **56**, 638 (1934).

[b] From equilibrium measurements in gas phase, Kistiakowsky, G. B., and Smith, W. R., *J. Am. Chem. Soc.*, **58**, 766 (1936).

[c] Olson, A. R., and Maroney, W., *J. Am. Chem. Soc.*, **56**, 1320 (1934). Equilibrium measurements in gas phase.

[d] Corruccini, R. J., and Gilbert, E. C., *J. Am. Chem Soc*, **61**, 2925 (1939).

[e] Hartley, G. S., *J. Chem. Soc.*, 633 (1938).

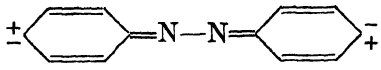
[f] These values do not represent a true comparison since the heat of combustion of the *cis* compound is that for a liquid while for the *trans* it is that of a solid.

[g] If the heat of fusion of *trans*-stilbene (7.5 kcals./mole) is added to the heat of combustion, the ΔH (*cis* → *trans*) for the liquid state becomes −2.7 kcals./mole.

The entropy difference between *cis* and *trans* compounds may be expected to be small and, where it has been measured (butene), it has been found to be about 1–2 cals./mole deg. Therefore the value of ΔH will be the quantity primarily concerned in determining the position of the equilibrium. From the data of Table 41 and from a large number of qualitative observations, it may be said more or less unequivocally that in the solid state the *trans* isomer is practically always the more stable one, and that the difference in energy between the two solid forms is of the order of 5 to 10 kcals./mole. This difference includes of course the differences in the intermolecular forces and lattice energies. In general, it seems that in the vapor phase the difference in energy will be somewhat smaller, but the direction of the difference remains the same, except in a few special cases.

This instability of the *cis* compound can be understood in terms of two main types of forces; the purely steric repulsion of the large groups when they find themselves both on the same side of a more or less rigid double bond and the dipolar electrostatic interaction, when polar groups are present, which always tends to make the compound with the smaller dipole moment (*trans*) the more stable. These effects and the exceptions are well-illustrated by the two cases in which the absolute configuration of a pair of *cis-trans* isomers has been determined by x-ray or electron diffraction measurements.

The crystal structure and molecular configuration of *cis*- and *trans*-azobenzene has been satisfactorily determined by Robertson[35] with the result shown in Figure 45. The *trans*-azobenzene molecule in the crystal is entirely in one plane and has the normal dimensions as shown in Figure 45A. This coplanar configuration is to be expected if the states represented by



and the intermediate electron configurations are to be important contributors to the resonance in the molecule. If now an attempt is made to obtain the coplanar *cis* molecule by simply rotating one half of the molecule 180° with respect to the other half around the double bond, as in Figure 45B, it is found that the distance between ortho carbon atoms in the phenyl groups is only 1.3 Å. This is even less than the normally bonded carbon-carbon distance of 1.54 Å

[35] Robertson, J. M., *J. Chem. Soc.*, 232 (1939).

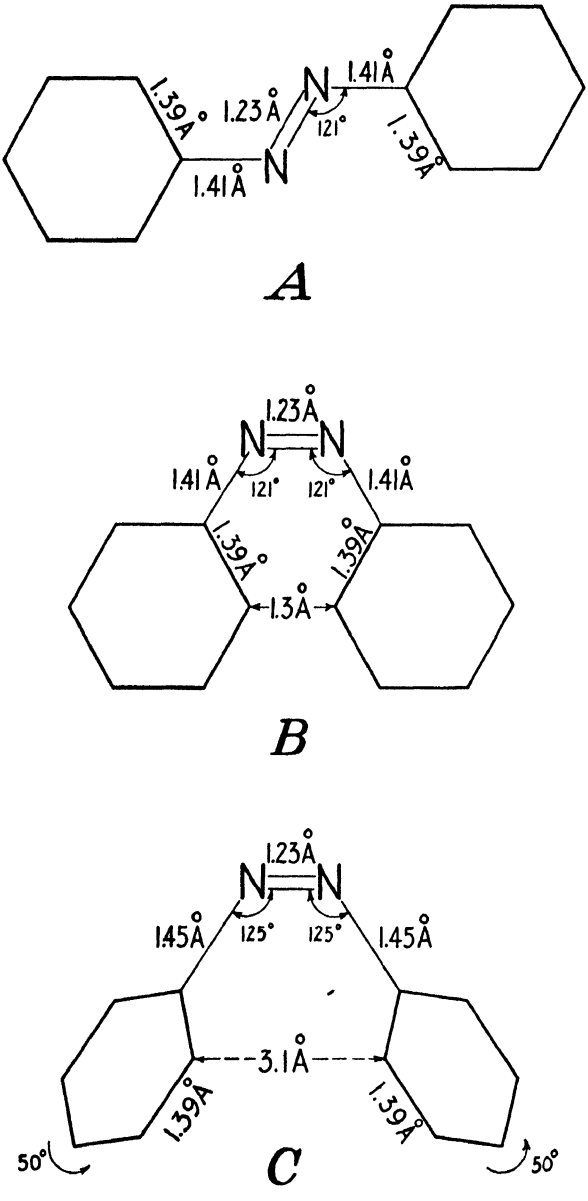


Figure 45. The structure of *cis* and *trans* azobenzene. *A*, *trans* (experimental); *B*, *cis* (hypothetical); *C*, *cis* (experimental).

and very much too small to accommodate two C—H bonds, which would require something greater than $2 \times 1.07 = 2.14$ Å. Actually

the *cis*-azobenzene molecule is found to have a configuration shown in Figure 45C in which the phenyl groups are rotated around the C—N axis and out of the C—N=N—C plane by an angle of about 50°. In this configuration the distance between ortho carbon atoms is 3.1 Å which is ample to accommodate the hydrogen atoms, especially since they are not on the line joining the two ortho carbon atoms. But this rotation is not accomplished without the expenditure of some energy, since the non-coplanar configuration must reduce the resonance energy contribution of the above-mentioned ionic forms. Thus the *cis* form must be unstable with respect to the *trans* form. In a similar manner a construction of the butene-2 molecule using the ordinary distances and angles assigned to carbon-carbon bonds brings the two methyl carbon atoms to a distance of about 2.9 Å in the *cis* compound. The distance of closest approach of CH_3 groups in crystals of such a molecule as hexamethylbenzene is about 4.0 Å. This distance (4.0 Å) can thus be taken as the distance of separation of the carbon atoms of a pair of methyl groups when they are lying at the van der Waals' minimum, and are experiencing a maximum of attraction for each other. Any attempt to move them closer would encounter repulsion. Thus the distance of 2.9 Å calculated for *cis*-butene-2 is too small, and *cis*-butene-2 would be unstable with respect to the *trans* compound.

On the other hand, the electron diffraction studies of the dichloroethylenes give the Cl—Cl distance in the *cis* compound as 3.6 Å and in the *trans* compound as 4.6 Å. This distance of 3.6 Å in the *cis* compound is just the van der Waal's distance of closest approach for bound chlorine atoms obtained from various sources. In this case, therefore, and also in the case of the bromoethylenes, the energy resulting from the attraction of the halogen atoms at the best distance of separation is sufficient to make the *cis* compounds slightly more stable than the *trans* compound.

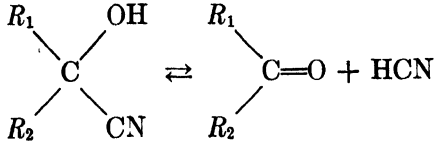
35. EQUILIBRIUM IN THE ADDITION TO THE DOUBLE BOND

We have already examined the equilibrium between the carbon-carbon double bond and molecular hydrogen as expressed in terms of the heat of hydrogenation. As an example of an equilibrium in the simple addition to a double bond, in which the equilibrium concentrations are directly measurable, we may take the addition to the C=O bond of a simple addend like HCN to form a cyanohydrin,

This is the reaction for which the most extensive data are available. Lapworth[36] and his co-workers determined the equilibrium constant

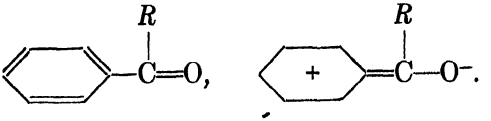
$$K = \frac{[\mathrm{HCN}][R_1R_2\mathrm{C{=}O}]}{[R_1R_2\mathrm{C(OH)CN}]}$$

for the reaction



at 20°C. in 96 per cent ethyl alcohol (4 per cent H_2O) for a large number of ketones and aldehydes. A careful examination of their results is very illuminating, since it conforms to the principles we have already outlined and also illustrates how complexities may enter into even what is apparently a very simple and straightforward case. In Table 42 are reproduced a pair of sequences showing the effect of the phenyl group and of successive substitution of carbon for hydrogen on the carbon atom attached to the carbonyl group.

The most striking effect is that of the phenyl group in stabilizing the carbonyl compound. This is undoubtedly due to the resonance possible in the carbonyl compound.



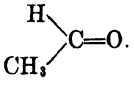
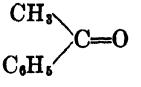
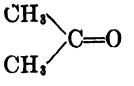
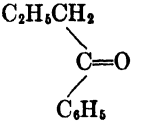
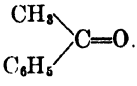
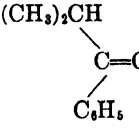
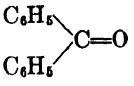
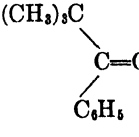
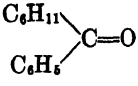
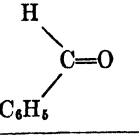
This possibility is removed in the cyanohydrin. When two phenyls are attached to the C=O group (benzophenone), no cyanohydrin formation could be detected. This is not simply a steric effect, i.e. a masking of the C=O group by the large phenyl groups, since the phenyl cyclohexyl ketone shows an even greater tendency to cyanohydrin formation than does acetophenone. This increase of the cyanohydrin stability produced by the substitution of cyclohexyl for methyl is the effect of increasing the number of carbon atoms

[36] Lapworth, A., and Manske, R. H. F., *J. Chem. Soc.*, 2533 (1928); Lapworth, A., and Manske, R. H. F., *J. Chem. Soc.*, 1976 (1930).

attached to the carbon atom directly bonded to the C=O group. This effect is clearly shown in the right-hand half of Table 42, where the successive introduction as R_1 of CH_3, n-C_3H_7, iso-C_3H_7, *tert*-C_4H_9, increases the stability of the cyanohydrin.

TABLE 42

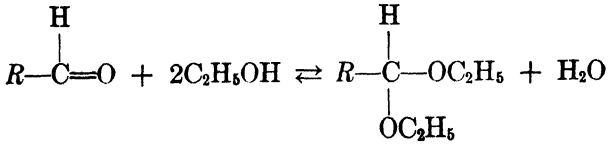
THE DISSOCIATION CONSTANT, $K = \frac{[HCN][R_1R_2C{=}O]}{[R_1R_2C(OH)CN]}$, OF SOME CYANOHYDRINS IN 96 PER CENT AQUEOUS ALCOHOL AT 20°C.

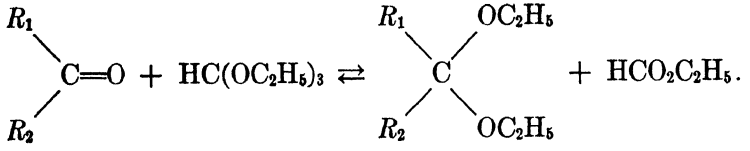
Carbonyl Compound	$K \times 10^2$	Carbonyl Compound	$K \times 10^2$
	0.28[a]		130
	3.05		90
	130		25
	∞ (no appreciable formation of cyanohydrin)		9
	40		0.47

[a] This value is estimated from the relative constants of acetaldehyde and acetone in aqueous solution reported by Jones, W. T., *J. Chem. Soc.*, 1560 (1914): $K_{\text{acetone}} \cong 11K_{\text{acetaldehyde}}$.

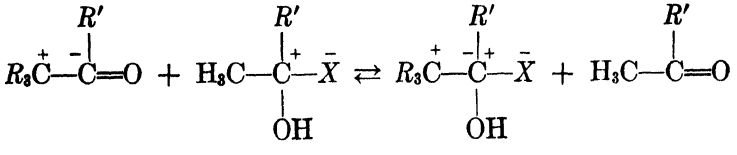
This order of primary, secondary and tertiary carbon atom effects is an interesting reversal of what is usually observed. In considering the heats of hydrogenation of unsaturated hydrocarbons it was found that the substitution of carbon for hydrogen attached to an unsaturated carbon atom acted so as to increase, apparently, the stability of the compound containing the double bond. An exactly similar

order of effects is found in the equilibria for the formation of acetals from aldehydes or ketones:[37]





In the case of the reaction of aldehyde with ethanol, the per cent conversion into acetal in a mixture of five moles of alcohol with one mole of aldehyde is, for acetaldehyde, 78 per cent; for dimethylacetaldehyde, 71 per cent; and for trimethylacetaldehyde 56 per cent. Similarly, when the ketone is allowed to react with ethyl orthoformate to form the ketal, the order of decreasing amount of ketal formed is dimethyl ketone, methylethyl ketone, diisopropyl ketone, methyl *tert*-butyl ketone, ethyl *tert*-butyl ketone, *tert*-butyl isopropyl ketone and di-*tert*-butyl ketone. Thus one is led to expect that the tertiary carbon atom will stabilize the compound containing the double bond (the C=O in this case) more than it will the compound containing no double bond. There appears to be some sort of conjugation between the tertiary carbon atom and the double bond, as has been pointed out in section 30a. The explanation of the reversal of this effect in the case of the addition of HCN is to be found in the high polarity of the CN group. The substitution of alkyl for hydrogen may act in two ways on the equilibrium of carbonyl compounds with their addition products. The first way is the one we have already mentioned in which the carbonyl compound is stabilized with respect to its addition products, i.e. the equilibrium



[37] Adkins, H., *Gilman's Organic Chemistry*, vol. 1, p. 823. John Wiley & Sons, New York, 1938.

is shifted toward the left because of the conjugation effect of the R_3C group with the double bond. On the other hand, the dipolar interaction of $R_3\overset{+}{C}—\overset{-}{C}$ and $\overset{+}{C}—\overset{-}{X}$ would tend to shift the equilibrium toward the right. This second effect becomes important only when X is a highly polar group, so that, when X is OR as in the acetal formation, the first effect predominates, whereas when X is CN the second effect becomes important.

When the tendency to cyanohydrin formation becomes very great, i.e. when K becomes very small, complexities arise which may often be very confusing. For example, the dissociation constant of

TABLE 43

THE DISSOCIATION CONSTANTS FOR SOME SUBSTITUTED BENZALDEHYDE CYANOHYDRINS AT 20°C. IN 96 PER CENT C_2H_5OH (4 PER CENT H_2O)

$XC_6H_4CH(OH)CN \rightleftarrows XC_6H_4CHO + HCN$

X	$K \times 10^2$
H	0.47
p-NO_2	1.81
m-NO_2	0.27
p-Cl	0.49
m-Cl	0.25
p-CH_3O	3.12
m-CH_3O	0.43
p-OH	7.66
m-OH	0.48
p-CH_3	1.03
m-CH_3	0.60
p-$(CH_3)_2N$	39.0

benzaldehyde cyanohydrin is already very small ($K = 0.47 \times 10^{-2}$), and Lapworth and Manske had already noticed that the effects of p-NO_2 and p-$(CH_3)_2N$ on this constant were both in the same direction, whereas in practically all other comparable cases these two groups have antipodal effects. This discrepancy appeared with other substituents but to a lesser degree. In Table 43 are reproduced some of the results on substituted benzaldehydes obtained by Lapworth and Manske. We have given only m and p substitutions, since we have already seen that o substitutions may have all sorts of vagaries depending on the particular group and reaction concerned.

In order to evaluate the quantitative effects of these groups, we can make use of the linear relations discussed in Chapter VI where

it was shown that the effect of a substituent on the acid strength of a particular type of acid could be expressed by

$$\log K_\sigma = \log K_u + \sigma\rho,$$

where σ is a constant characteristic of the group and ρ is a constant characteristic of the type of acid. Later on in Chapter IX we shall see how this relationship has been generalized to include the effects of structural changes on rates of reactions as well as on equilibria.

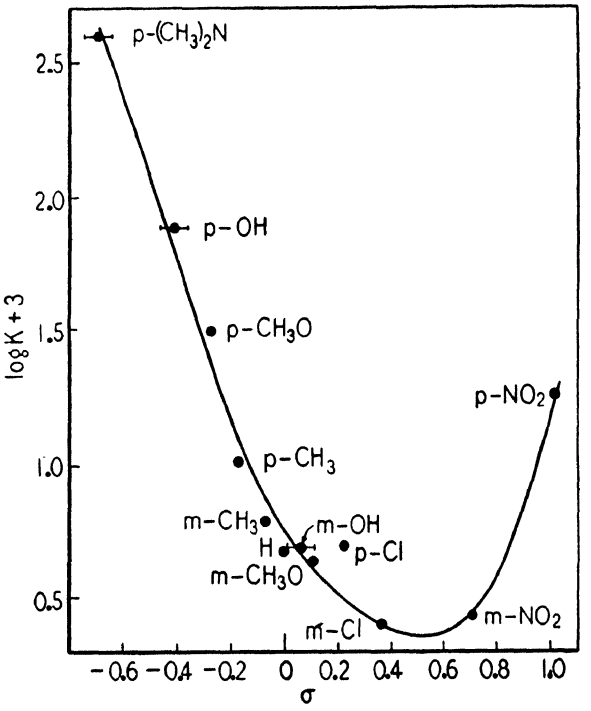


Figure 46. The effects of substitution on the dissociation of cyanohydrins.

The value of ρ for this particular reaction is as yet not known, but we have values for σ determined from the effects of groups on acid strengths or, better yet, values given in Chapter IX, which are averages from many types of equilibria and rates. Using the values given in Table 46, Chapter IX, $\log K_\sigma$ for the dissociation of the substituted benzaldehyde cyanohydrins is plotted as ordinate against the corresponding σ value as abscissa in Figure 46. The general shape of the curve is quite definite. It possesses a minimum and seems to pass into a straight line, at least on the left of the minimum.

The slopes of the ends and the position of the minimum are, however, very uncertain. It should be noted that most of these measurements are in the very region where the determination of K is least certain. When K is less than 10^{-2}, equimolecular mixtures of carbonyl compound and HCN react more than 90 per cent to form the cyanohydrin.

It is possible, at least, to understand this result without the introduction of any new principles if the conditions of the experiment are examined a bit more closely. The experiment was done by mixing alcoholic solutions containing measured quantities of aldehyde and HCN and allowing them to come to equilibrium, at which time an analysis was made for the free (uncombined) HCN. The equilibrium constant was then calculated by taking the proper differences, assuming that for each mole of HCN which had combined, 1 mole of aldehyde had reacted, the concentration of the remaining aldehyde being used as the concentration of free aldehyde, $[XC_6H_4CHO]$, in the equation

$$K = \frac{[\mathrm{HCN}][XC_6H_4CHO]}{[XC_6H_4CH(OH)CN]}.$$

Now it has been demonstrated, on the basis of refractive index and density measurements, that it is very probable that acetaldehyde in alcohol solution exists entirely as the semiacetal. The results on benzaldehyde[38] and anisaldehyde are not so readily interpreted, but semiacetal formation is indicated. This is to be expected, since the same factors which influence the stability of the cyanohydrin are operative in determining the stability of the semiacetal, and the stabilities of acetaldehyde cyanohydrin and benzaldehyde cyanohydrin are not very different. So, when the tendency to form cyanohydrin becomes very great, it will be necessary to consider also the possibility of semiacetal formation, especially since in these experiments the alcohol is present in much greater concentration than is the HCN. Thus the system may be described in terms of any two of the following three related equilibria:

(1)
$$X\text{—}C_6H_4\text{—}\underset{\displaystyle CN}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\text{—OH} \overset{K_1}{\rightleftarrows} X\text{—}C_6H_4\text{—}\overset{\displaystyle H}{\overset{|}{C}}\!=\!O + \mathrm{HCN};$$

$$K_1 = \frac{[\mathrm{HCN}][XC_6H_4CHO]}{[XC_6H_4CH(OH)CN]}.$$

[38] Adkins, H., and Broderick, A. E., *J. Am. Chem. Soc.*, **50**, 499 (1928).

$$X\text{—}C_6H_4\text{—}\underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{C}}\text{—}OH + C_2H_5OH \overset{K_2}{\rightleftarrows} X\text{—}C_6H_4\text{—}\underset{\underset{OC_2H_5}{|}}{\overset{\overset{H}{|}}{C}}\text{—}OH + HCN; \tag{2}$$

$$K_2' = \frac{[HCN][XC_6H_4CH(OH)OC_2H_5]}{[XC_6H_4CH(OH)CN][C_2H_5OH]}.$$

Or, since the concentration of the alcohol is practically constant, being present in an overwhelming excess over the other constituents,

$$K_2 = \frac{[HCN][XC_6H_4CH(OH)OC_2H_5]}{[XC_6H_4CH(OH)CN]}.$$

$$X\text{—}C_6H_4\text{—}\underset{\underset{OC_2H_5}{|}}{\overset{\overset{H}{|}}{C}}\text{—}OH \overset{K_3}{\rightleftarrows} X\text{—}C_6H_4\overset{\overset{H}{|}}{C}{=}O + C_2H_5OH; \tag{3}$$

$$K_3 = \frac{[XC_6H_4CHO]}{[XC_6H_4CH(OH)OC_2H_5]}.$$

The constant actually measured is

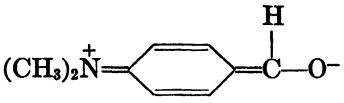
$$K = \frac{[HCN][XC_6H_4CHO + XC_6H_4CH(OH)OC_2H_5]}{[XC_6H_4CH(OH)CN]}$$

which can be expressed in terms of the existing equilibria as

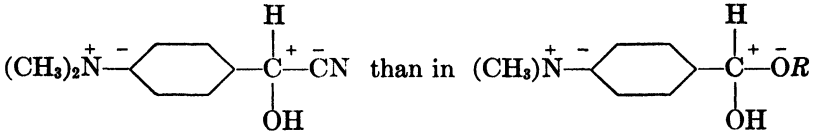
$$K = K_1 + K_2 \left(\text{and } K_2 = \frac{K_1}{K_3}\right).$$

The only conditions which need be satisfied in order that a curve such as that shown in Figure 46, containing a minimum, be obtained are (1) that K_1 and K_2 be somewhat of the same order of magnitude and (2) that the effect of a substituent on K_2 be the opposite of its effect on K_1. The first condition can be expected to be fulfilled even though K_2' might be very small; i.e., even though the cyanohydrin is certainly more stable than the semiacetal, the large constant value of the alcohol concentration which is incorporated into K_2 will bring its value up to the same order of magnitude as K_1. The second condition is not so readily apparent just from a consideration of the molecules involved, but let us examine more closely the two extreme substitutions NO_2 and $N(CH_3)_2$. The $N(CH_3)_2$ will increase K_1;

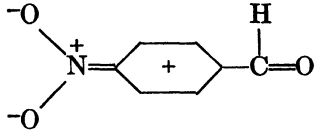
i.e., it will stabilize the aldehyde, mainly because of a large resonance interaction through the phenyl group, with the form



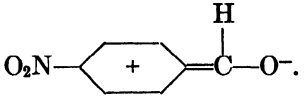
an important contributor. On the other hand, K_2 would be reduced, since the purely polar interactions will be greater in



because of the greater polarity of CN. The NO_2 group will decrease K_1 ; i.e., it will make the aldehyde less stable, since its resonance with the benzene ring is in competition with that of the carbonyl group. Thus the form



will reduce the contribution of the form



The polar interactions, on the other hand, are in the direction to increase K_2, since in this case the NO_2 dipole is in the opposite direction from both CN and O*R* dipoles and the CN dipole is much the larger.

We thus have the conditions necessary for the appearance of the minimum in Figure 46 fulfilled, but the position of that minimum as well as the slopes of the curve on either side of it depend on a knowledge of ρ_1 and ρ_2 for the two equilibria K_1 and K_2, and these are not known.

Chapter VIII

THE RATE FACTOR IN CHEMICAL BEHAVIOR

A compound cannot be prepared, under equilibrium conditions, in good yield by a reaction whose equilibrium does not favor the required substance; but even if the equilibrium is favorable, the reaction may be too slow to be of any practical use. Further, in any mixture of organic substances a countless number of reactions are conceivable. If complete equilibrium were reached there would be no appreciable concentration of any single compound, with the exception of a few especially stable substances. However, as most of the conceivable reactions are very slow, we do get appreciable and sometimes almost theoretical yields of the products of the fastest reactions, even though these products may not be the most stable thermodynamically. The successful preparation of a substance depends not only on the free energy changes involved in the reaction, but also on its rate. The relationship between the chemistry and the structure of a compound is, therefore, the result of thermodynamic and kinetic factors.

To understand the kinetic factors it is necessary to consider the laws of reaction velocities. Unlike the free energy, the rate of a reaction depends on its path. Consequently an understanding of the relationship between reaction rate and structure requires a knowledge of the mechanism of the reaction. The change of rate with change of structure depends on the path, and one should make comparisons not only between analogous stoichiometric reactions but also between corresponding paths for the reactions. For instance, the reaction $R\text{Cl} + \text{OH}^- \rightarrow R\text{OH} + \text{Cl}^-$ may proceed by two paths, one dependent and the other independent of the hydroxide ion concentration. The former is faster for ethyl chloride than for isopropyl chloride, but the latter is faster for isopropyl chloride than for ethyl chloride. The relative rates of the overall reactions are therefore not very significant.

The mechanism of a reaction is deduced from the way the rate changes with experimental conditions. In general, the assumed mechanism is not a unique explanation of the facts. We are, therefore, never quite certain of the mechanism of a reaction. This in-

creases the difficulty in relating reaction rate and molecular structure. It is therefore not surprising that, although many important generalizations connecting rate and structure have been made, they are qualitative in nature, and exceptions to them are not rare.

36. THE VARIATION OF RATE WITH CONCENTRATION

The rate of a reaction depends on the concentrations of the reactants. In reactions far from equilibrium, it is often found that the rate of increase of the concentration of a product, or the rate of decrease of the concentration of a reactant, is closely proportional to the product of some integral powers of the concentrations of all or some of the reactants. This product of concentrations can include that of a catalyst.

This rate law can be expressed as

$$\frac{dx}{dt} = k[A]^a[B]^b \cdots \tag{1}$$

where x is the concentration of a product of the reaction. The proportionality constant is called the velocity or rate constant. The product $[A]^a[B]^b \cdots$ is the rate function, and the sum of the indices is the order of this function. The apparent order of the rate law can be decreased by the use of a large excess of a reactant so that its concentration is constant during the course of a reaction and can be included in the velocity constant. Thus the rate law for the reaction of an acid chloride and alcohol is second-order, but by using alcohol as the solvent it can be made first-order. The rate function is then pseudo-first-order, and the reaction pseudo-unimolecular.

The first- and second-order rate laws can be expressed as

$$\frac{dx}{dt} = k(a - x), \qquad \frac{dx}{dt} = k(a - x)(b - x), \tag{2}$$

in which a and b are initial concentrations of reactants and x is the concentration of a product at any time. These concentrations are expressed in equivalents as given by the equation for the reaction. Then $(a - x)$ is the concentration of a reactant at any time. If concentrations are expressed in moles per unit volume, $(a - nx)$ must be substituted for $(a - x)$, n being the number of moles of reactant used up per mole of product formed. When equivalent quantities of reactants are used, $(a - x)$ equals $(b - x)$ and the second-order law becomes

$$\frac{dx}{dt} = k(a - x)^2.$$

This is also true when the reaction depends on the square of the concentration of one reactant.

By integrating the first- and second-order rate equations, we obtain:

$$k = \frac{1}{t} \ln \frac{a}{a - x} \quad \text{and} \quad k = \frac{1}{t(a - b)} \ln \frac{(a - x)b}{(b - x)a}. \tag{3}$$

When $a = b$, the second-order equation becomes

$$k = \frac{1}{t} \frac{x}{(a - x)a}.$$

The constancy of k when experimental values are put into an integrated rate equation can be the criterion of the order of a rate function.

The order of a rate law is not necessarily given by the number of molecules of reactants taking part in the stoichiometric reaction. In fact, the rate function need not have a definite order, and even though the reverse reaction is negligible, concentrations of products can appear in the function. Their appearance is due to the possibility of a reaction being not a single event but the result of a succession or combination of reactions. It is generally assumed that, for any single step, the rate function has an order corresponding to the molecularity, i.e. the number of molecules taking part in the simple step. The first-order function for a step indicates a unimolecular reaction, the second-order a bimolecular reaction, and so on.

For a combination or succession of simple reactions the rate function can be derived from those of the simple processes. The result may be a rate function corresponding to some definite molecularity. A simple rate function therefore does not necessarily mean a simple reaction. The steps in a reaction are not normally more than bimolecular, as the chances are against a simultaneous collision of more than two molecules.

36a. Reversible reactions. When a reversible reaction approaches equilibrium, the net rate is lowered by the reverse reaction. The rate is given by the equation

$$\frac{dx}{dt} = k_1 v_1 - k_2 v_2 \tag{4}$$

where v_1 and v_2 are the rate functions and k_1 and k_2 are the constants of the forward and backward reactions, respectively. At equilibrium the two reactions are equal and $\frac{v_2}{v_1} = \frac{k_1}{k_2}$. This equality holds not

only for the total reaction; it may be assumed to be true for any path. For, since a path may be catalyzed independently of other paths, the equilibrium could be disturbed by a catalyst if the equality did not hold for all paths. At equilibrium the mass-law function $\frac{[C]^c[D]^d}{[A]^a[B]^b}$ (see section 21) is also equal to a constant, so that $\frac{v_2}{v_1}$ is equal to the equilibrium constant or a power of it. It is not necessary that v_2 and v_1 be respectively powers of numerator and denominator of the mass-law function, nor that at some distance from equilibrium $\frac{v_2}{v_1}$ be a power of the mass-law function. For instance, if $A \rightleftarrows B$ goes by both a unimolecular and a bimolecular path, the rate laws of forward and backward reactions would be

$$\frac{d[B]}{dt} = k_1'[A] + k_1''[A]^2 \quad \text{and} \quad \frac{d[A]}{dt} = k_2'[B] + k_2''[B]^2.$$

These can be expressed as

$$\frac{d[B]}{dt} = k_1'[A]\left(1 + \frac{k_1''}{k_1'}[A]\right) \quad \text{and} \quad \frac{d[A]}{dt} = k_2'[B]\left(1 + \frac{k_2''}{k_2'}[B]\right).$$

The rate functions v_1 and v_2 are then

$$[A]\left(1 + \frac{k_1''}{k_1'}[A]\right) \quad \text{and} \quad [B]\left(1 + \frac{k_2''[B]}{k_2'}\right),$$

and $\frac{v_2}{v_1}$ is not a power of the mass-law function. At equilibrium,

$$k_1'[A]\left(1 + \frac{k_1''[A]}{k_1'}\right) = k_2'[B]\left(1 + \frac{k_2''[B]}{k_2'}\right).$$

Hence $\frac{v_2}{v_1} = \frac{k_1'}{k_2'}$; but, since by the unimolecular paths equal quantities of A and B are being formed, $k_1'[A] = k_2'[B]$, and $\frac{k_1'}{k_2'} = \frac{[B]}{[A]}$, so $\frac{v_2}{v_1} = \frac{[B]}{[A]}$ = mass-law function. In other examples, rate functions that are valid far from equilibrium are simpler than the numerator and denominator of the mass-law function. These simple rate functions are approximations. The full expressions for the rate functions are such that $\frac{v_2}{v_1}$ would reduce to the mass-law function or a power of it when the concentrations are those of an equilibrium mixture.

A mass-law function when expressed in concentrations is not strictly a constant at equilibrium. In the true equilibrium function, activities replace concentrations. In consequence, a change that increases the activity of the reactant but not that of the resultant increases the rate of the forward reaction relative to the reverse reaction. For this reason it has been suggested that rate functions should be expressed in terms of activities instead of concentrations. However, such a change does not greatly simplify kinetics. If we use concentration rate functions, it is necessary to assume activity effects on the rate constants, but when we use activity rate functions it appears that they are not successful. This can be seen from the attempts to express the rate of reactions independently of the solvent by multiplying the rate constant by the solubility product of the reactants in the solvent. This sometimes leads to a fairly constant quantity, but more often does not.

36b. Simultaneous reactions. Where a reaction goes by more than one independent path, the rate of the reaction is the sum of the rates by the several paths. When the laws that govern the paths are the same, we cannot distinguish them and have no way of knowing that there are more paths than one unless they happen to have very different temperature coefficients. When the paths lead to different rate laws, we can favor one path over another by a change in concentrations and, by noting the resulting difference in rate, we can distinguish the paths and measure their individual rates.

When simultaneous reactions give different products, each is formed independently of the other; but, as the reactions compete for some common reactant, the yield of each product is reduced by the formation of the other. The general law is

$$\frac{d[P_1]}{dt} = k_1 v_1 \quad \text{and} \quad \frac{d[P_2]}{dt} = k_2 v_2.$$

If there are several simultaneous reactions of the same order, v_1 and v_2 are the same functions, the proportions of P_1 and P_2 do not change during the reaction, and the fractional yield of P_1 is $\frac{k_1}{k_1 + k_2}$, or $\frac{k_1}{k_1 + k_2 + k_3 \cdots}$. The relative yields of various products can then be used as a measure of the relative rates when the competing reactions are of the same order.

When the reactions have different orders, it is difficult to calculate

the relative yields from the rate constants. They then depend also on the initial concentration. High initial concentrations favor the formation of the products from the higher order reactions.

When the reactions are reversible, equilibrium is reached between the various products if the solution is allowed to stand. The relative yields then depend on the relative free energies of the products.

36c. Successive reactions. The vagaries of kinetics chiefly result from a reaction going in successive stages. In a two-step irreversible unimolecular reaction, $A \xrightarrow{k_1} B \xrightarrow{k_3} C$, the rate of removal of A is proportional to the concentration of A, or

$$\frac{d[A]}{dt} = -k_1[A],$$

while that of the formation of C is proportional to the concentration of B, or

$$\frac{d[C]}{dt} = k_3[B].$$

The rate of formation of B is the difference between these two rates, or

$$\frac{d[B]}{dt} = k_1[A] - k_3[B].$$

The removal of A follows the same course as an ordinary unimolecular reaction, but the rate of formation of C starts at zero, increases to a maximum, and then decreases with time. The rate of formation of B starts at $k_1[A]$ and decreases to zero, when its removal as C becomes as fast as its formation from A. The concentration of B therefore rises to a maximum value, which is reached when $k_1[A] = k_3[B]$.

When the concentration of B has reached a maximum, then

$$\frac{[B]}{[A]} = \frac{k_1}{k_3}, \tag{5}$$

but the concentration of A is dropping while that of B is for the moment stationary. Hence the ratio $\frac{[B]}{[A]}$ increases and the reaction $B \rightarrow C$ becomes faster than the reaction $A \rightarrow B$. Thereafter B decreases in concentration. The changes of concentration of A, B, and C with time are shown in Figure 47.

When k_1 is not small with respect to k_3, the intermediate compound, B, can be obtained in appreciable yield. The maximum yield is determined by the ratio of the two constants k_1 and k_3. The maximum fractional yield is

$$\frac{[B]_{\text{max.}}}{[A]+[B]+[C]} = Re^{-\frac{R}{R-1}\ln R} \tag{6}$$

where $R = \dfrac{k_1}{k_3}$.

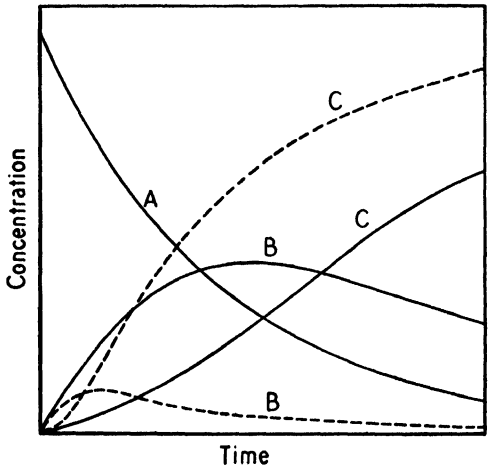


Figure 47. The concentration of the several species in the reaction $A \underset{}{\overset{k_1}{\rightleftarrows}} B \overset{k_3}{\rightleftarrows} C$. The solid lines are for the condition that k_3 is of the same order of magnitude as k_1. The dotted lines correspond to a tenfold increase in k_3.

The time taken to obtain the maximum yield is

$$t = \frac{1}{k_1 - k_3} \ln R \tag{7}$$

The above equations can be obtained by integrating the differential equation

$$d\left(\frac{[B]}{[A]}\right) = \frac{[A]\dfrac{d[B]}{dt} - [B]\dfrac{d[A]}{dt}}{[A]^2}\,dt = \frac{[A]k_1[A] - [A]k_3[B] + [B]k_1[A]}{[A]^2}\,dt$$

$$= \left(k_1 + (k_1 - k_3)\frac{[B]}{[A]}\right)dt.$$

This gives as the time required to achieve any given value of $\frac{[B]}{[A]}$:

$$t = \frac{1}{k_1 - k_3} \ln\left(1 + \frac{k_1 - k_3}{k_1}\frac{[B]}{[A]}\right) \tag{8}$$

The concentration of A is given by the standard equation for a unimolecular reaction, $[A] = A_0 e^{-k_1 t}$, where A_0 is the original concentration of A. The concentration of the final product, $[C]$, is

$$A_0 - [A] - [B],$$

and so the time taken to reach any given value of $\frac{[B]}{[A]}$ and the concentrations of all components at this time can be calculated in terms of k_1 and k_3 alone. The special case of $k_1 = k_3$ gives $[B]_{\max.} = \frac{A_0}{e}$. This condition is reached when

$$t = \frac{1}{k_1}, \qquad [A] = \frac{A_0}{e} \quad \text{and} \quad [C] = A_0 - \frac{2A_0}{e}.$$

Cases to which the above equations may be applied are not uncommon in organic reactions. As a rule they are pseudo rather than true unimolecular reactions. The equations can also be applied to cases in which the rate of the first step varies in the same way with respect to other substances present as the second step does. For instance, in a bromination of a substance that can form a mono- and a dibromo derivative, if the rates of the two steps vary in the same way with the bromine concentrations, the maximum fractional yield of the monobromide would be equal to $Re^{-\frac{R}{R-1}\ln R}$, where R is the ratio of the two rate constants. To get this yield, if a large excess of bromine is used the reaction must be stopped when the maximum concentration of the monobromide has been obtained, i.e. after the time $\frac{\ln R}{(k_1 - k_3)[\mathrm{Br}]}$; or by using $2 - 2e^{-\frac{R}{R-1}\ln R} - Re^{-\frac{R}{R-1}\ln R}$ equivalents of bromine and allowing the reaction to proceed until all the bromine is used up. It may be noted that the best yield of monobromide is obtained when less than one equivalent of bromine is used. When the order of the first step with respect to the reactant is different from the order of the second step with respect to the inter-

mediate (e.g., $2A \rightarrow B \rightarrow C$), the maximum yield of the intermediate is obtained when $\frac{[B]}{[A]^2} = \frac{k_1}{k_3}$. The yield depends not only on the ratio of the rate constants but also on the initial concentration. High yields are favored by high initial concentrations.

The course of two reactions of the type $A \xrightarrow{k_1} B \xrightarrow{k_3} C$ is shown in Figure 47. The full lines represent the case in which B is obtainable in quantity; the dotted lines represent the cases in which $[B]$ is always small. For these curves it has been assumed that the first step, $A \rightarrow B$, has the same rate in both reactions, so that a single curve gives the concentration of A for both reactions. But the dotted lines are for the case when the second step, $B \rightarrow C$, is ten times as fast as it is in the reaction for which the full lines were drawn. The necessary condition for a reaction of the type represented by the dotted lines is that $k_3 >> k_1$. B then can never have a high concentration, for at its maximum

$$\frac{[B]}{[A]} = \frac{k_1}{k_3} \ll 1.$$

Further, this maximum is obtained very shortly after the start of the reaction. Shortly after reaching the maximum concentration of B, the ratio of concentrations $\frac{[B]}{[A]}$ becomes constant, at the value $\frac{k_1}{k_3 - k_1}$. That is,

$$\frac{[B]}{[A] + [B]} = \frac{k_1}{k_3}. \tag{9}$$

Since $\frac{k_1}{k_3}$ and $\frac{k_1}{k_3 - k_1}$ are very nearly equal, and since B is seldom analytically distinguishable from A, $\frac{k_1}{k_3}$ is generally taken as the value of the constant ratio. When this constant ratio is reached, the reaction is said to have reached a steady state and the rate can be expressed as a comparatively simple function of the concentrations, and this function does not change as the reaction proceeds until equilibrium is approached. Thus, in Figure 47 the dotted lines are curves characteristic of unimolecular reactions shortly after the naximum concentration of B has been reached.

In many reactions in which an intermediate is formed in small

concentration, the first step is reversible; i.e., $A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_3} C$. When the maximum concentration of B is reached,

$$\frac{[B]}{[A]} = \frac{k_1}{k_2 + k_3}.^{1}$$

After $\frac{[B]}{[A]}$ has reached its maximum value, it changes but little as the reaction proceeds. If any other substances but A and B are involved in the reaction, then the concentrations of these substances appear as their appropriate powers in the equation for the steady state. For instance, if the successive reactions are

$$A + X \underset{k_2}{\overset{k_1}{\rightleftarrows}} B + Y, \qquad B + Z \xrightarrow{k_3} C,$$

then at the steady state, when B is small,

$$\frac{[B]}{[A]} = \frac{k_1[X]}{k_2[Y] + k_3[Z]}.$$

When B is not formed in equimolar quantities from A, the maximum concentration of B is reached at an almost steady ratio of $\frac{[B]^b}{[A]^a}$, where a and b are the numbers of molecules of A and B in the first reaction. Thus, for

$$2A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_3} C, \qquad \frac{[B]}{[A]^2} = \frac{k_1}{k_2 + k_3}$$

at the maximum concentration of B, and this condition changes very slowly as the reaction proceeds when $(k_2 + k_3) \gg k_1$.

When the reverse reaction $C \rightarrow A$ becomes appreciable with respect to $A \rightarrow C$, i.e. when equilibrium is approached, the steady-state ratios increase to the equilibrium ratio. Thus in

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \underset{k_4}{\overset{k_3}{\rightleftarrows}} C,$$

$\frac{[B]}{[A]}$ reaches $\frac{k_1}{k_2}$ at equilibrium.

[1] Sometimes A is introduced as an equilibrium mixture of A and B. The same steady state is obtained, but only after a decrease in the concentration of B and of the rate $\frac{d[C]}{dt}$.

The theory of the steady state allows us to set up the rate laws for any assumed set of successive reactions in terms of the concentrations of reactants and resultants, in quantities that are determined by analysis. The rate law is first set up in terms of the concentration of the intermediate, and this is replaced by its value, from the steady-state equation, in terms of compounds present in large quantities. For instance in $A + X \underset{k_2}{\overset{k_1}{\rightleftarrows}} B + Y$, $B + Z \xrightarrow{k_3} C$, the net reaction being $A + X + Z \rightarrow Y + C$, we first write

$$\frac{d[C]}{dt} = k_3[B][Z]; \quad \text{but } \frac{[B]}{[A]} = \frac{k_1[X]}{k_2[Y] + k_3[Z]},$$

so that

$$\frac{d[C]}{dt} = \frac{k_1 k_3[A][X][Z]}{k_2[Y] + k_3[Z]}, \tag{10}$$

in which $[A]$, $[X]$, and $[Z]$ are concentrations of reactants and $[Y]$ and $[C]$ are concentrations of products. This rate law is valid only after sufficient time has been allowed to reach, or nearly reach, the steady state.

The above equation often simplifies, as $k_2[Y]$ and $k_3[Z]$ may have different orders of magnitude. Thus, if $k_2[Y] \gg k_3[Z]$,

$$\frac{d[C]}{dt} = \frac{k_1 k_3}{k_2} \frac{[A][X][Z]}{[Y]} = K_e k_3 \frac{[A][X][Z]}{[Y]}, \tag{11}$$

where K_e is the equilibrium constant of the reaction $A + X \rightleftarrows B + Y$. The steady state is then an equilibrium. In this case the intermediate B is called an Arrhenius intermediate. However, if $k_3[Z] \gg k_2[Y]$, then

$$\frac{d[C]}{dt} = k_1[A][X] \tag{12}$$

and the rate of the reaction is determined by the first step, which is called the master or rate-determining step. The intermediate B in this case is called a van't Hoff intermediate. It should be noted that, if this reaction is measured over a sufficient range of concentrations of Y and Z, B is sometimes an Arrhenius and sometimes a van't Hoff intermediate. At equilibrium all intermediates belong to the Arrhenius type.

36d. Catalysis. In a series of successive reactions it is possible that a reactant in one step is a resultant in another, and therefore

is not used up as the reaction proceeds. Such a substance is a catalyst. When it enters the reaction the product is an intermediate, and this intermediate can equally well be considered as the catalyst. In fact, catalysis is effected by a pair or series of compounds rather than by a single compound.

Reduced to its simplest form, a catalytic reaction can be represented as

$$A + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_3} D + C,$$

followed by $C + A \rightarrow B \rightarrow D + C$, etc. Either C or B can be considered as the catalyst, or better, C and B can be considered a catalytic couple. In this catalysis, B can be an Arrhenius or a van't Hoff intermediate. The method of steady states can be applied to catalytic reactions. Thus, in the example, if the amount of catalyst added is small and remains chiefly as C,

$$\frac{d[D]}{dt} = \frac{k_3 k_1 T_c [A]}{k_2 + k_3} \tag{13}$$

where T_c is the amount of catalyst added per unit volume. When, however, $k_1[A]$ is $\gg (k_2 + k_3)$, nearly all of the catalyst is in the form B, and

$$\frac{d[D]}{dt} = k_3 T_c . \tag{14}$$

Similarly, if the catalyst is added in large quantities with respect to the reactant and $k_1 \gg (k_2 + k_3)$, nearly all of the reactant is combined as B and the rate is independent of further addition of catalyst, and

$$\frac{d[D]}{dt} = k_3 [A]. \tag{15}$$

When a catalyst affects the formation of a van't Hoff intermediate but not the follow reaction, it increases the rate of the reaction by changing the steady-state ratio. It can increase this only to the equilibrium ratio; and, once this is reached, further addition of the catalyst does not increase the rate of the reaction. At this stage the intermediate belongs to the Arrhenius type. Thus, if the steps of a reaction are $A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$ catalyzed by C, and $B \xrightarrow{k_3} D$, the rate is given by the equation

$$\frac{d[D]}{dt} = \frac{k_1 k_3 [A][C]}{k_2[C] + k_3},$$

which becomes

$$\frac{d[D]}{dt} = K_e k_3 [A]$$

when $k_2[C]$ is very large with respect to k_3.

As a reaction proceeds, it may form a catalyst. This is known as autocatalysis. The reaction starts at the low speed of the uncatalyzed reaction, but is accelerated as it proceeds. The reaction has an induction period. Reference to Figure 47 shows that there is an induction period for the formation of the final product in the case of successive reactions. This can be distinguished quite easily from the induction period due to autocatalysis. In autocatalysis, the induction period applies both to the formation of the product and the removal of the reactant; for succesive reactions there is no delay in the removal of the reactant.

36e. Chain reactions. When an intermediate that can enter into a catalytic cycle is formed from the reactants and can be removed occasionally by another reaction, the catalytic cycle can be repeated many times every time the preliminary step occurs. The intermediate reaches a steady state that depends on the relative rates of the preliminary step and the final reaction or reactions that remove the intermediate. Thus, when a mixture of hydrogen and chlorine is exposed to light, the dissociation of chlorine to Cl atoms can occur. The chlorine atom is a reactant in the catalytic cycle

$$\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{H} + \mathrm{HCl},$$
$$\mathrm{H} + \mathrm{Cl_2} \rightarrow \mathrm{Cl} + \mathrm{HCl}.$$

It can be removed by the reactions

$$\mathrm{Cl} + \mathrm{Cl} \rightarrow \mathrm{Cl_2},$$

$$2\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{H} + \mathrm{HCl} + \mathrm{Cl} \rightarrow 2\mathrm{HCl},$$

and

$$2\mathrm{Cl} + 2\mathrm{H_2} \rightarrow 2\mathrm{HCl} + 2\mathrm{H} \rightarrow 2\mathrm{HCl} + \mathrm{H_2};$$

or by a reaction between either member of the catalytic couple Cl and H and some other substance that has been added. Reactions of this type are called chain reactions.

There are three essential parts in a chain reaction: (1) the preliminary step, (2) the catalytic cycle, and (3) the chain-terminating reaction. For a chain mechanism to be effective, the catalytic cycle must be fast with respect to the chain-terminating reaction.

The rate law for any assumed chain mechanism can be deduced by the steady-state method. The rates of the preliminary and chain-terminating steps determine a steady-state concentration of the intermediate, and the rate of formation of the products of the catalytic cycle can be given as a function of the steady-state concentrations. For instance, the simplest possible chain mechanism would be $A \xrightarrow{k_1} C$, $C + B \xrightarrow{k_3} D$, $D \xrightarrow{k_4} E + C$, and $C \xrightarrow{k_2} A$, with $k_3 \gg k_2$. The preliminary reaction is $A \rightarrow C$; the catalytic cycle is $C + B \rightarrow D$ and $D \rightarrow E + C$; the chain-terminating reaction is $C \rightarrow A$. The steady-state concentration of C is determined by

$$k_1[A] = k_2[C] \text{ or } [C] = \frac{k_1}{k_2}[A],$$

and

$$\frac{d[E]}{dt} = k_3[C][B] = \frac{k_1}{k_2} k_3[A][B].$$

In this simple case the chain mechanism is equivalent to the reaction $B \rightarrow E$ catalyzed by A.

The rate of a chain reaction is also given by the product of the rate of the preliminary reaction and the length of the chain. The latter is the average number of catalytic cycles that occur before the chain is broken. In the simple example above, the length of the chain is $k_3[B]/k_2$, and

$$\frac{d[E]}{dt} = k_1[A] \frac{k_3[B]}{k_2}.$$

As a rule, chain reactions are not as simple as this, but the same principles can be used to obtain the rate law from the assumed mechanism. These laws can be expressed by the general equation:

$$\text{Rate} = k \frac{v_1 v_3}{v_2} \qquad (16)$$

where v_1, v_2, and v_3 are the rate functions for the preliminary, chain-terminating, and catalytic reactions, respectively.

36f. Inhibitors. Many instances of a small amount of an impurity decreasing the rate of a reaction are known. The impurity is said to be an inhibitor for the reaction. In typical examples of inhibition, the reaction is delayed for a time but eventually acquires a normal rate. At this stage the inhibitor has been destroyed. The

phenomenon is best explained by assuming that the reaction has a chain mechanism and the inhibitor reacts with one of the intermediates and thereby terminates the chain. If without the inhibitor the rate of the reaction is given by some law as

$$\frac{dx}{dt} = k_1[A]\frac{k_3[B]}{k_2},$$

with the inhibitor the reaction rate becomes

$$\frac{dx}{dt} = k_1[A]\frac{k_3[B]}{k_2 + k_4[I]} \tag{17}$$

in which $[I]$ is the concentration of the inhibitor. Inhibitors are very often found for oxidations by oxygen. These reactions are generally chain reactions, often with very long chains. The inhibitors are substances that can be oxidized by the intermediate oxygen compounds, producing no chain or only a short chain. Resorcinol, hydroquinone, various alcohols, anthracene, and iodide ion are often strong inhibitors of auto-oxidation. Often very minute quantities of inhibitors have very large effects. Thus the oxidation of benzaldehyde by oxygen can be practically stopped by concentrations of inhibitors as low as one part in a hundred thousand.

The above theory of the mechanism of inhibitors has been clearly demonstrated in certain cases by Alyea and Bäckström.[2] Where an inhibitor is oxidized only in the process of inhibition, the rate of decrease of its concentration is a measure of the number of chains terminated by the oxidation of the inhibitor. When the concentration of the inhibitor is sufficiently great, all chains are terminated by oxidation of the inhibitor, and the rate of oxidation of the inhibitor does not increase further with its concentration. Further, this rate is the rate of the preliminary step, and is not only independent of the concentration of the inhibitor but also of what the inhibitor is, provided it meets the specification of being oxidized only in a chain-terminating process. The concentration of inhibitor needed to obtain the constant rate depends on the strength of the inhibitor. The concentration is less the stronger the inhibitor. The inhibition of the auto-oxidation of sulfite ion by isopropyl, butyl, or benzyl alcohol is an example of this ideal type of inhibition. All three alcohols, when in sufficient concentration, are oxidized at the same constant rate, and this rate is the rate of the preliminary step of the reaction.

[2] Alyea, H. N., and Bäckström, H. L. J., *J. Am. Chem. Soc.*, **51**, 90 (1929).

The rate of a chain reaction divided by the rate of the preliminary reaction equals the average length of the chain, so that the length of the chain can be obtained from the above measurements. Similarly, even if the inhibitor is oxidized by some process other than a chain-terminating step, a minimum length of the chain can be obtained for the uninhibited reaction by dividing the normal rate of the reaction by the rate of removal of the inhibitor.

In photochemical reactions the preliminary step involves the absorption of a quantum of light. Hence the rate of a photochemical chain reaction divided by the rate of absorption of light in quanta equals the length of the chain.

The best criteria of whether a reaction has a chain mechanism are the temporary inhibition of the reaction by a small quantity of an impurity, and the formation of a large amount of product per quantum of light absorbed in a photochemical reaction.

37. THE TEMPERATURE COEFFICIENT OF REACTION RATE

The rate constant of a reaction generally increases very rapidly with temperature. This increase can be fairly accurately expressed for nearly all measurable reactions by the equation

$$\frac{d \ln k}{dT} = \frac{A}{T^2}, \tag{18}$$

where A is a constant characteristic of the reaction. This expression fulfills the equilibrium requirement that the equilibrium constant be $K = \frac{k_1}{k_2}$, for $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$, where ΔH is fairly constant with temperature and $A_1 - A_2$ can be put equal to $\frac{\Delta H}{R}$. The quantity A is therefore an energy divided by R, and

$$\frac{d \ln k}{dT} = \frac{\epsilon}{RT^2}. \tag{19}$$

It is therefore assumed that it is necessary for reactants to absorb energy before they can go over to the products, whether the heat content of reactants or of products is the greater. This energy is known as the heat of activation. For reactions that go slowly in both directions, the heat of activation is generally much larger than ΔH for the reaction, and it is not related to ΔH except by the condi-

tion that ΔH is the difference of the heats of activation of the forward and backward reactions.

If $\frac{d \ln k}{dT} = \frac{\epsilon}{RT^2}$, k is proportional to $e^{-\epsilon/RT}$; i.e., $k = be^{-\epsilon/RT}$. Insofar as the differential equation is accurate, the proportionality constant is independent of the temperature. It is often called the temperature independent factor. Every reaction rate has two characteristic constants: the temperature independent factor and the heat of activation. Actually neither b nor ϵ is quite independent of the temperature, but they are sufficiently so for practical purposes.

In the corresponding equation for an equilibrium constant, $K = ae^{-\Delta H/RT}$, the proportionality constant is $e^{\Delta S/R}$, so that $\frac{b_1}{b_2} = e^{\Delta S/R}$, where b_1 and b_2 are the temperature independent factors of the velocity constants of the forward and backward reactions and ΔS is the change of entropy in the reaction. The quantity b is therefore related to probability.

To account for the above relationship of rate and temperature, Arrhenius[3] proposed the theory of an activated intermediate. The reacting molecule or molecules first react to form a high energy intermediate which passes over to the products with loss of energy. In this theory the second step has been assumed to be the slower or master reaction, and hence $k = K_a k_a$, where K_a is the equilibrium constant for the change Reactants $\rightarrow$ Active Intermediate, and k_a is the rate constant for the reaction Intermediate $\rightarrow$ Product. There are certain difficulties in the theory that the intermediate is an actual compound. For instance, if we write $k_1 = K_a k_a$ and $k_2 = K_b k_b$ for the rate constant of a reaction and its reverse, then

$$\frac{K_a}{K_b} = K = \frac{k_1}{k_2} = \frac{K_a k_a}{K_b k_b}, \text{ and } k_a = k_b;$$

but k_b is the rate constant of the de-activation of the intermediate to reactant, which we have to assume to be large with respect to k_a in order that the intermediate shall reach an equilibrium rather than a steady state. The theory would then require that the velocity constant increases as equilibrium is approached, but for many reversible reactions the rates are given over a wide range by $\frac{dx}{dt} = k_1 v_1 - k_2 v_2$, where v_1 and v_2 are functions of the concentrations of reactants and

[3] Arrhenius, S., *Z. physik. Chem.*, **4**, 226 (1889).

products, respectively. These difficulties are now avoided by not considering the intermediate as an ordinary compound but as a state of the molecules defined by their internal energy. It is then assumed that, in order for a molecule or system of molecules to react in some given way, its internal energy must equal or exceed some critical energy. There are therefore two energies associated with a reaction, the critical energy and the heat of activation. The critical energy can be defined as above. Its definition is then in terms of a theory of reaction, and by definition it is independent of the temperature. The heat of activation can be defined in many ways, but about the simplest method is to define it by the equation

$$\epsilon = \frac{d \ln k}{dT} RT^2. \tag{19a}$$

A definition of the heat of activation then depends on the mathematical law which is derived from the assumption of the necessity of a critical energy. One of these definitions is that it is the difference between the average energy of activated molecules and the average energy of all molecules. In this definition it is not quite clear what is meant by an activated molecule. An activated molecule could be one with enough energy to react, or one that meets this and other requirements for reaction. By the above definition, the heat of activation is independent of the temperature only to the extent that $\frac{d \ln k}{d(1/T)}$ is constant.

37a. Unimolecular reactions. Several gas-phase unimolecular reactions are known. Most of these are decompositions or isomerizations and follow very closely the law $k = be^{-\epsilon/RT}$. The importance of obtaining unimolecular reactions in the gas phase is that we then know that the rate constant is independent of the concentration of any species of molecule. In a unimolecular reaction in a solution, we cannot tell whether the reaction is or is not dependent on the concentration of the solvent except insofar as that could be assumed if the rate is independent of the nature of the solvent. It has been shown that these reactions acquire energy of activation from collisions. The number of collisions per unit volume per second varies with the square root of the temperature, but this change with temperature is small with respect to the change of reaction velocity and so is a poor test of whether the collision rate is or is not a factor in the rate. However, there is a much better way of showing that the velocity constant does not depend on the collision rate. The latter

depends on the square of the concentration of molecules and is the same for any kind of molecules of the same size. Hence, if the rate of a unimolecular reaction depends on the frequency of collision, the rate constant would increase with pressure, whether produced by reactant or extraneous molecules. As this constant is independent of pressure except at very low pressure, the activated state is an Arrhenius intermediate, and has a much greater chance of returning to a normal molecule than of decomposing into the products.

In the preceding section we pointed out the difficulty of considering an active isomer as an Arrhenius intermediate. This difficulty does not exist in Lindemann's conception of the activated molecule.[4] He assumes it to be a molecule that has sufficient internal energy in all its degrees of freedom to allow it to react, but, unless this energy accumulates in the right degree of freedom before it is dissipated to other molecules by collisions, the molecule does not form products but merely returns to the starting point. It is assumed that the chance of an activated molecule losing its energy to other molecules and returning to its original state is large with respect to the chance of the energy accumulating in a degree of freedom that permits reaction. The reversible reaction $A \rightleftarrows B$ can then be represented as $A \underset{k_2}{\overset{k_1}{\rightleftarrows}} A' \underset{k_4}{\overset{k_3}{\rightleftarrows}} B' \underset{k_6}{\overset{k_5}{\rightleftarrows}} B$, where A' and B' represent molecules with their energies so distributed that A' normally returns to A and B' to B. The rate of $A \rightarrow B$ is then $\frac{k_1}{k_2} k_3[A]$ or $K_a k_3[A]$, and the rate of the reverse reaction is $\frac{k_6}{k_5} k_4[B]$ or $K_b k_4[B]$. These are rate equations for Arrhenius intermediates.

When, as in the original Arrhenius conception, A' and B' are treated as a single substance, the ratio of the equilibrium constants of A and B with the intermediate has to equal the equilibrium constant of the reaction $A \rightarrow B$, and the de-activation to A becomes the slow step in the reaction $B \rightarrow A$, while the de-activation to B becomes the slow step in the reaction $A \rightarrow B$. This leads to a self-contradiction; i.e., to maintain an Arrhenius intermediate, one rate constant has to be assumed both equal to and larger than another one. When the slow step in the reaction is the redistribution of the energy in the molecule, this contradiction is not met, whether the reaction is unimolecular in both directions or is a unimolecular decomposition.

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[4] Lindemann, F. A., *Trans. Farad. Soc.*, **17**, 599 (1922).

When the rate of the unimolecular reaction is put equal to $K_a k_3[A]$, K_a is the fraction of the molecules that have enough energy to react, and this fraction is $e^{-\epsilon_c/RT}$, where ϵ_c is the critical energy. But k_3 is not necessarily independent of the temperature, for the probability of the activated molecule reacting instead of being de-activated increases with the energy of the molecule. In consequence, the heat of activation as defined by the equation $\epsilon = RT^2 \frac{d \ln k}{dT}$ is greater than the critical energy. Expressions have been derived theoretically for the chance of the reaction occurring as a function of the degree of activation of the molecule, and complex equations for the unimolecular reaction have been obtained.[5] These theories are beyond the scope of this book. In general, the simple equation $k = be^{-\epsilon/RT}$ is as close an approximation as is warranted by the accuracy of measurement. The value of ϵ determined from the experimentally measured temperature coefficient of the rate constant is better not identified with the critical energy, but may be called the heat of activation.

If the heat of activation can exceed the critical energy, then the heat of activation for the breaking of a bond can exceed the bond energy. From the requirement that $\frac{k_1}{k_2} = K$, we can further deduce the possibility that the formation of a bond could be a reaction with a heat of activation. The dissociation of hexaphenylethane has been found to have a greater temperature coefficient than corresponds to the expression $\frac{d \ln k}{dT} = \epsilon/RT^2$ if ϵ is put equal to the heat of the dissociation. This dissociation is accompanied by large changes in resonance, and it could well be that there is an energy barrier between the products of dissociation and the original compound.

With decrease in pressure, the chance that an activated molecule will lose its energy decreases more rapidly than the chance of the energy becoming so distributed as to allow a reaction to occur. Consequently, at low pressures the rates of unimolecular reactions cannot remain independent of the pressure. The activated molecule tends to become a Van't Hoff intermediate, and the rate to depend on the collision frequency. This corollary of Lindemann's theory has been

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[5] See Kassel, L. S., *J. Phys. Chem.*, **32**, 225, 1065 (1928); Rice, O. K., and Ramsperger, H. C., *J. Am. Chem. Soc.*, **50**, 617 (1928); Rice, O. K., *Proc. Nat. Acad. Sci.*, **14**, 118 (1928).

experimentally observed by Ramsperger[6] and others. The best example is the decomposition of azomethane. The rate of this decomposition varies with the pressure in close agreement with the theories of Rice and Ramsperger.

37b. Bimolecular reactions. The rate of a primary bimolecular reaction depends on the rate of collision of the reactive molecules. The number of collisions between the spherical molecules A and B per cc. per second is given by the equation

$$Z_{A,B} = n_A n_B \sigma_{A,B}^2 \left\{\frac{8\pi RT}{N\mu_{AB}}\right\}^{\frac{1}{2}}, \qquad (20)$$

where n_A and n_B are the numbers of molecules per cc. for A and B, respectively; $\sigma_{A,B}$ is the sum of the radii of A and B; μ_{AB} is the reduced mass of the molecules A and B; N is Avogadro's number; and RT is expressed in ergs. Should A and B be the same, the expression on the right-hand side should be divided by two, since it is the number of molecules of A multiplied by the collision rate of one of them with molecules of B, and if A and B are identical this method would count every collision twice. Since a collision of molecules at unreactive points would be very unlikely to result in a reaction, $\sigma_{A,B}$ is better considered as the sum of the radii of atoms directly concerned in the reaction.

The dependence of Z on the temperature is negligible with respect to the change of rate of a bimolecular reaction. The bimolecular rate constant changes with temperature in much the same way as a unimolecular constant, $\frac{d \ln k}{dT}$ being approximately $\frac{\epsilon}{RT^2}$. It may be assumed, therefore, that the energy of a reacting system whether composed of one, two, or more molecules must exceed a critical value, ϵ_c, for the reaction to occur. In a bimolecular reaction this energy can be taken as all obtained from the collision. It is then the sum of the kinetic energies of the molecules as measured by an observer who is at rest with respect to the center of mass of the two molecules. It may also be expressed as $\frac{1}{2}\mu v^2$, where μ is the reduced mass and v is the relative velocity parallel to the line joining the centers of the molecules.

The fraction of collisions that meet this energy condition is $e^{-\epsilon_c/RT}$. If only collisions and sufficient energy are the requirements for a reaction, the rate in molecules per cc. is $Ze^{-\epsilon_c/RT}$ and the velocity con-

[6] Ramsperger, H. C., *J. Am. Chem. Soc.*, **49**, 912, 1495 (1927).

stant in moles per liter is

$$k = \frac{N}{1000}\sigma_{A,B}^2\left\{\frac{8\pi R}{N\mu_{AB}}\right\}^{\frac{1}{2}} T^{\frac{1}{2}} e^{-\epsilon_c/RT}, \tag{21}$$

and the rate of change of k with T is given by the equation

$$\frac{d \ln k}{dT} = \frac{1}{2T} + \frac{\epsilon_c}{RT^2}.$$

For reactions that are slow enough to be measured, $1/2T$ is generally negligible with respect to ϵ_c/RT^2.

Even if we take $\sigma_{A,B}$ of such dimensions that collisions at unreactive parts of the molecules are ignored, the rate cannot equal $Ze^{-\epsilon_c/RT}$ unless all collisions involving the reactive molecules are effective in producing a reaction. Since $\sigma_{A,B}$ in those cases would not vary very much from one reaction to another, the rates of bimolecular reactions would be governed only by the values of ϵ_c. This is not true for reactions in liquid phase, even when the reactions are very similar in type and involve molecules of nearly the same size. Thus the reaction $CH_3CH_2CH_2Cl + I^- \rightarrow CH_3CH_2CH_2I + Cl^-$ in acetone solution has the same heat of activation as the reaction

$$CH_3COCH_2Cl + I^- \rightarrow CH_3COCH_2I + Cl^-$$

in acetone solution, but the latter reaction is about 30,000 times as fast as the former.

Similarly, the relation Rate $= Ze^{-\epsilon_c/RT}$ can be directly tested from measurements of the rate and its temperature coefficient. It is found that this relation leads to fairly reasonable values of $\sigma_{A,B}$ for bimolecular reactions in the gas phase and for certain types of reactions in the liquid phase; e.g.,

$$RI + RO^- \rightarrow ROR + I^-.$$

However, in general, reactions in liquid phase would need absurd values of $\sigma_{A,B}$ to fit the law. It is not uncommon that a reaction rate is less than one millionth of what would be calculated if $\sigma_{A,B}$ were taken as the sum of the radii of the molecules. It is thus apparent that for a reaction to occur it may not only be necessary for the resulting molecules to collide with a necessary energy, but also that some other condition must be fulfilled during the collision. Presumably it is necessary for the atoms to get into a configuration favorable for reaction before the colliding molecules rebound. For each reaction there is a probability that this condition will be met.

It is therefore necessary to introduce a probability factor, characteristic of the particular reaction, into the expression for the rate constant. The rate constant in moles per liter per second for a bimolecular reaction then becomes

$$k = \frac{NP}{1000}\sigma_{A,B}^2\left\{\frac{8\pi R}{N\mu_{AB}}\right\}^{\frac{1}{2}} T^{\frac{1}{2}} e^{-\epsilon_c/RT}, \tag{22}$$

or, if $A = B$,

$$k = \frac{N}{1000}\frac{P}{2}\sigma^2\left\{\frac{16\pi R}{NM}\right\}^{\frac{1}{2}} T^{\frac{1}{2}} e^{-\epsilon_c/RT},$$

where P is a constant for the particular reaction. As P is assumed to be independent of the temperature, its inclusion does not alter the value of $\frac{d \ln k}{dT}$. We need not go into the question of whether P or ϵ is entirely independent of the temperature. It is sufficient to say that measurements of $\frac{d \ln k}{dT}$ seldom vary from $\frac{1}{2T} + \frac{\epsilon_c}{RT^2}$ to an extent greater than can be attributed to experimental error.

Equation 22 was developed on the assumption that ϵ_c is the energy of a special configuration of the pair of reacting molecules. The special configuration is supposed to be the lowest energy arrangement which can spontaneously react. The alternative is that ϵ_c is not a critical energy but a heat of activation, i.e. the difference in average heat content attained by molecules that are about to react and the average heat content of all the molecules. We shall, throughout the rest of this book, assume the latter to be the case. Actually there is not much evidence on this point. The evidence for this energy being a critical energy is that in many reactions the probability factor is unity. This may mean that these are reactions for which the probability is very small when little more than sufficient energy has been acquired but becomes large at higher activation energies. Therefore, most of the reaction occurs with high enough activation energies to remove other restrictions to a reaction.

The evidence for the theory that ϵ is not a critical energy is that in many reactions the probability factor is very small, indicating that there are very restrictive prerequisites for a reaction other than sufficient energy. Again, a structural change that might well be supposed to introduce a stabilizing resonance in activated molecules, as for instance the introduction of a doubly bonded system on one of the atoms of the reacting bond, often greatly increases the rate

without decreasing the activation energy. The effect of pressure is also of interest in this connection. The rate constants of many simple bimolecular reactions are increased by pressure. When this occurs, the activation energy is sometimes increased and sometimes decreased.[7] Thus at 3000 kg./cm^2 the esterification of acetic anhydride is seven times its normal speed, and the heat of activation is 3.5 kcals. less than its value at one atmosphere. On the other hand, the quaternization of pyridine by *n*-butyl bromide is eight times as fast, but the activation energy is 1.4 kcals. higher at 3000 kg./cm^2 than at one atmosphere. The critical energy considered as the potential energy of a special configuration is not affected by pressure, so that the opposite effects in the two reactions would have to be attributed to opposite effects of pressure on the heat contents of the two pairs of reactants. If ϵ is considered as the average energy difference between reacting and other molecules, the difference is not surprising, for pressure must produce great differences on the probabilities of reaction of different configurations. Where the probability is low, as in the quarternization, the reaction is already occurring through low energy configurations and pressure is apt to increase the proportion of reaction by higher energy forms. The higher probability and higher activation energy of the esterification suggests an increase in reaction by pressure through lower energy forms, and a consequent decrease in activation energy.

37c. The temperature coefficient of a complex reaction. A reaction may be the result of successive steps. The rate constant is then a function of the rate constants of the steps and their reversals up to and including the step that is so slow that what happens afterwards does not affect the rate of the reaction. The temperature coefficient of the overall reaction can be deduced from those of the component steps. Thus in the reaction $A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_3} C$, if $k_3 < k_2$,

$$k = \frac{k_1 k_3}{k_2} = be^{-(\epsilon_1 - \epsilon_2 + \epsilon_3)/RT}$$

and the heat of activation is $\epsilon_1 - \epsilon_2 + \epsilon_3 = \Delta H_B + \epsilon_3$, where ΔH_B is ΔH for the reaction $A \rightleftarrows B$; but if $k_3 > k_2$, $k = be^{-\epsilon_1/RT}$, and the heat of activation is equal to ϵ_1. When k_3 and k_2 have the same order of magnitude, the overall heat of activation lies between $\Delta H_B + \epsilon_3$ and ϵ_1.

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[7] Perrin, M. W., *Trans. Farad. Soc.*, **34**, 144 (1938).

The rate law often includes powers or roots of systems that are the reactants of a preliminary step. Thus, for

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2B, \qquad B \xrightarrow{k_3} C, \quad \text{and for} \quad A + 2B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C, \qquad 2C \xrightarrow{k_3} D,$$

the rate laws are, respectively,

$$\frac{d[C]}{dt} = \left(\frac{k_1}{k_2}\right)^{\frac{1}{2}} k_3[A]^{\frac{1}{2}} \quad \text{and} \quad \frac{d[D]}{dt} = \left(\frac{k_1}{k_2}\right)^{2} k_3([A][B]^2)^2,$$

if $k_2 \gg k_3$. In these cases the heats of activation are obtained by multiplying those of the preliminary reactions by the indices which their rate constants have in the rate equation and adding this product to the heat of activation of the master reaction. Thus the heats of activation for the two examples cited are

$$\epsilon = \tfrac{1}{2}\epsilon_1 - \tfrac{1}{2}\epsilon_2 + \epsilon_3 = \tfrac{1}{2}\Delta H + \epsilon_3$$

and

$$\epsilon = 2\epsilon_1 - 2\epsilon_2 + \epsilon_3 = 2\Delta H + \epsilon_3, \text{ respectively.}$$

38. TRANSITION STATE

The concepts of an activation energy and a probability factor for a reaction suggest the idea that there is an intermediate formed in every reaction. The intermediate cannot be an ordinary compound, and for this reason it is known as a transition state rather than as an intermediate substance. On the other hand, it is not merely a collection of reactant molecules having energies greater than some given value. In discussing unimolecular reactions we saw that it was not sufficient to get the requisite energy; it was also necessary that this energy be distributed in a special way for the reaction to occur. Similarly in a bimolecular reaction the energy of activation alone is not sufficient, but a particular range of atomic configurations is also needed. If we imagine all configurations and modes of motion depicted in some many-dimensional space, some domain could be identified as the transition state, distinct from the domains of reactants and products. The domain of the transition state would have extension in all dimensions but the one representing the reaction path. In this dimension it is a point, and in this sense the transition state cannot be considered as a substance. The two-dimensional analogue of this picture is a line for the transition state, separating two areas for the reactants and products, respectively.

The points of likeness of the transition state to an ordinary substance has suggested giving it the properties of free energy and entropy. If a certain velocity of passage across the transition state is imagined, and called v, and an equality of passage is assumed in both directions, a rate constant can be expressed as

$$k = \tfrac{1}{2}ve^{-\Delta F_T/RT}, \quad \text{or as} \quad k = \tfrac{1}{2}ve^{\Delta S_T/R}e^{-\Delta H_T/RT},$$

where ΔF_T, ΔH_T, and ΔS_T are the usual thermodynamic quantities for the reaction Reactants $\rightarrow$ Transition state. This equation obviously satisfies the requirement that $K = \dfrac{k_1}{k_2}$, where K is the equilibrium constant and k_1 and k_2 are the rate constants of the reaction and its reversal. This equation identifies the heat of activation with a ΔH at the temperature of the reaction and hence permits variation of the heat of activation with temperature.

The advantage of this thermodynamic treatment is that, knowing the origin of the transition state, we know something of its properties. For instance, if the reaction is one between similarly charged ions, the transition state has a charge equal to the sum of the charges of the reacting ions and ΔF_T for Reactants $\rightarrow$ Transition state is decreased by addition of salt to the solution, and the reaction rate is increased by salt.

The energies and configurations of reactants, products, and transition state depend on the laws of bond formation, so that if these laws could be fully formulated we could picture the whole process of reaction. Although we are very far from this state of knowledge, we can use what we know about the interactions of atoms to picture the transition state and the process of reaction. We shall consider the transition state and the reaction from two points of view. First, we will consider them on the basis of the concepts of the Lewis structural theory with the inclusion of the postulate of resonance. This theory is essentially qualitative, and the resulting picture of reaction is qualitative, and must remain so unless empirical formulas for bond formation, molecular repulsion, and resonance are introduced. As the second point of view we shall consider the application of quantum mechanics to the problem. Here it is possible to use equations that are formally quantitative. Actually the problem is too complicated to obtain more than a qualitative picture from quantum mechanics. By introducing empirical equations, some increase in accuracy is obtained, but even then no great advance has been made. The rest of this section should be considered as qualita-

tive rather than quantitative, even though the language may have an occasional quantitative timbre.

Let us consider a reaction between a saturated molecule $A—B$ and an unsaturated one, C. The reacting system $A—B + C$ is distinguished from the resulting system $A + B—C$ by the relative distance of B from A and C, respectively. In all arrangements of A, B, and C the alternative bond arrangements $A—B\ \ C$ and $A\ \ B—C$ contribute, but the former is more important when B is near A and far from C, and the latter when B is nearer C than A. This resonance decreases the energy of the system, but its effect is small in either extreme atomic configuration, that of reactants or that of resultants. The resonance energy can be increased by pulling B from A towards C or pushing C towards B. The first of these processes requires work against the bond; the second requires work against the repulsive forces between the molecules.

If for all configurations of A, B, and C the work done in stretching the bond and that done in compressing the molecules are together greater than the increase of the energy of the resonance ($A—B\ \ C$, $A\ \ B—C$), there is a complete energy barrier between reactants and products. For each separation of A and C, B can take a position for which the bonds $A—B$ and $B—C$ are equal. When this condition is reached, there is no force on B driving it to A or to C. The aggregate of these configurations which fulfill this last condition can be called the transition state. It is necessary to pass through the transition state to get the reaction $A—B + C \rightarrow A + B—C$ or its reversal.

There is a transition state configuration that has a minimum energy. The energy of this configuration less that of $A—B$ with C far away is the critical energy for the reaction $A—B + C \rightarrow A + B—C$. This critical energy must be reached or exceeded for the reaction to occur. The heat of activation as measured by the equation $\frac{d \ln k}{dT} = \frac{\epsilon}{RT^2}$ is the difference between the average energy of molecules passing through the transition state and the average energy of the reactants.

We shall assume that we are dealing with a system that maintains a constant number of unpaired electrons and is not interacting with light. The potential energy is then determined by the relative positions of the atoms, as the electrons reach their most stable arrangement much faster than the atoms move. The potential energy of any configuration in which B is more bonded to A than to C, measured

from the starting point *A*—*B* (equilibrium distance) and *C* (at infinity), is the sum of the energy necessary to separate *B* from *A* against the bond force and that needed to force *C* near to *A* and *B* without bonding, minus the energy obtained from the resonance resulting from the alternative bond arrangement *A B*—*C*. The potential energy of a configuration with *B* bonded more to *C* than to *A* is composed of the corresponding energies measured from the starting point *A* and *B*—*C*. It will be assumed that the easiest way to get *A*, *B* and *C* close together is to have them in a linear configuration.

With the aid of this theory of the factors on which the energy of the reacting system depends, we have constructed a diagram (see Figure 48) showing how the potential energy changes with the configuration. The abscissa gives the distance between *A* and *B*, it being assumed that *B* moves along the bond towards *C*. The ordinate is the energy of the system. Each of the curves I_1, I_2, etc. is a graph of the energy against the distance between *A* and *B*, the distance between *A* and *C* being fixed. Each of the curves corresponds to a different distance between *A* and *C*. This distance is successively less from I_1 to I_5. Curve I_1 is for the case in which the effect of *C* on *A*—*B* is negligible.

Each curve shows two minima. These minima represent the reactants (*A*—*B C*) and the products (*A B*—*C*), respectively. As we pass from curves I_1 to I_5, the minima are situated at higher energies on account of the repulsion between *A*—*B* and *C* for the minima on the left and that between *A* and *B*—*C* for the minima on the right. The distances between *A* and *B* are shown in the diagram, so that the line joining the right-hand minima shows the energy of repulsion between the products as a function of the distance between the molecules in the product, measured from the center of *A* to the center of *B* in *B*—*C*. This curve has been drawn in the diagram and is curve II. The corresponding curve for the energy of the repulsion of the reactant molecules does not appear in the diagram, but the left-hand minima are slightly displaced from the perpendicular to indicate an effect on the bond distance of *A*—*B* when *C* is near.

Between their minima, curves I_1 to I_5 rise to maxima. At these maxima *B* is held equally by *A* and *C*, and the points represent transition states between reactants and products. Curve III is a line joining the maxima. It is a graph of the energy of the transition state as a function of the distance between *A* and *B*. The minimum of this curve gives the lowest energy for the transition state, and its height above the left-hand minimum of curve I_1 is the critical energy

of the reaction. Curve III shows the energy for a vibration of the transition state in which B remains fixed and A and C move simultaneously towards and then simultaneously away from B. This is one of the vibrations in which the transition state can behave like a stable molecule. That it is not a stable molecule can be seen from

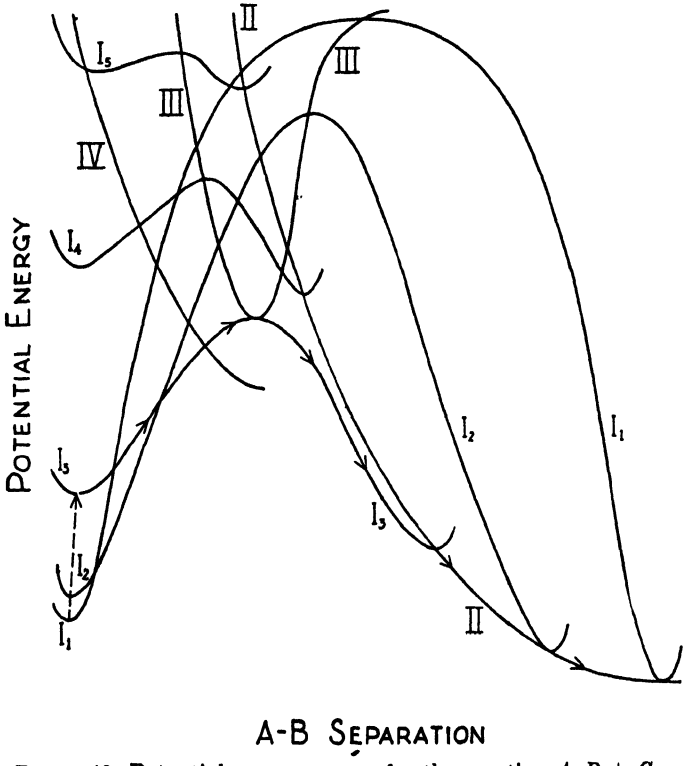


Figure 48. Potential energy curves for the reaction A–$B + C \rightarrow A + B$–C for a number of limiting conditions. Each of the curves I_1, I_2, I_3, I_4, and I_5 corresponds to the motion of B from A to C for a fixed distance between A and C. The other curves are derived from these as explained in the text. Except for curve IV, they correspond to cross-sections of surface shown in Figure 49.

the downward slope of the potential-energy curve corresponding to a displacement of B either towards A or C.

In this figure A, B, and C have been assumed to lie in a line. This is the most advantageous arrangement, for it allows B to bond with A and C with a minimum of interference between A and C. One can construct similar diagrams with any angle between the lines A—B and B—C. In these diagrams, curves corresponding to III

lie at higher energies. The minimum of curve III therefore lies at the bottom of a pit. There are, therefore, elastic forces in a transition molecule that tend to make the molecule linear. It should be noted that the tendency of the transition state to be linear will be diminished by the presence of any interactions other than those between the three atoms concerned in the reaction.

The steepness of the walls of curve III is related to the probability factor of the reaction. The probability is low when the walls are steep. The same is true of the pit which would replace this curve if the angle of approach of C were included in the picture.

Curve I_3 has its maximum at the minimum of curve III. The lowest point on the energy barrier between reactants and resultants lies on curve I_3, and a reaction occurs with the minimum of activation by passing through this point. An imagined course of the reaction is traced by arrows. From the left-hand minimum of curve I_1 the energy rises to the minimum of curve I_3 as C approaches A—B. The energy then rises along curve I_3 as B moves towards C. From here the reaction proceeds spontaneously with loss of energy, at first along curve I_3 by the motion of B towards C until the second minimum of curve I_3 is reached, and then along curve II by the repulsion of A from B—C until B—C is independent of A, i.e. at the second minimum of curve I_1. Of course this is merely a formal separation of the reaction into stages; presumably these stages would not be separate in an actual reaction. Nor would it usually proceed by this most efficient path. The average reaction would probably pass through a somewhat higher energy portion of the transition curve.

If ϵ_n is the energy of a point on the I_n curve corresponding to a given separation, q, of A and B, with C at the distance characteristic of the I_n curve, and ϵ_1 is the energy of a point on the I_1 curve corresponding to the same separation, q, with C far away, and ϵ_n^0 and ϵ_1^0 are minimal energies of the two curves (I_n and I_1), then the quantity $\epsilon_n + \epsilon_1^0 - \epsilon_1 - \epsilon_n^0$ is the energy of the resonance (A—B C, A B—C) with B at the distance q from A, and with C at the distance characteristic of the I_n curve, neglecting the small resonance present even when A and B are separated by their normal bond distance. Curve IV is a plot of this quantity for the left-hand limb of curve I_3. The energy at a point of this limb of curve I_3 is the sum of an A—B bond energy shown in curve I_1, the resonance energy shown in curve IV, and a repulsion energy whose curve is not shown in the diagram but is very similar to curve II.

The critical energy depends on the repulsive energy between A—B and C, the bond energy of A—B and the lowering of energy by resonance. Strong repulsions and high bonding energies mean high critical energies, but strong resonance at small separation of A and B results in low critical energies. The stronger the bond between B and C, the more rapidly will the resonance increase with separation of A and B. Low critical energies and fast reactions are then associated with a reagent that combines strongly with B, and slow reactions are probable when B is already strongly combined.

It is only at separations corresponding to the maximum of curve I_3 that the bond energies of A—B and B—C determine the critical energy. At greater separation these bond energies determine the shape of the transition curve (III), and the probability of the reaction. Thus if curve I_1 were drawn flatter at the top but not changed for smaller separations of A and B, the maximum of curve I_3 would not be changed, but the maxima of curve I_1 and I_2 would be lowered. The reaction corresponding to such a curve would have the same critical energy as that depicted in Figure 48, but would have a higher probability. Curve I_1 is a typical Morse curve and its shape is characteristic of energy curves for the dissociation of diatomic molecules, but the curves for complicated organic molecules, especially in the presence of solvents, and possibly dissociating into ions, may have very different shapes. The reaction rate is therefore not determined by the critical energy nor by the bond energies discussed above. It must depend in a complicated way on the entire functional relationship between energy and configuration, and such functions cannot be universally depicted by a set of curves varying in only a few parameters.

The transition state and energy barriers can also be shown by an energy contour map. Figure 49 is such a map drawn to correspond to the graphs of Figure 48. In this map the distances of B and C from a fixed A are the coordinates. The line III is the transition state and separates the field into two parts: that on the left is A—B C; that on the right is A B—C. The length of III between contour lines is a measure of the probability factor of the reaction. The lowest energy contour line touching III is the critical energy of the reaction.

The same formal course for the reaction indicated by arrows in Figure 48 is shown by arrows in the contour map. An actual course for the reaction would be quite different. When C meets A—B, B is not at rest. It may be moving away or towards A, and may change

its direction of motion more than once during the approach and separation of A and C. Similarly, the change from kinetic to potential energy and back does not occur in the regular way shown by the arrows, as the interchange of kinetic and potential energy of B does not keep in step with that of C. The system zig-zags its way across the contour map during the reaction. Further, during the collision, energy may pass to or from the other degrees of freedom and still further complicate the situation. This randomness is a justification for assigning an entropy to the transition state.

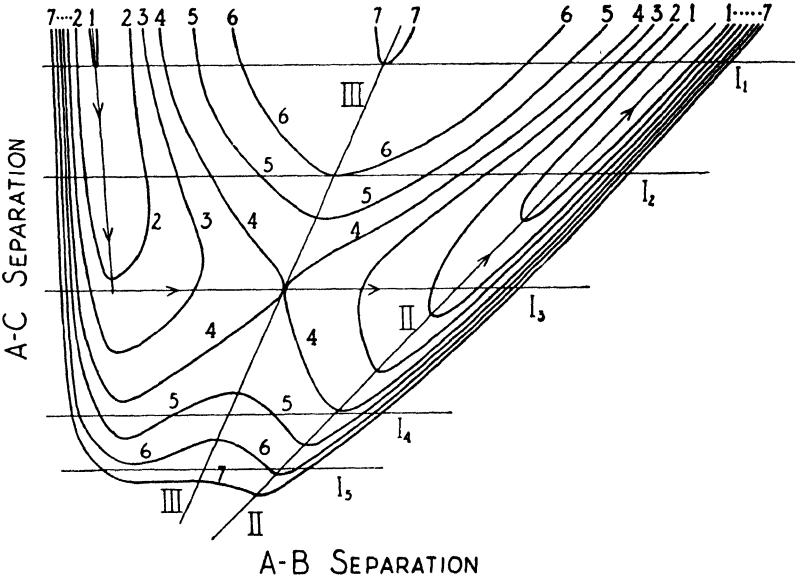


Figure 49. Potential energy surface for the reaction A–$B + C \rightarrow A + B$–C. The Roman numbers represent the sections whose contours are shown in Figure 48.

Contour energy maps of this type are generally drawn with the central atom stationary and the two dimensions are the distances of A and C, respectively, from B. We have taken A as fixed, so that any section parallel to the B axis gives an I_1 curve in Figure 48, by plotting the contour energies against the distance along the section. If the same thing is done for a section of the almost vertical ravine on the left-hand side of the map, an energy curve for the repulsion of C by A—B can be obtained. Curve II of Figure 48 can be obtained from a section along the slanting ravine on the extreme right, and curve III of Figure 48 can be drawn from the section along the saddle marked III in Figure 49.

39. MOLECULAR ASSOCIATION

In preceding chapters we have assumed the association of molecules by a hydrogen bond to be a resonance phenomenon. The formation of these and other molecular associations should be understandable in terms of a reaction theory that includes the resonance principle.

In order to simplify the discussion of the reaction $A—B + C \rightarrow A + B—C$, we neglected the energy of the resonance ($A—B\ \ C$, $A\ \ B—C$) where B is at its equilibrium bond distance from one of the other atoms. Actually this resonance has a finite energy for all distances. This means that the repulsion curve II, Figure 48, includes a small resonance effect, and the resonance curve (IV) gives the change in resonance energy as B is moved from an equilibrium point, rather than the whole resonance energy. If we do not neglect this resonance, the repulsion curve (II) should be drawn with a shallow minimum, as the forces of attraction (coulombic and resonance) are more persistent than those of repulsion. This minimum should be situated at a separation of A and $B—C$ where the repulsion is negligible, but small attractions (van der Waal's forces) are still left.

In a reaction for which the repulsion curve is less steep than that shown in the figure, the repulsion is negligible at a smaller molecular separation. From this it follows that the residual resonance energy, the increase of energy on infinite separation, and the depth of the minimum in the repulsion curve are all greater in the new case than in the old. If these phenomena are sufficiently extreme, a definite compound of A and $B—C$ is obtained. There are two molecular associations, $A—B \cdots C$ and $A \cdots B—C$, and they are separated by an energy barrier and a transition state.

The factors—low repulsions and high resonance energies—that tend to produce these molecular associations are those that lower the energy barrier so that if two isomeric molecular compounds $A—B \cdots C$ and $A \cdots B—C$ existed, the change from one to the other would be rapid, and the separation of the isomers would be difficult or impossible.

The restoring force excited by the displacement of a bonded atom is at first proportional to the displacement (Hooke's law); then it increases less rapidly and reaches a maximum; thereafter it decreases with the displacement. As a first approximation, the forces on B in the system $A—B + C \rightarrow A + B—C$, with A and C stationary,

can be taken as the resultant of the A—B and B—C bonding forces. Unless A and C are very close to each other, the net force on B becomes zero at three places in the displacement from the normal A—B bond distance to the normal B—C bond distance. Two of these are positions of stable equilibrium with respect to the motion of B, and correspond to slightly displaced A—B and B—C bonds. The third is a position of metastable equilibrium and corresponds to a transition configuration. From this it follows that, in the molecular association A—$B \cdots C$, the separation of A and B is slightly greater than it is in A—B.

However, if A and C are sufficiently close together, it is possible to have a configuration such that any displacement of B results in an increase of energy. This configuration is one of stable equilibrium with respect to a motion of B, and it is the only stable or metastable equilibrium that can be obtained with the given distance between A and C. This case corresponds to an I_n curve that has only one energy minimum and no maximum. Curve I_5, Figure 48, approximates but does not quite reach this condition. If the reactants and products are so anomalous that A and C, when brought sufficiently close to give a single stable position for B, do not excite stronger repulsions than can be compensated by resonance or other attractions, there is only one stable configuration of A, B, and C. This is a molecular association that is neither more nor less A—$B \cdots C$ than it is $A \cdots B$—C. Further, between A—$B + C$ and $A + B$—C there is no transition state. Reactants and products are the results of two modes of dissociation of the compound ABC.

Every substitution reaction implies a molecular association, and we can separate the reactions into three types. In the first the association is so weak that the association corresponding to any particular reaction is lost among those corresponding to the numerous reactions possible to any assembly of molecules. In the second the association is strong and forms definite molecular species. There are two associations—one of reactants and one of products—though either one of these may be weak. Between these two associations a transition state exists. The third type is also a strong association, but only one compound exists, and there is no transition state. The compound has, however, two sets of dissociation products, corresponding to A—B C and A B—C.

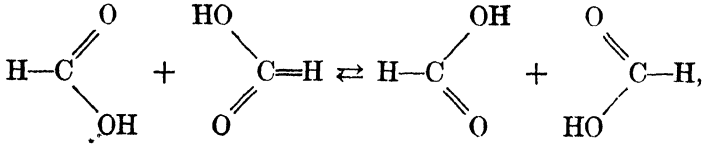
The chief deductions that can be made concerning a molecular association and the reaction that has been assumed for it are (1) that if the association is strong, the reaction from which it is derived

is fast, (2) that the atomic configuration of the molecular association is one that would favor the reaction, (3) that the atomic distances are greater than normal bond distances, (4) that if the reaction has a transition state, there are isomeric associations for unsymmetrical reactions and, in place of isomerism, a non-central position of the intervening atom if the reaction is symmetrical: e.g., $A—B + A \rightleftarrows A + B—A$, and (5) that if the reaction has no transition state, there is no isomerism but, instead, a centrally placed atom for a symmetrical reaction. Unfortunately the relationships (4) and (5) which distinguish the two types of strong associations are often beyond actual experimental test. Lack of isomerism is only negative evidence, and in cases where low energies are to be expected for transition states it is quite unconvincing. A few examples of these deductions are given below.

Substitution reactions of hydrogen are generally faster than those of methyl, so that we would not expect the compound $CH_3F_2^-$ from the reaction $F—CH_3 + F^- \rightarrow F^- + CH_3—F$, but do expect HF_2^- from $F—H + F^- \rightarrow F^- + HF$. Triiodide ion is probably derived from $I^- + I—I \rightarrow I—I + I^-$ and should be linear. If R_3NI_2 is derived from $R_3N + I—I \rightarrow R_3\overset{+}{N}I + I^-$, then the structure is $N—I—I$, but if the reaction is $I—\overset{+}{N}R_3 + I^- \rightarrow I^- + \overset{+}{N}R_3I$, the structure is

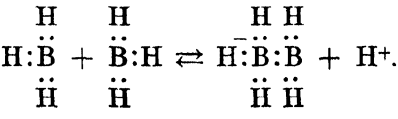
$$\begin{array}{c} I \\ | \\ R_3N—I. \end{array}$$

This has never been tested, but the former is by far the more probable of the alternatives. The distances between atoms bonded by protons are greater than the sum of the covalent radii of the bonded atoms. If the evidence that the connecting protons are not centrally located between the molecules of diformic acid is accepted, the compound is derived from the reaction

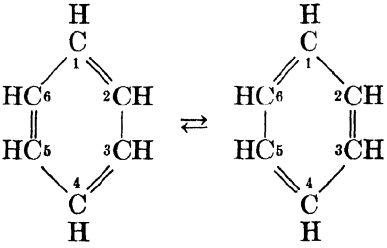


and this reaction has a transition state. If the hydrogen is central in HF_2^-, the reaction $F—H + F^- \rightleftarrows F^- + H—F$ has no transition state. There is no direct evidence of this; the assumption is made

because the fluorines in HF_2^- are unusually close for proton-linked atoms. The ethane-like structure with a somewhat high boron-to-boron distance of B_2H_6 suggests that it is a simultaneous derivative of the six forms resulting from the reactions of the type



This way of considering the formation of molecular association as derived from reactions is applicable to ordinary resonating compounds like benzene. The only difference is that in a compound like benzene the reaction is an intramolecular one, and strong association is easier to obtain, as the repulsion forces have already been overcome by bond formation. Benzene is then the association complex of the diene-type reaction in which the conjugate diene 3,4,5,6 reacts with the ethylene 1,2:



The evidence for the equal distances between the carbon atoms shows the lack of a transition state.

Actually there is nothing in the organic theory of molecular resonance proving that there is only one energy maximum in the I_n curves. If we imagine that curve I_3, Figure 48, has two maxima, there is a minimum between them. The intermediate would then be stable to any small change of configuration, and would be a definite compound. However, it seems simpler and better to assume a single maximum unless definite evidence for a stable intermediate has been obtained. In that case the reaction would be complex and there would be transition states for each successive step.

40. THE QUANTUM MECHANICAL TREATMENT

A quantum mechanical treatment of chemical reaction was first attempted by London.[8] It has since been greatly extended by

[8] London, F., *Z. Elektrochem.*, **35**, 555 (1929).

others, most notably by Eyring and Polanyi.[9] The problem is so complicated that simplification is necessary.[10] The process is assumed to occur so slowly that the particles are practically at rest, and the energies are, therefore, all potential. From the way these energies change, it is shown that there are energy minima corresponding to reactants and products and an energy barrier between them. The system travels from reactants to products through a pass in this barrier. The rate of the reaction depends on the height and shape of this pass.

The energy of a system of two atoms can be divided into two parts,

$$E = Q_{AB} + \alpha_{AB}, \tag{23}$$

both being integral functions involving the eigenfunctions of the undisturbed atoms, ψ and ϕ, and the potential energy function V.

$$Q_{AB} = \int \psi^2(x) V \phi^2(y)\, dx\, dy \tag{24}$$

and

$$\alpha_{AB} = \int \psi(x)\phi(x) V \psi(y)\phi(y)\, dx\, dy. \tag{25}$$

The first quantity may be called the coulombic energy and the second the exchange energy. Both quantities depend on the distance between the atoms. At the distance for which E is at a minimum, we have an unexcited molecule, and $Q_{AB} + \alpha_{AB}$ is the potential energy of the bond A—B, or the energy of dissociation at absolute zero less the zero-point energy.

If we introduce a third atom, the system becomes a combination of the six possible functions Ψ_1, Ψ_2, etc. of the type $\psi(x)\phi(y)\chi(z)$, $\psi(x)\phi(z)\chi(y)$, etc., where $\psi(x)$, $\phi(y)$, and $\chi(z)$ are functions for the three atoms.

The secular equation is:

$$\begin{vmatrix} W_{11}-E & W_{21} & W_{31} & W_{41} & W_{51} & W_{61} \\ W_{12} & W_{22}-E & W_{32} & W_{42} & W_{52} & W_{62} \\ W_{13} & W_{23} & W_{33}-E & W_{43} & W_{53} & W_{63} \\ W_{14} & W_{24} & W_{34} & W_{44}-E & W_{54} & W_{64} \\ W_{15} & W_{25} & W_{35} & W_{45} & W_{55}-E & W_{65} \\ W_{16} & W_{26} & W_{36} & W_{46} & W_{56} & W_{66}-E \end{vmatrix} = 0 \tag{26}$$

where $W_{ij} = \int \Psi i V \Psi j\, dx\, dy\, dz$.

[9] Eyring, H., and Polanyi, M., *Z. physik. Chem.*, **B12**, 279 (1931).

[10] For a more detailed discussion and further references, see the Symposium on "Reaction Kinetics" published in *Trans. Faraday Soc.*, **34** (January, 1938).

$$\text{When } i = j,\ W_{ii} = \int \psi^2(x)\phi^2(y)\chi^2(z)V\,dx\,dy\,dz$$
$$= \int \psi^2(x)\phi^2(y)V\,dx\,dy \int \chi^2(z)\,dz$$
$$+ \int \psi^2(x)\chi^2(z)V\,dx\,dz \int \phi^2(y)\,dy$$
$$+ \int \phi^2(y)\chi^2(z)V\,dy\,dz \int \psi^2(x)\,dx \qquad (28)$$

and in each term one integral is that for the coulombic energy of the two atoms making a bond, and the other is unity. Hence

$$W_{ii} = Q_{AB} + Q_{AC} + Q_{BC}, \qquad (28)$$

and is the coulombic energy, Q_{ABC}, for the combination of the three atoms. When $i \neq j$,

$$W_{ij} = \int \psi(x)\chi(x)\psi(y)\phi(y)\phi(z)\chi(z)V\,dx\,dy\,dz \qquad (29)$$

or a similar integral with one of the functions squared, e.g.,

$$W_{ij} = \int \psi^2(x)\phi(y)\chi(y)\phi(z)\chi(z)V\,dx\,dy\,dz. \qquad (30)$$

When the former of these values for W_{ij} is broken into three terms, as was done above for W_{ii}, each term is multiplied by $\int \psi(z)\chi(z)\,dz$ or another integral of two functions for one co-ordinate. These integrals are approximately zero, so W_{ij} of this type equals 0. When the other type of W_{ij} is broken into terms, two are equal to zero as above, but the other is of the type

$$\int \psi(y)\chi(y)\phi(z)\chi(z)V\,dy\,dz \int \phi^2(x)\,dx$$

where $\int \phi^2(x)\,dx = 1$, and $\int \phi(y)\chi(y)\phi(z)\chi(z)V\,dy\,dz$ is the exchange integral for making a bond between two atoms. The secular equation then becomes:

$$\begin{vmatrix} Q_{ABC}-E & 0 & 0 & \alpha_{BC} & \alpha_{AC} & \alpha_{AB} \\ 0 & Q_{ABC}-E & 0 & \alpha_{AC} & \alpha_{AB} & \alpha_{BC} \\ 0 & 0 & Q_{ABC}-E & \alpha_{AB} & \alpha_{BC} & \alpha_{AC} \\ \alpha_{BC} & \alpha_{AC} & \alpha_{AB} & Q_{ABC}-E & 0 & 0 \\ \alpha_{AC} & \alpha_{AB} & \alpha_{BC} & 0 & Q_{ABC}-E & 0 \\ \alpha_{AB} & \alpha_{BC} & \alpha_{AC} & 0 & 0 & Q_{ABC}-E \end{vmatrix} = 0. \qquad (31)$$

The only acceptable roots of this equation are:

$$E = Q_{AB} + Q_{BC} + Q_{AC}$$
$$\pm\sqrt{\alpha_{AB}^2 + \alpha_{BC}^2 + \alpha_{AC}^2 - \alpha_{AB}\alpha_{BC} - \alpha_{BC}\alpha_{AC} - \alpha_{AC}\alpha_{AB}}. \qquad (32)$$

London showed that this would give minimal energies when two atoms are near and the other distant, and that the easiest approach of the third atom is along the bond line. For this type of approach he assumed the interactions of the distant atoms to be zero, and neglected the coulombic energy. This gives:

$$E = \sqrt{\alpha_{AB}^2 + \alpha_{BC}^2 - \alpha_{AB}\alpha_{BC}}. \qquad (33)$$

The lowest point in the energy barrier is reached when $\alpha_{BC} = \frac{\alpha_{AB}}{2}$, and the energy is $\left(1 - \frac{\sqrt{3}}{2}\right)\alpha_{AB}$ above the level for the compound A—B. The critical energy is then estimated as 0.134 of the exchange part of the bond energy.

The conclusions that we can draw from London's theory are: (1) that the main interactions of three monovalent groups, A, B, and C, yield three compounds, AB, BC, and AC, but not ABC; (2) that the reaction of the spare atom with one of these compounds occurs through an end-on rather than a broadside collision; (3) that this reaction requires a much smaller energy of activation than that necessary to dissociate the molecule; and (4) that this energy can be expressed as a function of the energies of the three possible bonds, A—B, B—C, and A—C. Although the theory was developed for valences due to odd electrons, presumably the above conditions hold for valences arising from unshared pairs of electrons, and from incomplete valence shells.

The above conclusions are similar to those that might be drawn from the qualitative resonance theory of the preceding section. London's equation for the critical energy, $\epsilon_c = \alpha_{AB} - \frac{\sqrt{3}}{2}\alpha_{AB}$, where α_{AB} is the energy of the normal A—B bond, makes the rate a function of the A—B bond but not of the B—C bond, except insofar as it is necessary for this bond to be so strong that at some distance α_{BC} can equal $\frac{\alpha_{AB}}{2}$. This does not agree with our previous treatment, in which the tendency of B to bond with C was an important factor. The discrepancy arises from the over-simplification used to obtain $\epsilon_c = \alpha_{AB} - \frac{\sqrt{3}}{2}\alpha_{AB}$.

40a. The Eyring-Polanyi method. Eyring and Polanyi[11] have

[11] Eyring, H., *Naturwissenschaften*, **18**, 914 (1930); Eyring, H., and Polanyi, M., *Z. physik. Chem.*, **12B**, 279 (1931); Eyring, H., *J. Am. Chem. Soc.*, **53**, 2537 (1931).

avoided some of London's assumptions. They start with equation 32 and the conclusion that the end-on collision is by far the most effective. They obtain α from the equation for the bond energy:

$$Q + \alpha = D[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}] \qquad (34)$$

where D is the heat of dissociation plus the zero point energy, r_0 is the equilibrium bond distance, r is the distance between the atoms, and a is equal to a constant for all bonds multiplied by the frequency of the lowest vibrational level and the square root of $\frac{\mu}{D}$, where μ is the reduced mass. This empirical equation is the Morse function for bond energies.[12] The constants in it are generally obtainable for diatomic molecules. The coulombic energy is obtained by assuming that it is 10 or some lower per cent of the total binding energy. Conclusions are considered valid only when reasonable variations in the per cent of the coulombic energy make little difference.

With these assumptions the energy for any linear arrangement of A, B, and C can be calculated. All these arrangements can be depicted in two dimensions, usually the distances of A and C from the central atom, and the energies put in as contour lines. The map shows two valleys separated by a saddle. The height of the lowest point in this saddle above the lowest point in the valley for reactants is the critical energy. With this method the heat of activation of the reaction H_2 (ortho) + H $\rightarrow$ H_2 (para) + H was calculated, and the result agreed with the observed value within a few thousand calories.

The calculations show a shallow depression between two maxima in the transition from H—H H to H H—H. This corresponds to the molecule H_3. Kassel[13] considers that this depression is not real but due to a sensitiveness to error in this neighborhood.

The method can be used for reactions between saturated molecules; e.g., $A—B + C—D \rightarrow A—C + B—D$. The energy for four atoms is

$$E = Q_{AB} + Q_{CD} + Q_{AC} + Q_{BD} + Q_{AD} + Q_{BC}$$
$$+\sqrt{\tfrac{1}{2}[(\alpha_{AB} + \alpha_{CD} - \alpha_{AC} - \alpha_{BD})^2 + (\alpha_{AB} + \alpha_{CD} - \alpha_{AD} - \alpha_{BC})^2 + (\alpha_{AC} + \alpha_{BD} - \alpha_{AD} - \alpha_{BC})^2]}. \qquad (35)$$

The stable configurations are the atoms combined in pairs. The best approach for the reaction is $A—B$ and $C—D$ in the same plane,

[12] Morse, P. M., *Phys. Rev.*, **34**, 57 (1929).

[13] Kassel, L. S., *Kinetics of Homogeneous Gas Reactions*, page 57. Chemical Catalog Co., New York, 1932.

with A near C and B near D. In this type of reaction four atomic centers are involved simultaneously in the transition state, whereas in the reaction previously discussed only three atomic centers were concerned. These two types can be called four-center and three-center reactions, respectively.

A four-center reaction always has the alternative mechanism of the dissociation of a molecule followed by the reaction of its parts with the other molecule. Eyring showed by calculation that the energy of activation of hydrogen directly reacting with iodine is less than what would be needed for a dissociation into atoms followed by a reaction of an atom with a molecule; but that the latter type of mechanism would require less heat of activation than the direct combination of H_2 and Cl_2. This deduction is in agreement with experiment.

Chapter IX

THE REACTIONS OF ACIDS AND BASES WITH NEUTRAL SUBSTANCES—THREE-CENTER REACTIONS

The critical energy is lower for reactions involving a saturated molecule and groups whose valences are not all satisfied than for those between entirely saturated molecules, and the former reactions are generally faster than the latter. Consequently, not only do we find many reactions whose equations show that they are three-centered, but even when the equations suggest four centers, the mechanism includes at least one step of the three-center type. Groups with incompletely satisfied valences fall into three types: the odd molecule, the base, and the acid, characterized respectively by the presence of an unpaired valence electron, the presence of an unshared pair of valence electrons, and the deficiency of a pair of valence electrons.

One of the products of a simple reaction between an odd molecule and a saturated one is another odd molecule. This is more likely to react with a saturated molecule than to become inert by reacting with another odd molecule whose concentration is in most cases very low. These conditions are apt to lead to a chain reaction. The rates of chain reactions depend on so many factors that the relationships between structure and rate are complex. On the other hand, acids and bases reacting with saturated molecules do not generally form chains, and, though the reactions are usually complex, their rates and the structures of the reactants are more simply related than are those of chain reactions. Further, acids and bases are comparatively common substances and a great number of common reactions are wholly or in part the breaking of a bond by an acid or base with the formation of another acid or base. For these reasons we shall ignore the reactions of odd molecules[1] and consider those of acids and bases.

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[1] For a review of the appearance of free radicals in organic reactions, see Wittig, G., *Z. angew. Chem.*, **52**, 89 (1939).

In the sense of a reactant, we do not confine the term "acid" to a hydrogen compound but use it in the generalized sense to denote a substance that has a strong affinity for unshared valence-electron pairs of an atom of some other molecule. Some objection may be raised to the implication that this property implies an unsaturated valence. One might choose to consider the valence of a hydrogen in an acid like H_3O^+ as satisfied, and classify its compounds as molecular associations. However, we do not consider the forces that lead to molecular association as fundamentally different from other bond-forming forces, and there is no reason to believe that these forces act differently in reactions. Similarly, we do not need to distinguish between the acidity of an atom that has less than eight valence electrons and that of an atom that has eight valence electrons but can have an expanded valence shell. Thus hydrogen ion, the boron of BF_3, the hydrogen of H_3O^+, the sulfur of SO_3, the iodine of I_2 (note its tendency to form brown compounds with R_3N, I^-, ROH) are all acidic atoms and can show their acidity by practically instantaneous reaction with bases, or may function as acids in reactions with more saturated molecules.

41. THE MECHANISMS OF THE REACTIONS

Before comparing the rates of analogous acidic and basic reactions, we should consider some of their peculiarities and possible mechanisms. Had we a solution for the relationship of rate and structure, the mechanisms of reactions could be deduced from it. In special cases this has been done, as for instance the deduction of the mechanisms of the reactions of hydrogen and halogens by Eyring (section 40a). However, at the present time the answer to the question of the relationship of rate and structure must depend chiefly on our ability to compare the rates of analogous processes and hence on a knowledge of the mechanisms of reactions. This knowledge is often indefinite even when the kinetics of the reaction have been investigated. The comparison of rates and the elucidation of the kinetics of reactions must be used to supplement one another.

According to the transition-state theory, the rate of a simple reaction is proportional to the equilibrium constant of the formation of the transition state from the reactants (Chapter VIII, page 377). The mechanism is important only insofar as it shows the composition or structure of the transition state of the rate-determining step. The rate depends on the equilibrium between the reactants involved up to this stage of the reaction, on the one hand, and on the transition

state and products formed at this stage of the reaction, on the other hand. This principle is often of value in simplifying the problem. Thus we shall find it unnecessary to consider whether the valence-unsaturated reagent (acid or base) is a catalyst or a reactant. The complex reactions all end with a rapidly attained equilibrium between the acids and bases present. Whether, after this equilibrium has been reached, the original reagent is largely neutralized or practically unchanged is not pertinent to the relation of rate to structure, but determines whether the reagent is a catalyst or reactant.

41a. The Walden inversion. In the last chapter we showed that for the reaction of an odd molecule with a bonded pair of atoms, an approach along the bonding line is most favorable for a reaction. This is in general the best type of approach for the reaction of a valence-unsaturated atom with a saturated molecule, whether the unsaturation of the valence is due to an unpaired electron, to an unshared pair of electrons, or to a lack of electrons. Consequently, in a simple substitution the new group takes a position which is the mirror image of that previously occupied by the replaced group. On an asymmetrical atom this type of substitution changes a dextro to a laevo configuration. That this inversion sometimes occurs was first shown by Walden,[2] who found that, in the cycle Malic acid → Chlorosuccinic acid → Malic acid, the laevo malic acid is changed to its dextro isomer. Olson[3] has assumed that, in any simple reaction of the type $A—B + C \rightarrow A + B—C$, a Walden inversion occurs, and if B is an asymmetric atom it can be observed. This assumption has been fully substantiated by experiment. It does not mean that every substitution of a group on an asymmetric atom must produce a different configuration, for in that case Walden's cycle, d form → Intermediate → l form, would not be possible. The products of a reaction may be the result of a series of steps. If there is an even number of steps and a Walden inversion occurs at each, the product has the same configuration as the original substance. Further, it has not been shown that the reaction type $A—B + C—D \rightarrow A—C + B—D$ necessarily leads to a Walden inversion. According to Eyring, a broadside collision with C near A and B near D is the most favorable one for this type of reaction. This mechanism does not favor an inversion.

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[2] Walden, P., *Ber.*, **26**, 210 (1893); **29**, 133 (1896).

[3] Olson, A. R., *J. Chem. Phys.*, **1**, 418 (1933); Bergman, E., Polanyi, M., and Szabo, A. L., *Trans. Faraday Soc.*, **32**, 843 (1936); Olson, A. R., and Long, F. A., *J. Am. Chem. Soc.*, **56**, 1294 (1934).

The Walden inversion is a valuable test for a suggested mechanism. Any mechanism that assumes a single step of the type $A—B + C \rightarrow A + B—C$ must be discarded if the reaction does not lead to inversion. The theory also shows that if steric factors make the attack from the back difficult, the reaction is slow. As a by-product of the theory, Olson was able to obtain the rate of reaction $Cl—R + Cl^- \rightarrow Cl^- + R—Cl$ from the rate of racemization where the halogen is bonded to an asymmetric carbon atom in R. A more generally applicable method of measuring the rate of an exchange reaction is to use radioactive halide ions. It has been shown that the two methods give the same result.[4]

41b. The differentiation of rate-determining and preliminary reversible reactions. In considering an acidic or basic complex reaction, it is necessary to decide whether or not the actual reaction of the acid or base is the rate-determining step, before comparing the rates of analogous reactions. Otherwise we do not know whether the reactions are truly analogous or not.

If the reaction of the acid or base with the substrate is a preliminary slow step, or a simple reaction, then $k = k_1$, where k is the rate constant of the overall reaction and k_1 is the constant for the acidic or basic reaction. If, however, the reaction of acid or base with the substrate is a preliminary equilibrium reaction, then $k = Kk_3$, where K is the equilibrium constant of the acidic or basic reaction and k_3 is the rate constant of a slow follow reaction involving a product of the first equilibrium. In the rare coincidence that $k_3 \doteq k_2$, where k_2 is the constant for the reversal of the acidic or basic reaction, the rate constant is $k = k_1 \dfrac{k_3}{k_3 + k_2}$.

A kinetic study of the reaction may determine whether the acidic reaction is rate-determining or not. The mechanism of the reaction is, in general:

$$nA + mB \rightleftarrows sI + pC, \qquad qI + rD \rightarrow E.$$

If the first step determines the rate, the velocity function for the reaction is $[A]^n[B]^m$. If the first step is fast enough to maintain equilibrium, this function is $\dfrac{[A]^{nq/s}[B]^{mq/s}[D]^r}{[C]^{pq/s}}$. However, for acidic

[4] Hughes, E. D., Juliusburger, F., Masterman, S., Topley, B., and Weiss, J., *J. Chem. Soc.*, 1525 (1935); Hughes, E. D., Juliusburger, F., Scott, A. D., Topley, B., and Weiss, J., *J. Chem. Soc.*, 1173 (1936); Cowdrey, W. A., Hughes, E. D., Nevell, T. P., and Wilson, C. L., *J. Chem. Soc.*, 209 (1938).

reactions it is not rare for q/s to be unity, p to be zero, and r to be zero, and then a simple kinetic study does not decide whether the reaction with acid is rate-determining or a preliminary fast reversible step. This also applies to reactions with bases.

When a substrate is an acid of appreciable strength and one of its reactions is catalyzed by a base, the dissociation constant of the substrate will be included in the rate function. By itself this kinetic peculiarity does not tell us whether the reaction is one of the ion of the substrate or a base-catalyzed reaction of the undissociated substrate. The neutralization of the substrate will be a fast reversible reaction, and the same rate laws will hold for either alternative. The same principle holds when a substrate is a base of appreciable strength and the reaction is catalyzed by acid. For instance, if the auto-oxidation of catechol in alkaline solution is the auto-oxidation of the negative ion $C_6H_5O_2^-$, or is a reaction of catechol, oxygen, and hydroxide ion, the rate at constant oxygen pressure is in both cases proportional to $\frac{A[OH^-]}{K_a[OH^-] + K_w}$, where A is the known sum of the concentrations of $C_6H_5O_2^-$ and $C_6H_6O_2$ and K_a is the first dissociation constant of catechol. A study of the rate as a function of A and $[OH^-]$ does not distinguish between these mechanisms, but can be used to measure K_a.

41c. The salt effect. The relative rate constants for the reaction $A + B \rightarrow C$ in two solvents can be expressed as $\frac{k}{k_0} = \frac{K_\tau}{K_{0\tau}}$, where K_τ and $K_{0\tau}$ are the concentration equilibrium constants for the formation of the transition state in a given solvent and in a reference solvent, respectively. In dilute solutions in the reference solvent we can arbitrarily put the activities of A, B, and τ equal to their concentrations. Then $K_{0\tau}$ is also the thermodynamic equilibrium constant independent of solvent. The activities in the other solvent are then $\gamma_A[A]$, $\gamma_B[B]$, and $\gamma_\tau[\tau]$, where γ is the activity coefficient. Then

$$K_{0\tau} = \frac{[\tau]_0}{[A]_0[B]_0} = \frac{\gamma_\tau[\tau]}{\gamma_A[A]\gamma_B[B]} = \frac{\gamma_\tau}{\gamma_A\gamma_B}K_\tau, \quad \text{and} \quad k = k_0\frac{\gamma_A\gamma_B}{\gamma_\tau}.$$

This equation is valuable only when we can predict something about the activity coefficient of the transition state.

When the standard environment is a highly dissociating solvent such as water, we know how the activity coefficient of an ion is changed by the addition of small quantities of a salt. As a first

approximation for dilute solutions, the effect of the salt is the same for all salts in solutions of the same ionic strength (the sum of the products cZ_e^2 for all species of ions), and the activity coefficient of an ion is affected by the ionic strength according to the square of the ionic charge. For water solutions at 25°C., this degree of approximation leads to the equation

$$\log \gamma = -0.5 Z_e^2 \sqrt{c} \quad ,$$

where Z_e is the charge of the reacting ion and c is the concentration of a uni-univalent salt.

In a reaction between ions, we know the charges of the ions and hence the charge on the transition state. We can then apply the above equation and obtain an approximate value for the effect of added salt on the reaction rate when the concentrations of all ions are small. Then, if the reaction is between ions of the opposite charge, the reaction is slower in salt solution than in pure water, while the reverse is true if the reacting ions have the same sign. If the reaction is between an ion and a neutral substance, the charge on the transition state is the same as on the reacting ion, and the rate is the same in water and a salt solution. These deductions can be summarized by the equation

$$\log k = \log k_0 - 0.5\sqrt{c}[Z_{eA}^2 + Z_{eB}^2 - (Z_{eA} + Z_{eB})^2],$$

where the sign of Z_e is determined by the sign of the charge on the ion. This equation has been confirmed experimentally in dilute solution. The above is Brönsted's theory of the primary or exponential salt effect. Salts affect the activity coefficients of neutral substances, and affect the activity coefficients of small ions more than those of large ones. Besides, each salt has its own specific effect on a reaction. There are, therefore, secondary and specific salt effects as well as primary ones, but we shall not discuss these.

The primary salt effect is sufficiently large and well substantiated to be used as a test for a suggested mechanism of a reaction. It does not necessarily distinguish a rate-determining reaction of ions from preliminary fast reactions of ions followed by a rate-determining step. For instance, $A^+ + B^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB^{++}$, $C + AB^{++} \xrightarrow{k_3} D^{++}$ has the same primary salt effect when $k_3[C] \gg k_2$ as when $k_2 \gg k_3[C]$. The equilibrium constants for $A^+ + B^+ \rightarrow r$ and $A^+ + B^+ \rightarrow AB^{++}$

are equally affected by salt, and k_3 has no salt effect. On the other hand, the mechanism $A^+ + B^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} C^+ + D^+$, $C^+ + E \xrightarrow{k_3} F^+$ has a different salt effect according as $k_3[E] > k_2[D^+]$ or $k_2[D^+] > k_3[E]$. The former case gives a positive salt effect; the latter, none. The salt effect is determined by the reactants used and products formed up to the transition state of the rate-determining step. In the above-mentioned four possibilities, the salt effects are determined by the equilibria of the following reactions $A^+ + B^+ \rightarrow \tau_{AB^{++}}$, $A^+ + B^+ + C \rightarrow \tau_{ABC^{++}}$, $A^+ + B^+ \rightarrow \tau_{AB^{++}}$, and $A^+ + B^+ + E \rightarrow \tau_{CE^+} + D^+$. The first three reactions are the formations of divalent ions from pairs of similarly charged monovalent ions and must have positive primary salt effect. The last is the formation of two monovalent ions from two monovalent ions and should have no primary salt effect.

41d. Reaction with both hydrogen ion and undissociated acid. Many solvents react rapidly with acids or bases or both. For instance, water reacts with either acid or base. If then water is the solvent and an acid is the reagent, three different acids are present: H_2O, H_3O^+, and the acid that was added. The substrate reacts with all three acids, and the reaction is the sum of three reactions. In the same way, in an aqueous solution of a base, three bases—H_2O, OH^-, and the added base—are present. All of these bases may react with the substrate. The separate reactions may lead to the formation of the same products, so that the analysis of the products does not always distinguish the reactions.

The rates of individual simultaneous reactions can often be obtained from a series of measurements of the rates of the overall reaction at various concentrations. This can be done for the reactions of the mixture of acids obtained when an acid is added to water or a similar solvent. Assuming a first-order rate function with respect to each reactant, the rate is

$$\frac{dx}{dt} = k_1[H_3O^+][S] + k_2[HA][S] + k_3[S],$$

where S is the substrate, HA is the undissociated acid, k_1 is the constant for the reaction with hydronium ion, k_2 is that with the acid, and k_3 is that for the reaction with water, and includes the constant concentration of water. The values of $[HA]$ and $[H_3O^+]$ can be obtained from the amount of acid added and the dissociation constant of the acid. By measuring the rate at different concentra-

tions of acid, the resulting simultaneous equations can be solved for k_1, k_2, and k_3.

Another method of varying the concentrations of H_3O^+ and HA is by adding the salt of HA, thus decreasing H_3O^+ and increasing HA. Similarly, if the acid HA is weak, we can increase H_3O^+ without much affecting the concentration of HA by adding a strong acid. In these methods it may be necessary to assume reactions with hydroxide ion and the ion of the added acid. These introduce new unknown constants into the rate laws, but where the dissociation constants are known this presents no difficulty. When salts are added the rates should all be measured at the same ionic strength to compensate for salt effects. The same methods can be used for basic reactions.

The method is of course at fault if the rate laws are not those assumed. Such errors can be detected, for if the assumed rate laws are wrong, we do not obtain constants over wide ranges of concentrations.

If it is found that the undissociated acid reacts as well as the hydronium ion that it forms, the assumed reaction mechanism must be such that the acid as well as its hydrogen ion is included in the transition state of the master reaction. Thus if the reaction $C—B \rightarrow C + B$ is catalyzed by both hydronium ion and acetic acid, we may assume for the acetic-acid-catalyzed reaction the mechanisms

$$C—B + HAc \underset{k_2}{\overset{k_1}{\rightleftarrows}} C—BH^+ + Ac^-, \qquad C—BH^+ \xrightarrow{k_3} C + B + H^+,$$

with $k_3 \gg k_2$;

$$C—B + HAc \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + BHAc, \qquad BHAc \xrightarrow{k_3} B + HAc,$$

with $k_3 \gg k_2$ or $k_2 \gg k_3$;

or

$$C—B + HAc \underset{k_2}{\overset{k_1}{\rightleftarrows}} C—BHAc \xrightarrow{k_3} C + B + HAc,$$

with $k_3 \gg k_2$ or $k_2 \gg k_3$;

but we cannot assume the mechanism

$$C—B + HAc \underset{k_2}{\overset{k_1}{\rightleftarrows}} C—BH^+ + Ac^-, \qquad C—BH^+ \xrightarrow{k_3} C + B + H^+,$$

with $k_2 \gg k_3$,

because, in this last mechanism, $C—BH^+$ can be obtained in equilibrium concentration by the reaction $C—B + H_3O^+ \rightarrow C—BH^+ + H_2O$, and its concentration is determined by those of $C—B$ and H_3O^+. In the other mechanisms the master reaction is sometimes the preliminary and sometimes the follow step, but in every case its transition state includes acetic acid, its composition being either $C—BHAc$ or $BHAc$.

41e. Reaction of substrate with either acid or base. Hydrolyses and similar reactions are often accelerated by both acids and bases. This is not surprising in view of the three-center theory of acidic and basic reactions. The bond of $A—B$ is polarized, i.e. one of its ionic components A^+B^- or A^-B^+ is more important than the other. If A^+B^- is the preferred component, hydroxide ion breaks the bond by an attack on A and hydrogen ion by an attack on B, and in both cases the products are AOH and BH or their ions. Similarly, if the acid or base first unites with $A—B$ without breaking the bond, the base tends to join the A group and the acid to join the B group. The electrostatic effect of both these additions enhances the importance of the A^+B^- component of $A—B$ and increases the tendency for the bond to be split into the products of A^+ and B^-, i.e. into AOH and BH.

Acceleration of a reaction by both acid and base is not restricted to hydrolysis, ammonolysis, and alcoholysis, but is also found for reactions of quite different type, such as tautomeric changes, condensations, etc.

The rate of such a reaction is the sum of the rates of the reactions of the positive ion, the negative ion, and the undissociated acid. For instance, in a hydrolysis,

$$\frac{dx}{dt} = k_1[H_3O^+][S] + k_2[OH^-][S] + k_3[H_2O][S].$$

Since water is the solvent, its concentration is almost constant and $[H_2O]$ can be included in the constant of the last term. There is a fixed relationship between $[H_3O^+]$ and $[OH^-]$, for $[H_3O^+][OH^-] = K_w$, so we can write

$$\frac{1}{[S]}\frac{dx}{dt} = k_a[H_3O^+] + \frac{k_b}{[H_3O^+]} + k_c,$$

where $k_a = k_1$, $k_b = k_2K_w$, and $k_c = k_3[H_2O]$. This equation gives a minimum value for $\frac{1}{[S]}\frac{dx}{dt}$ at $[H_3O^+] = \left(\frac{k_b}{k_a}\right)^{\frac{1}{2}}$. At this minimum the

acidic and basic reactions have identical rates. It is called the isocatalytic point.

If we have two concentrations of hydrogen ion giving equal rates, the relations become

$$\frac{1}{[S]}\frac{dx}{dt} = k_a[H_3O^+]_1 + \frac{k_b}{[H_3O^+]_1} + k_c = k_a[H_3O^+]_2 + \frac{k_b}{[H_3O^+]_2} + k_c,$$

which reduces to $[H_3O^+]_1[H_3O^+]_2 = \frac{k_b}{k_a}$, which is the square of the hydrogen ion concentration at the isocatalytic point. The sum of the logarithms of the two hydrogen ion concentrations for which the rates are equal is twice the logarithm of the isocatalytic hydrogen ion concentrations. Hence the curve of $\frac{1}{[S]}\frac{dx}{dt}$ against pH is symmetrical about a minimum. This curve is a catenary.

The solvent ions (H_3O^+ and OH^-) are produced by adding an acid or base. If this acid or base in its undissociated form is a catalyst and its conjugate (e.g., the ion of an acid) is also a catalyst, the partial reactions due to these catalysts must be included, and

$$\frac{1}{[S]}\frac{dx}{dt} = k_1[H_3O^+] + k_2[OH^-] + k_3[H_2O] + k_4[HA] + k_5[A]$$

where HA and A^- are the added acid and its conjugate base. By adding varying amounts of HA and NaA, or some completely ionized acid whose ion is ineffective (the best is $HClO_4$), or NaOH, a wide variation in the relative concentrations of H_3O^+, OH^-, HA, and A^- is possible and a sufficient number of simultaneous equations can be obtained to permit a solution for k_1, k_2, k_3, k_4, and k_5.

When a constant quantity, A_0, of HA is used, the pH of the solution may be changed by adding varying quantities of NaA. If HA is sufficiently weak so that $[HA] = A_0$, the above equation reduces to

$$\frac{1}{[S]}\frac{dx}{dt} = k_a[H_3O^+] + \frac{k_b}{[H_3O^+]} + k_c$$

with

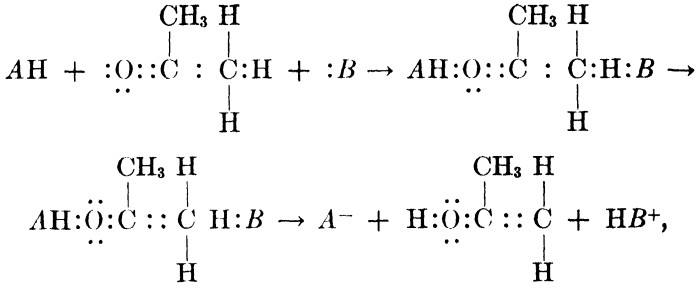
$$k_a = k_1, \qquad k_b = k_2K_w + k_5K_{HA}A_0,$$

and

$$k_c = k_3[H_2O] + k_4A_0.$$

The plot of $\frac{1}{[S]}\frac{dx}{dt}$ against pH is a catenary with a minimum at the isocatalytic point, $[H_3O^+] = \left(\frac{k_b}{k_a}\right)^{\frac{1}{2}}$.

41f. Lowry's mechanism. Lowry[5] has proposed the theory that reactions that are produced by both acid and base are in reality produced by the combined action of acid and base. The acid attacks one part of the molecule, the base another. The acid attracts electrons and repels nuclei; the base repels electrons and attracts nuclei. The reaction follows as the consequence of electrons and protons moving in the resultant field. Thus, the sequence



followed by the rapid achievement of the neutralization equilibrium between A^-, $CH_3C(OH)=CH_2$ and HB^+, would represent the change of acetone to its enol form.

The experimental basis of this theory is that many tautomeric changes that are catalysed by bases, say pyridine, do not occur in the presence of pyridine in a solvent that has been freed from impurities that might function as acids, but do occur when acidic impurities are present. The most striking example is the mutarotation of tetramethylglucose[6] which is brought about by tautomeric changes. In chloroform this reaction is very slow when either the base pyridine or the acid cresol are added, but is quite rapid if both are added. Water, being an amphoteric substance, can function either as the acid, the base, or both.

An interesting case of a Lowry mechanism is the reaction of ethylene oxides with water, hydronium ion, chloride ion and hydrochloric acid. Brönsted and the Kilpatricks[7] found that if the con-

[5] Lowry, T. M., *J. Chem. Soc.*, **127**, 1371 (1925).
[6] Lowry, T. M., and Richards, E. M., *J. Chem. Soc.*, **127**, 1385 (1925).
[7] Brönsted, J. N., Kilpatrick, Mary, and Kilpatrick, M., *J. Am. Chem. Soc.*, **51**, 428 (1929).

stants for these four reactions are k_1, k_2, k_3 and k_4, respectively, then $k_1/k_2 = k_3/k_4$. This they could explain only on the assumption of the Lowry mechanisms:

$$H_2O + C_2H_4O + H_2O \xrightarrow{k_1} C_2H_6O_2 + OH^- + H^+,$$

$$H_2O + C_2H_4O + H_3O^+ \xrightarrow{k_2} C_2H_6O_2 + H^+ + H_2O,$$

$$H_2O + C_2H_4O + Cl^- \xrightarrow{k_3} C_2H_5OCl + OH^-,$$

and $$H_3O^+ + C_2H_4O + Cl^- \xrightarrow{k_4} C_2H_5OCl + H_2O,$$

for the four reactions. The relationship was found for more than one ethylene oxide derivative and for more than one halogen.

According to this general theory, the rate of a reaction catalyzed by an acid and its ion in aqueous solution would be given by an equation involving terms for all combinations of the acids and bases present. Assuming first order with respect to each reactant:

$$\frac{1}{[S]}\frac{dx}{dt} = k_1[H_3O^+][H_2O] + k_2[OH^-][H_2O] + k_3[H_2O][H_2O] + k_4[HA][H_2O] + k_5[A^-][H_2O] + k_6[H_3O^+][A^-] + k_7[HA][A^-] + k_8[H_3O^+][OH^-] + k_9[HA][OH^-].$$

As H_2O is constant, and $[H_3O^+][OH^-] = K_w$, and $\frac{[A^-][H_3O^+]}{[HA]} = K_a$, this reduces to

$$\frac{1}{[S]}\frac{dx}{dt} = k_a[H_3O^+] + k_b[OH^-] + k_c + k_d[HAc] + k_e[A^-] + k_f[A^-][HA].$$

Only in the last term does this equation differ from that derived for the individual action of an acid or a base. The existence of this term has not been shown for the enolization of ketones in aqueous solution.

A linear four-center transition state can be assumed for a reaction going by a Lowry mechanism, and the reaction considered as similar to those with three-center linear transition states. Any molecule having basic or acidic properties when present in a reaction mixture must affect a three-center transition state, an acidic molecule stabilizing the transition state for a basic reaction and a basic molecule that

of an acid one, as suggested by Lowry. When this perturbation is great, the reaction must be treated from Lowry's point of view, but when small the simpler three-center treatment is to be preferred.

41g. Unimolecular and bimolecular hydrolysis. That one can notice the effect of an acid or base on the rate of a reaction in water or similar solvent can only mean that that acidic or basic reaction is faster with stronger than with weaker acids or bases, for water is both an acid and a base and is at a much higher concentration than that of the reagent added. If, for any particular substrate, this is not true, the reaction might well use up the added reagent and yet its rate be independent of the acidity or basicity of the solution. This condition is found in the alkaline hydrolyses and alcoholyses of many organic halides. For instance, the reaction $(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$ is independent of the hydroxide ion concentration. The equation for the similar hydrolysis of ethyl chloride has the same form, $RCl + OH^- \rightarrow ROH + Cl^-$, but in this case the reaction is kinetically different, the rate being proportional to the hydroxide ion concentration. Both reactions are proportional to the concentration of the alkyl halide. They are called, respectively, uni- and bimolecular alkaline hydrolyses of alkyl halides. They are examples of two distinct types of hydrolysis.

The difference between the uni- and bimolecular hydrolyses does not lie in the relative rates of preliminary and follow reactions. It cannot be assumed that the first step is a reversible reaction, $RCl \underset{k_2}{\overset{k_1}{\rightleftarrows}} R^+ + Cl^-$, followed by $R^+ + OH^- \xrightarrow{k_3} ROH$ in both cases, but that $k_3[OH^-] \gg k_2[Cl^-]$ in the unimolecular type and $k_2[Cl^-] \gg k_3[OH^-]$ in the bimolecular type. In that case the reactions would be unimolecular and bimolecular, respectively, but the rate of the latter would be inversely proportional to the chloride ion concentration, which it is not. The bimolecular hydrolyses are accepted as simple three-center basic reactions. The most generally accepted theory for the unimolecular hydrolysis is that it is a slow ionization, $RCl \rightarrow R^+ + Cl^-$, followed by a fast reaction, $R^+ + OH^- \rightarrow ROH$.

The other facts concerning these two types of reactions are that the bimolecular reaction is accompanied by a complete Walden inversion, but in the unimolecular reaction there is only partial inversion. If one starts with a dextro form of the halide, the unimolecular reaction produces both forms of the alcohol with the laevo in excess, but a bimolecular reaction yields only the laevo form. Another

important fact is that if a unimolecular reaction is carried out in a mixture of water and alcohol, the rate is

$$\frac{1}{[S]}\frac{dx}{dt} = k_1 \alpha_{H_2O} + k_2 \alpha_{C_2H_5OH},$$

where α is the activity.[8] However, the product of the action of a mixture of alcohol and water[9] has a greater ratio of ether to alcohol than $\frac{k_2 \alpha_{C_2H_5OH}}{k_1 \alpha_{H_2O}}$.

The heats of activation of many of the unimolecular reactions are small compared to the values that might be assumed to correspond to the breaking of the bond into ions.

Finally, it is possible for a substrate to undergo both types of reaction simultaneously. The rate law is then $\frac{1}{[S]}\frac{dx}{dt} = k_1 + k_2[OH^-]$. By varying the concentration of alkali, both velocity constants can be determined.

There has been a great deal of controversy concerning the mechanism of the unimolecular reaction. Ingold, Hughes, and their coworkers claim that the mechanism is $RX \underset{k_2}{\overset{k_1}{\rightleftarrows}} R^+ + X^-$, $R^+ + OH^- \xrightarrow{k_3} ROH$, with $k_3[OH^-] \gg k_2[X^-]$. Olson and Halford claim that it is pseudo-unimolecular, being $RX + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} R\overset{+}{O}H_2 + X^-$, $R\overset{+}{O}H_2 + OH^- \xrightarrow{k_3} ROH + H_2O$, with $k_3[OH^-] \gg k_2[X^-]$; or $RX + H_2O \rightarrow ROH + HX$. Neither mechanism is quite in accordance with the observations. Thus the ionization theory does not explain (1) the preponderance of inversion, for $R_1R_2R_3\overset{+}{C}$ has a planar configuration, (2) the heat of activation being less than would be expected from an ionization, (3) the rate of the reaction with a mixture of alcohol and water being a function of the activities of the components of the solvent. The second mechanism does not explain (1) the preponderance of ether formation over that expected from the relative rates of the alcohol and water reactions, (2) greater racemization in unimolecular than in bimolecular hydrolyses, (3) the substrate reacting with the weakly basic solvent rather than the strong base hydroxide

[8] Olson, A. R., and Halford, R. S., *J. Am. Chem. Soc.*, **59**, 2644 (1937).

[9] Bateman, L. C., Hughes, E. D., and Ingold, C. K., *J. Am. Chem. Soc.*, **60**, 3080 (1938).

ion. On the other hand, the difficulties encountered by both theories are not insuperable. The facts, however, suggest (1) that the transition state of the master reaction includes more than one molecule of solvent, (2) that the configuration of the transition state is such that at least one molecule of solvent is not far displaced from the line of the carbon-to-halogen bond, and on the other side of the carbon from the halogen, and (3) that the transition state does not include hydroxide ion unless it also includes hydronium ion. The evidence for (1) is that the alcoholysis is catalyzed by water; for (2), that inversion, though not complete, is predominant; and for (3), that the rate is independent of the hydroxide ion. The proviso for (3) is necessary. In Lowry's theory of combined acid and base catalysis, one of the possible transition states is $OH^-RCl\ H_3O^+$. If the hydrolysis is one that is only rapid when both a very strong acid and a very strong base react with the substrate, then in an amphoteric solvent neither an acid nor a base is a good catalyst. The rate equation would be $\frac{1}{[S]}\frac{dx}{dt} = k[OH^-][H_3O^+] = kK_w$. Other amphoteric solvents would give similar rate equations but with a different constant.

41h. Slow and fast reactions. As was mentioned in the previous chapter, P in the equation $k = PZe^{-\epsilon/RT}$ is often very small in reactions carried out in solution, but sometimes it is not very much less than one. Reactions where P has an order of magnitude less than 10^{-2} have been grouped together as the "slow" reactions, the others being called "fast" or "normal" reactions. The nomenclature is very unfortunate, as a "fast" reaction can be much slower than a "slow" one. The "fast" reactions have also been called ionic three-center reactions, because when they are found in the liquid phase they are generally bimolecular reactions of an ion with an uncharged molecule. However, bimolecular reactions of an ion with an uncharged molecule are also found among the "slow" reactions.

The assumption usually made is that a collision having the critical energy normally leads to a reaction, but in "slow" reactions some steric factor causes a variation from the norm. We shall assume that a "fast" reaction is one that occurs with a heat of activation far in excess of the critical energy, and in consequence the energy barrier between reactants and products is surmounted over a wide area. This implies that no very precise configuration of reactants is required in the transition state and hence the steric or probability factor, P, is close to unity. If, however, the reaction path is through

a rather narrow region in the barrier, the activation energy may be reduced considerably toward the value of the critical energy, but the narrowness of the pass implies a rather precise configuration in the transition state and hence a small value of P, i.e. a "slow" reaction.

42. THE STRENGTH OF THE REACTING ACID OR BASE (C)

The formation of a transition configuration for the reaction $A{:}B + C \rightarrow A + B{:}C$, where C and A are acids, necessitates a partial breaking of the $A{:}B$ bond and a partial formation of a bond between $B{:}$ and C. Therefore, the stronger is the $A{:}B$ bond, the slower the reaction, and the stronger is the $B{:}C$ bond, the faster is the reaction. The acidity of C is the driving force of the reaction and that of A is part of its resistance. Whether the basicity of $B{:}$ helps or hinders the reaction is indeterminate, depending on whether its interaction with C from a large distance to the distances in the transition configurations is greater or smaller than its interaction with A from the bond distance to those in the transition state.

It is not possible to define acidity and basicity quantitatively in a completely general way. But the free energies of the reactions of A and C with water to produce hydrogen ion can be taken as rough measures of the tendency of A to combine with $B{:}$ to form $A{-}B$ from the transition state and that of C to unite with $B{:}$ to the extent that C and $B{:}$ are combined in the transition state. Hence if A and $B{:}$ are kept constant and C is varied, there should be a direct correlation between the strengths of the C's as acids and the rates of their reaction with $A{-}B$. Also, if B and C are kept constant and A is varied, there should be an inverse correlation between the acid strengths of the A's and the rates of reaction of their $B{:}$ compounds with the acid C. If $B{:}$ is varied and A and C are constant, we may expect either a direct or an inverse relationship between the basic strengths of the $B{:}$'s and the reaction rates, depending on the choice of A and C. One must even consider the possibility of a change from a direct to an inverse correlation when $B{:}$ is varied for a single choice of A and C.

What has been written above concerning the effects of the acidities of A and C and the basicity of $B{:}$ on the rate of the acidic reaction $A{:}B + C \rightarrow A + B{:}C$ is applicable, by inversion, to the effects of the basicities of $A{:}$ and $:C$ and the acidity of B on the rate of the basic reaction $A{:}B + {:}C \rightarrow A{:} + B{:}C$. The basicity of $:C$ enhances the rate; that of $A{:}$ diminishes it; and the effect of the acidity of B is indeterminate.

We have seen in Chapter VI that the strength of a hydrogen acid can be fairly well estimated from its structure, so that effects of change of structure of A and C on the rate of the acidic and basic reactions of the type $A—B + C \rightarrow A + B—C$ can be predicted. These predictions are only rough approximations. Similar estimates of the effects of change of structure of A and C on the rates can be made from the experimental values of the acidic and basic constants. These are also rough approximations. The dissociation constants depend on the combinations and separations of acids and bases between equilibrium bond distances and infinity; the rates depend on similar combinations and separations, but only between equilibrium and transition-state distances or between transition-state distances and infinity.

The correlation between rates and acid strengths was noted by Snethlage[10] when it had become evident that acid catalysis could be separated into a catalysis by hydrogen ion and one by the undissociated acid. This correlation was expressed quantitatively by Taylor[11] by the equation $\frac{k_m}{k_H} = K_a^{\frac{1}{2}}$, where k_m and k_H are the rate constants of those parts of the reaction that depend on the undissociated acid and the hydrogen ion, respectively, and K_a is the dissociation constant of the acid. It is now known that the exponent in this equation is not invariant to a change of the substrate, but that for a number of acid-catalyzed reactions its value is not far from $\frac{1}{2}$.

42a. Brönsted's equation. Similar relations are found between the strengths of bases and the rate of base-catalyzed reactions. Brönsted expressed these, using a generalized system of acids and bases. In this system an acid reacts with water to form H_3O^+ and its conjugate base. If K_a is defined as $\frac{[\text{Base}]\,[H_3O^+]}{[\text{Acid}]}$, then K_a for H_3O^+ is 55.6 (the molality of water); K_a for water is $10^{-14}/55.6$; K_a for a simple hydrogen acid is its ordinary dissociation constant; and K_a for a positive ion is its hydrolysis constant. If K_a is a measure of the acidity of an acid, $\frac{1}{K_a}$ is a measure of the basicity of its conjugate base. Brönsted then expressed the rate constant of an acid-catalyzed reaction by $k_a = GK_a^x$ and the rate constant for a base-catalyzed reaction by $k_b = GK_a^{-x}$. G and x are constants determined

[10] Snethlage, H. C. S., *Z. physik. Chem.*, **85**, 211 (1913); *Z. Elektrochem.*, **18**, 539 (1912).

[11] Taylor, H. S., *Z. Elektrochem.*, **20**, 201 (1914).

by the reaction, and for the base-catalyzed reaction K_a is the acid constant of the conjugate acid. When a reaction is catalyzed by both acid and base, G and x need not be the same for the two catalyses. Exponents so far observed are all less than unity and, in general, the base-catalyzed reactions have the higher exponents. It may be noted that, if a reaction is catalyzed by both acid and base, it is experimentally difficult to observe the effects of weak acids or weak bases on the rate, when x is large. The contributions of these reactions are masked by the large contributions of those due to hydronium or hydroxide ions. For instance, if G and x for the acidic hydrolysis are 1 and 2, respectively, and G and x for the basic one are $10^{-17.5}$ and 1.5, respectively, the rate of the reaction for unit concentration of the substrate in a solution $1N$ with respect to the ion of an acid whose dissociation constant is 10^{-5}, with sufficient of the acid to make the solution neutral, is $10^{-12} + 10^{-10} + 10^{-3.5} + 10^{-0.9}$. These terms are the reactions due to the acid, its ion, hydronium ion, and hydroxide ion, respectively. The first two terms are quite negligible. Further, with these values of x they would be negligible with any choice of values for G, or at any other pH. No significance can be attached to the observation that x is always less than unity.

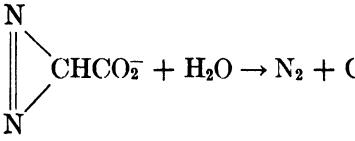
The equations for the effects of undissociated acid or base can be corrected for the probability factor that arises from the possibility of more than one acid or basic center.[12] From a theoretical standpoint, Brönsted's equation should be $k_a' = GK_a'^x$, where k_a' is the rate due to a single acidic center (point of dissociation) of the catalyst, and K_a' is the dissociation constant for the acid after it has been corrected for the probability factor due to multiplicity of acidic centers in the undissociated acid (called p) and of basic centers in the conjugate base (called q). Then $k_a = pk_a'$ and $K_a = K_a' \frac{p}{q}$, and $\frac{k_a}{p} = G\left(K_a \frac{q}{p}\right)^x$ or $k_a = GK_a^x q^x p^{1-x}$. Similarly, for a base-catalyzed reaction, $k_b = GK_a^{-x} p^x$. The formulas for the rates of acid- and base-catalyzed reactions are generally expressed in logarithmic form. Thus the simpler equations become $\log k_a = \log G + x \log K_a$, and $\log k_b = \log G - x \log K_a$. The results can then be plotted as a straight line, whose slope is x.

The correlation between the rates and the acidities or basicities of the reagents as given by the above equations has been experi-

[12] Pedersen, K. J., *J. Phys. Chem.*, **38**, 591 (1934).

mentally verified in all cases in which the rates for the individual acids or bases have been measured, and in which the acids or bases compared are of similar type, i.e. are derived from the same hydride (H_2O, NH_4^+, NH_3, etc.). There is even a marked correlation when the acids or bases compared do not belong to the same type. The correlation fails where something specific happens in the dissociation or reaction with substrate. Thus the basic catalytic constant of bicarbonate ion does not correspond to the ordinary first dissociation constant of carbonic acid (3×10^{-7}). This constant involves the reaction $H_2CO_3 \rightleftarrows CO_2 + H_2O$, but the interaction between bicarbonate ion and the substrate is independent of the decomposition of H_2CO_3.

We shall give in detail only a single example of generalized acid catalysis and one of generalized basic catalysis. They are shown in Tables 44 and 45. The first is the acid-catalyzed reaction



the second is the base-catalyzed reaction $NH_2NO_2 \rightarrow H_2O + N_2O$.

The correction for the multiplicities of acidic and basic centers have not been introduced. The constancy of G in Table 44 is improved if this is done. Although the constancy of G appears to be much greater for the decomposition of nitramide than for that of diazoacetate ion, it really is not. The range of rates covered by the measurements given on the diazoacetate reaction is much greater than that of the nitramide decomposition. If the latter were extended to include very strong bases, as for instance hydroxide ion, the value of G would not be so constant. Both reactions have some abnormalities in their kinetics.

The decomposition of nitramide is supposed to show some differences in the behavior of carboxylate ions and amines. Thus if the same value for x is used for both, as was done in Table 45, the average values of G for the two types of bases are slightly different. Also, when $\log k_b$ is plotted against $\log K_a$ the best lines for the two types of bases are slightly different.

The mutarotation of glucose is catalyzed by both acids and bases in general. The base-catalyzed reaction increases more rapidly with the strength of the base than the acid-catalyzed reaction increases with the strength of the acid. That is, x for the basic reaction is

TABLE 44

RATE OF $N_2CHCO_2^-$ + H_2O → N_2 + CH_2OHCO_2 CATALYZED BY ACIDS*

Acid	Log k_a	Log K_a	Log G = log k − 0.833 log K_a
H_2O	−6.0	−15.75	7.1
HPO_4^{--}	−2.3	−12.3	7.7
$C_5H_{10}NH_2^+$ (piperidinium ion)	−2.2	−11.1	7.1
C_6H_5OH	−0.35	−10.0	8.0
NH_4^+	−0.25	−9.3	7.5
CH_3CO_2H	+4.1	−4.8	8.1
H_3O^+	+8.45	+1.7	7.1

* King, C. V., and Bolinger, E. D., *J. Am. Chem. Soc.*, 58, 1533 (1936).

TABLE 45

RATE OF NH_2NO_2 → H_2O + N_2O CATALYZED BY THE CONJUGATE BASES OF SOME ACIDS*

Acid	Log k_b	Log K_a	Log G = log k_b + 0.85 log K_a
$^-O_2C(CH_2)_2COOH$	+0.2	−5.4	−4.4
$^-O_2CCH(OH)CH_2COOH$	−0.1	−4.9	−4.3
CH_3CH_2COOH	−0.2	−4.9	−4.4
CH_3COOH	−0.3	−4.8	−4.4
$HO_2C(CH_2)_2COOH$	−0.5	−4.2	−4.3
$C_6H_5CH_2COOH$	−0.7	−4.3	−4.4
C_6H_5COOH	−0.8	−4.2	−4.4
$^-O_2C(CHOH)_2COOH$	−0.8	−4.1	−4.3
$^-O_2CCOOH$	−1.0	−4.0	−4.4
$HO_2CCH_2CH(OH)COOH$	−1.2	−3.7	−4.3
$HCOOH$	−1.1	−3.7	−4.2
$HO_2C(CHOH)_2COOH$	−1.5	−3.3	−4.3
o-$C_6H_4(COOH)_2$	−1.6	−3.2	−4.3
o-$C_6H_4(OH)COOH$	−1.7	−3.0	−4.3
H_3PO_4	−2.2	−2.5	−4.3
p-$CH_3C_6H_4\overset{+}{N}H_3$	0.06	−5.1	−4.3
m-$CH_3C_6H_4\overset{+}{N}H_3$	−0.2	−4.8	−4.3
$C_6H_5\overset{+}{N}H_3$	−0.3	−4.7	−4.3
o-$CH_3C_6H_4\overset{+}{N}H_3$	−0.5	−4.5	−4.3
p-$ClC_6H_4\overset{+}{N}H_3$	−0.8	−4.1	−4.3
m-$ClC_6H_4\overset{+}{N}H_3$	−1.1	−3.5	−4.1
o-$ClC_6H_4\overset{+}{N}H_3$	−1.8	−2.7	−4.1

* Brönsted, J., and Pedersen, K., *Z. physik. Chem.*, 108, 185 (1924); Brönsted, J., and Duus, H. C., *Z. physik. Chem.*, 117, 299 (1925); Brönsted, J. N., *Trans. Faraday Soc.*, 24, 637 (1928).

greater than x for the acidic one. When $\log k_a$ and $\log k_b$ are plotted against $\log K_a$, oppositely sloping straight lines are obtained. The rate of the reaction in water falls on both lines; on the line for the basic reactions the abscissa is $\log K_a$ for hydronium ion, and on the line for acidic reactions it is $\log K_a$ for water. This fact has been noted[13] as exemplifying the amphoteric character of water. If these facts are correct, the rate constant for the water reaction is

$$k_w = G_a K_{H_2O}^{x_a} \quad \text{or} \quad k_w = G_b K_{H_3O^+}^{-x_b}.$$

The simple theory of independent acid and base reactions gives

$$k_w = G_a K_{H_2O}^{x_a} + G_b K_{H_3O^+}^{-x_b}.$$

Lowry's theory, that the reactions occur under the combined action of acid and base, makes k_a the constant for water acting as a base and the reagent as the acid, k_b the constant for water acting as an acid and the reagent as the base. The constant for water is then

$$k_w = G_a K_{H_2O}^{x_a} \quad \text{or} \quad k_w = G_b K_{H_3O^+}^{-x_b},$$

plus the added term for the combined action of hydroxide and hydronium ions. The latter term is negligible when x_a and x_b are small with respect to unity, and predominant when they are large with respect to unity. The observed value of k_w seems to indicate a Lowry mechanism for this reaction, but it is difficult to decide these points experimentally, for the errors involved in extrapolating the values of k_w from measurements with stronger acids and bases are as a rule large with respect to the value of k_w.

Lowry's theory that the substrate is attacked simultaneously by acids and bases leads to a variety of possibilities of hydroxide ion and hydrogen ion catalysis in aqueous solution according to the values of x_a and x_b in Brönsted's equations. With x_b large and x_a very small, the reaction is catalyzed by base but not by acid; with x_a large and x_b very small, the reaction is catalyzed by acid but not by base; with x_a and x_b of intermediate magnitudes, the reaction is catalyzed by both acids and bases; and with both x_a and x_b either very large or very small, the reaction is not apparently faster in the presence of either acids or bases.

The mechanisms of the reactions that show generalized acid-base

[13] Schwab, G.-M., Taylor, H. S., and Spence, R., *Catalysis from the Standpoint of Chemical Kinetics*. Van Nostrand, New York, 1937.

catalysis are not known with any degree of certainty. It is simpler, but not necessary, to assume that the reaction with the acid is the master reaction. If this is not done, it must be assumed that the entire acid is retained in the Arrhenius intermediate. When the latter is done and the thermodynamic properties of the transition state are assumed to govern the rate, it becomes immaterial whether the intermediate belongs to the Arrhenius or to the Van't Hoff type, as in either case generalized acid catalysis is to be expected.

Assuming that the reaction between acid and substrate is the master reaction, the mechanism for an acid-catalyzed hydrolysis of a substrate having an unshared pair of electrons may be

$$S\!: + \mathrm{H}\!:\!A \rightarrow S\!:\!\mathrm{H} + :\!A$$

followed by a rapid decomposition or hydrolysis of S:H to the final products, or

$$A\!:\!\mathrm{H} + :\!S \rightarrow A\!:\!\mathrm{H}\!:\!S_1 + S_2\,,$$

where S_1 and S_2 are the products of the scission of S, with water acting simultaneously or afterwards to yield the final products. Although there is no kinetic evidence favoring one of these mechanisms over the other, the latter is to be preferred for any hydrolysis that takes an appreciable time in the presence of H_3O^+, as the distribution of hydrogen ion between unshared electron pairs is normally a very rapid process, and it is unlikely that

$$S\!: + \mathrm{H}\!:\!A \rightarrow S\!:\!\mathrm{H} + :\!A$$

is slow enough to be the master reaction. However, it is not necessary that all generalized acid catalyses have the same mechanisms.

In general, what has been written above concerning the mechanism of generalized acid catalysis is applicable to generalized base catalysis. A special mechanism is applicable to the reaction of acyl compounds. These substances contain the carbonyl group, and a reaction that finally ends in the change of one acyl derivative to another may proceed through an attack on the carbonyl group. This is particularly likely in basic reactions, and the alkaline hydrolysis of an ester can be taken as a good example. A probable mechanism is:

$$\begin{array}{l} :\!\mathrm{O}\!: \\ \vdots\ \ \vdots \\ R\mathrm{C}\!:\!\mathrm{O}\!:\!R \\ \vdots \end{array} + \ddot{B} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \begin{array}{l} :\!\ddot{\mathrm{O}}\!:^- \\ \vdots\ \ \vdots \\ R\mathrm{C}\!:\!\mathrm{O}\!:\!R \\ \vdots\ \ \vdots \\ \ddot{B} \end{array}.$$

In this compound, the basic negatively charged oxygen atom can displace either $\ddot{B}$ or $:\ddot{\underset{\cdot\cdot}{O}}:R$. The equation for the latter process is

$$:\ddot{O}: \qquad\qquad :O:$$
$$R\ddot{C}:\ddot{O}:R \xrightarrow{k_3} R\ddot{C} + :\ddot{O}:R\,.$$
$$\ddot{B} \qquad\qquad \ddot{B}$$

If $\ddot{B}$ is hydroxide ion, the follow step forming RCO_2^- and HOR is rapid; or, if $\ddot{B}$ is a weak base,

$$RC\begin{matrix}\overset{O}{\overset{\|}{}}\\ \diagdown\\ \underset{B}{}\end{matrix}$$

is rapidly hydrolyzed and the products, after the acids and bases have reached equilibrium, are $RCO_2^- + ROH + \ddot{B}$. The rate is then equal to $k_1 \dfrac{k_3}{k_2 + k_3}[RCOOR][\ddot{B}]$. The greater the basicity of $\ddot{B}$, the greater is k_1 and the greater is the ratio $\dfrac{k_3}{k_2 + k_3}$. Hence, if $k_1 \dfrac{k_3}{k_2 + k_3}$ is made equal to $GK_{H:B}^{-x}$, x is large. In consequence, this is a type of reaction in which weak bases are very inefficient; and when a weak base is added, the ester is hydrolyzed chiefly by the hydroxide ion produced by the action of water on the weak base. Should the base $\ddot{B}$ contain a proton, so that $\ddot{B}$ is $\ddot{B}'$:H, then

$$:\ddot{O}:$$
$$R\ddot{C}:\ddot{O}:R$$
$$H:\ddot{B}'$$

is rapidly neutralized by any base in the solution (including itself) and forms

$$:\ddot{O}: \qquad\qquad H$$
$$R\ddot{C}:\ddot{O}:R \quad \text{or} \quad :\ddot{O}:$$
$$\ddot{B}': \qquad\qquad R\ddot{C}:\ddot{O}:R.$$
$$\ddot{B}':$$

Now, $\ddot{B}'$: is a much stronger base than $\ddot{B}'$:H and the chance of $:\ddot{O}:R$ being displaced instead of $\ddot{B}'$: is much greater than that of $:\ddot{O}:R$ being displaced instead of a base of the strength of $\ddot{B}'$:H. The base $\ddot{B}'$:H is therefore a more effective reagent than corresponds to its strength. The product, however, is $R\text{CO}B'$:, not $R\text{CO}_2^-$. Thus the hydrolysis of an ester in an aqueous solution of a tertiary amine is but little faster than that due to the hydroxide ion present, and the product is $R\text{CO}_2^-$, but in aqueous solutions of ammonia, primary and secondary amines react with esters faster than this, producing amides instead of carboxylate ions.

42b. Hammett's equation. An aromatic compound and its derivatives react in similar ways. Any one of these ways is a general reaction of the class of compounds that includes the aromatic compound and its derivatives. Hammett[14] has found that the rate or equilibrium constant of a general reaction for a member of a class of aromatic compounds is given approximately by the equation $\log k_\sigma = \log k_u + \sigma\rho$, where k_u is the rate or equilibrium constant of the general reaction for the unsubstituted member of the class, σ is a constant for the substitution, and ρ is a constant for the general reaction. Thus the rate constant for the reaction

$$p\text{-ClC}_6\text{H}_4\text{N(CH}_3)_2 + \text{CH}_3\text{I} \rightarrow p\text{-ClC}_6\text{H}_4\overset{+}{\text{N}}\text{(CH}_3)_3 + \text{I}^-$$

is given by the equation

$$\log k_\sigma = \log k_u + \sigma\rho,$$

where k_u is the rate constant for the reaction

$$\text{C}_6\text{H}_5\text{N(CH}_3)_2 + \text{CH}_3\text{I} \rightarrow \text{C}_6\text{H}_5\overset{+}{\text{N}}\text{(CH}_3)_3 + \text{I}^-,$$

ρ is a constant characteristic of the general reaction

$$X\text{C}_6\text{H}_4\text{N(CH}_3)_2 + \text{CH}_3\text{I} \rightarrow X\text{C}_6\text{H}_4\overset{+}{\text{N}}\text{(CH}_3)_3 + \text{I}^-,$$

and σ is a constant for the para substitution of chlorine.

In order to assign values to σ and ρ it is necessary to assume an arbitrary value of ρ for the rate or equilibrium constant of some

[14] Hammett, L. P., *J. Am. Chem. Soc.*, **59**, 96 (1937).

general reaction. Hammett has taken $\rho = 1$ for the equilibrium constants of the dissociation of benzoic acids.

Hammett's equation must be considered as an approximate empirical equation that is applicable only with certain limitations. It was applied in Chapter VI to the dissociation constants of aromatic acids. There it was found that it was not applicable to ortho substitutions, nor when the substituent group resonates with the atom from which the proton dissociates, as for instance in *p*-nitrophenol. The latter limitation can be expressed in a more general way. If the substituent group resonates with an atom directly concerned in the reaction, the σ value for the substitution must be changed or a term must be added to take account of the effect of this resonance. The equation is a good approximation when the effect of the sub-

TABLE 46
THE σ VALUES FOR GROUPS

Substitution	σ	Substitution	σ
p-NH_2	−0.660	*p*-Cl	+0.227
p-OCH_3	−0.268	*p*-Br	+0.232
p-OC_2H_5	−0.25	*p*-I	+0.276
m-$(CH_3)_2N$	−0.211	*m*-F	+0.337
p-$(CH_3)_2N$	−0.205	*m*-I	+0.352
p-CH_3	−0.170	*m*-Cl	+0.373
m-NH_2	−0.161	*m*-Br	+0.391
p-C_2H_5	−0.144	*p*-$C_6H_5N{=}N$	+0.640
p-CH_3S	−0.047	*m*-CN	+0.678
p-C_6H_5	+0.009	*m*-NO_2	+0.710
p-F	+0.062	*p*-NO_2(benzoic)	+0.778
m-OCH_3	+0.115	*p*-CN	+1.000
m-OC_2H_5	+0.15	*p*-NO_2(phenolic)	+1.27

stitution is chiefly due to a change of the electric charge on the aromatic carbon atom to which the reacting group is attached, directly or by a chain. The σ value for a substitution is then proportional to the difference between the polar constants for the substituted aromatic group and for the phenyl group. These polar constants of complex groups include the effects of the polarities of the atoms and of the resonances within the group. However, when the substitution introduces steric factors, directly transmitted polar effects, and important resonances other than those between the substituent group and the aromatic resonances, neither polar constants for complex groups nor σ values determined only by the substitution can be used without introducing appreciable error. In Table 46 we show the σ values assigned to some groups by Hammett.

The values given in the above table are averaged from several general reactions to which ρ values have been assigned. The abscissa values of the groups in Figure 39, Chapter VI, are also σ values, but averaged from the dissociation constants of benzoic and phenylboric acids and calculated on the assumption that $\rho = 1$ for the dissociation constants of the derivatives of phenylboric acid. The two sets of values should be proportional, but this is only approximately true. Both sets of σ values are only tentative. In Figure 39 the abscissa for the *p*-amino is less negative than that for the *p*-alkoxy group. The reverse order given by Hammett is probably correct. It may be noticed that in Figure 39 the points for these groups do not fall on the line, but would fit the line more accurately if the order of the abscissa values were reversed. On the other hand, Hammett's values for *m*-$N(CH_3)_2$ and *m*-NH_2 are probably erroneous. The values are too negative. The true values are probably near to zero for aqueous solutions. Hammett's value for *p*-$N(CH_3)_2$ is less negative than that for *m*-$N(CH_3)_2$. That this group puts a larger negative charge on the meta than on the para position is exceedingly unlikely. In general the $N(CH_3)_2$ group behaves like the NH_2 group but, if anything, appears to produce a greater negative charge in the ring. The relative effects of such groups as OH, OCH_3, NH_2, and $N(CH_3)_2$ should be markedly affected by the solvent, and by the *p*H of the solution. The hydrogenated groups OH and NH_2 interact with both acidic and basic atoms, and the other two only with acidic atoms. These interactions often go beyond the stage of forming divalent hydrogen. Thus reactions of phenols are often those of their ions, and those of anilines are due to anilinium ions. Hammett has given a definite order to the effects of *m*-Cl, *m*-Br, and *m*-I. The order is doubtful, since almost any order is found experimentally. However, the effects of these substitutions are never very different from each other. The cyano group, like the nitro group, resonates strongly with a basic atom in the para position. Hence two σ values, a benzoic and a phenolic, are as much justified for the cyano as for the nitro group.

The reason why the σ values assigned to the groups in Table 46 are open to criticism is that the relative effects of the groups are not constant except under the ideal conditions of lack of perturbing effects. This "normal" effect of the substituent is difficult to obtain because we cannot be sure of the lack of perturbation in any chosen general reaction. However, the qualitative order (1) *p*-O^-, (2) *p*-amino (NH_2, NR_2, etc.), (3) *p*-hydroxy (OH, OCH_3, etc.),

(4) *p*-alkyl (CH_3, C_2H_5, etc.), (5) *m*-alkyl, (6) *m*-amino, (7) *p*-F, (8) *m*-hydroxy, (9) *p*-Cl, (10) *p*-Br, (11) *p*-I, (12) *m*-carboxy (COOH, COOR), (13) *m*-F, (14, 15, 16, and 17) *m*-Cl, *m*-Br, *m*-I, and *p*-carboxy, (18 and 19) *m*-NO_2 and *m*-CN, (20 and 21) *p*-NO_2 and *p*-CN, in which no attempt has been made to distinguish between groups with nearly equal effects, is probably very close to the normal order. We can use Hammett's equation and, with the exceptions we have mentioned, his table of σ values, as a rough approximation to calculate the rate and equilibrium constants of the reactions of benzene derivatives. When the discrepancies between observed and calculated values are very great, we can seek the reasons for the perturbations.

If we consider σ to represent the charge imposed on an atom of the nucleus by the substitution, the ρ value for the dissociation constant of an aromatic acid is always positive. An inspection of Figure 36 will show that this is the case. It has been deduced from the transition state theory that the stronger the acidic or basic reactant, the faster is its reaction with the substrate. Hence ρ for the rate constant of a reaction of an aromatic acid is also positive, and ρ for the rate constant of a reaction of an aromatic base or ion of an aromatic acid is always negative.

In his article, Hammett quotes the following eleven examples of basic reactions with the reagent varied by meta and para substitutions: reaction of substituted anilines with dinitrochloronaphthalene in ethyl alcohol,[15] reaction of substituted anilines with dinitrochlorobenzene in ethyl alcohol,[16] reaction of substituted phenyldiethylphosphines with ethyl iodide in acetone,[17] reaction of substituted dimethylanilines with trinitrophenyl methyl ether in acetone,[18] reaction of substituted dimethylanilines with trinitrocresyl methyl ether in acetone,[19] reaction of substituted dimethylanilines with methyl iodide in aqueous acetone,[17] reaction of substituted anilines with benzoylchloride in benzene,[20] reaction of substituted anilines with formic acid in aqueous pyridine,[21] reaction of substituted phenolate ions with ethylene oxide in alcohol,[22] reaction of substituted phenolate

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[15] Van Opstall, H. J., *Rec. trav. chim.*, **52**, 901 (1933).
[16] Singh, A., and Peacock, D. H., *J. Phys. Chem.*, **40**, 669 (1936).
[17] Davies, W. C., and Lewis, W. P. G., *J. Chem. Soc.*, 1599 (1934).
[18] Hertel, E., and Dressel, J., *Z. physik. Chem.*, **B29**, 178 (1935).
[19] Hertel, E., and Dressel, J., *Z. physik. Chem.*, **B23**, 281 (1933).
[20] Williams, E. G., and Hinshelwood, C. N., *J. Chem. Soc.*, 1079 (1934).
[21] Davis, O. C. M., and Rixon, F. W., *J. Chem. Soc.*, **107**, 728 (1915).
[22] Boyd, D. R., and Marle, E. R., *J. Chem. Soc.*, **105**, 2117 (1914).

ions with propylene oxide in alcohol,[22] reaction of substituted phenolate ions with ethyl iodide in alcohol.[23] In every case the plot of log k against σ gives a fairly straight line, and ρ is negative.

No reactions of the type $A{:}B + C \rightarrow A + B{:}C$, where C is an aromatic acid, are included in Hammett's list of reactions that conform to his equation. In a reaction of this type, C is a hydrogen acid, and the product $B{:}C$ has a divalent hydrogen atom. The rapid follow reactions release C or its ion. These reactions are examples of generalized acid catalysis. When the acids used in a generalized acid catalysis are restricted to an aromatic acid and its meta and para derivatives, we have a general reaction for which the equation $\log k_\sigma = \log k_u + \sigma\rho$, with a positive value of ρ, holds.

42c. The relationship between Brönsted's and Hammett's equations. The last statement in the previous section implies a relationship between Hammett's and Brönsted's equations. Brönsted's theory requires that the rate constants for the reaction of an aromatic base and of one of its meta or para derivatives be given by the equations $\log k_u = \log G - x \log K_u$ and $\log k_\sigma = \log G - x \log K_\sigma$, where K_u and K_σ are the dissociation constants of the conjugate acids of the aromatic base and its derivative. But K_u and K_σ are related by the Hammett equation $\log K_\sigma = \log K_u + \sigma\rho'$. By combining these equations, one obtains $\log k_\sigma = \log k_u - \sigma\rho' x$. In this, x is determined by the substrate, and ρ' by the aromatic acids, so that $\rho' x$ is determined by a general reaction of a class of aromatic acids. That is, $\rho' x$ is ρ for this general reaction, and $\log k_\sigma = \log k_u + \sigma\rho$, where ρ is negative. Similarly, for reactions of aromatic acids, $\log k_\sigma = \log k_u + \sigma\rho' x = \log k_u + \sigma\rho$, where ρ is positive.

When ρ and ρ' are known, x can be calculated. If one uses the values given by Hammett for ρ and ρ', a wide variation of x is obtained even in reactions of the same base. Thus, for the reaction of aniline with formic acid in aqueous pyridine solution, ρ is -1.219, and, since ρ' for aniline is 2.73, $x = 0.48$; for the reaction of anilines with dinitrochloronaphthalene in ethyl alcohol, $\rho = 3.69$, and hence $x = 1.3$. The last example is important in that it shows that x can exceed unity. As the change from water to alcohol does not affect ρ' for aniline very greatly, x would be greater than one even if the reactions were both carried out in alcohol.

42d. Acids without hydrogen atoms. The strongest acids are

[23] Goldsworthy, L. J., *J. Chem. Soc.*, 1254 (1926).

not the hydrogen acids, but compounds with atoms whose valence shells can easily hold more electrons than they do, such as SO_3 and BF_3. The effects of these acids are difficult to observe in the presence of substances like water or alcohol. These strong acids produce reactions which, if catalyzed by hydronium ion, would go at immeasurably slow rates. Thus the C—O bond of diethyl ether is practically inert to aqueous acids, but is broken with the greatest ease by sulfur trioxide,

$$C_2H_5OC_2H_5 + SO_3 \rightarrow (C_2H_5O)_2SO_2 .$$

The catalytic effects of BF_3, $AlCl_3$, $ZnCl_2$, etc., may well be due to acidic three-center reactions of these powerful acids.

42e. Charged and neutral bases. The Brönsted equation for the rates of generalized acidic and basic reactions holds over wider ranges of structural changes in the acidic or basic reagents than might be expected from the transition-state theory. It does, however, fail when acids or bases of very different types are compared. Failure might be expected when acids or bases having different electric charges are compared, but the rates appear to show very little effect of a change of electric charge on the reagent. This can be seen in the constancy of G in Table 44 and Table 45. However, the change in the charge of the reacting base from an ion to a neutral amine produces a large effect on the relative values of the factors of the velocity constant, PZ and $e^{-\epsilon/RT}$. For reactions with the same rate, $e^{-\epsilon/RT}$ is smaller for the ionic than for the amine reaction. Hinshelwood[24] has accounted for the higher values of $e^{-\epsilon/RT}$ for the amine reactions by the stabilizing attraction of the charges in the transition state $\overset{-}{A} \cdots B \cdots \overset{+}{C}$. We shall restate this theory on the assumption that the activation energy is in general greater than is necessary to form the transition configuration of lowest energy. In doing this we shall also imagine the transition configurations for the reaction $A{:}B + {:}C \rightarrow A{:} + B{:}C$ to be formed from the separate groups instead of from $A{:}B$ and ${:}C$. The first step is to bring $A\overset{-}{:}$ and ${:}C$ to the required distance. The repulsion in this step is greater if ${:}C$ is negatively charged than if it is neutral, but this difference is more marked when the separation is small than when it is large. B^+ is now introduced between $A\overset{-}{:}$ and ${:}C$, making bonds with both. Where $A\overset{-}{:}$ and B^+ are constant and only ${:}C$ is varied, we can approxi-

[24] Hinshelwood, C. N., Laidler, K. J., and Timm, E. W., *J. Chem. Soc.*, 848 (1933).

mate by ignoring the effect of bond formation between $A\overline{:}$ and B^+. The energy obtained by bonding B^+ and $:C$ is only part of the $B—C$ bond energy, that obtained up to the distance between B^+ and $:C$ in the particular configuration. When this distance is large, a smaller proportion of the bond energy is available if $:C$ is neutral than if it is negatively charged. Thus a neutral base has an advantage over a negatively charged one because of the lower repulsion between $A\overline{:}$ and $:C$, but a negatively charged base has an advantage over a neutral one because its basicity is effective at a greater distance from B^+. The former advantage is diminished and the latter increased when there is a wide separation of the groups in the transition configuration, so that reactions with negatively charged bases occur more readily through the higher-energy and the more diffuse transition states than do those with neutral bases. This raises the average energy of activation for reactions with ions, but this rate-diminishing effect is compensated by the greater entropy of the diffuse transition state of the reaction with ions. In consequence, the activation energy and the probability are both less when the reacting base is an amine than when it is an ion. With equal basicities, the amine is the more reactive at low temperatures, and the ion at high temperatures.

42f. The polarizability effect. When the bases compared are derivatives of hydrides of elements having different numbers of electron shells, the Brönsted equation fails. Thus mercaptans are as readily formed from alkyl halides as alcohols are, although H_2S is more than 10^3 times as strong as water, and thioethers react with alkyl iodides fairly readily though their basicities are hardly demonstrable. The halides show similar anomalies. Thus C_2H_5Br reacts more rapidly with bases than C_2H_5Cl, while bromide ion is a more efficient basic reagent than chloride ion and HBr has a larger catalytic constant than HCl.[25] In every case the bromide reacts more rapidly than the chloride. Here the relative strength of the acids and bases involved cannot be the only factor that governs the relative rates of the three-centered acidic and basic reactions. The fact that Br^- is a more efficient basic reagent than Cl^- could be taken as evidence that HBr is a weaker acid than HCl. In that case alkyl chlorides would be expected to react faster than the bromides and HCl to have a higher catalytic constant than HBr.

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[25] Hantzsch, A., *Ber.*, **58**, 612 (1925).

Where the change of rate with the base strength is small, other factors besides base strength readily appear. For instance, the breaking of the C—O bond of epichlorohydrin is nearly as rapid with water as with acetate ion. The relative rates correspond to an x value of 0.15 as base-catalyzed reactions. The reaction with chloride ion is about twice as fast as that with acetate ion, and the reaction with iodide ion about a hundred times as fast as that with chloride ion.[26]

For three-center basic reactions it appears to be a general rule that, other factors being equal, an increase in the number of electron shells of either the reactant or the product base increases the rate. This is attributable to the accompanying increase of polarizability of the valence electrons. This can be deduced qualitatively from the theory of the transition state. A greater proportion of the total basicity of a pair of electrons is effective at a larger distance when they belong to a readily polarizable atom than when they belong to a difficultly polarizable one. In the reaction $A{:}B + {:}C \rightarrow A{:} + B{:}C$ the resistance of the A—B bond is effective only from the equilibrium to the transition distance and the total energy of this bond gives an exaggerated measure of the resistance when A is a readily polarizable atom. The driving force of the reaction, the formation of the B—C bond, is effective only from infinity to the transition distance. The more readily polarizable the base ${:}C$, the greater the proportion of the bond energy which is available at large distances. The result is that, apart from their base strengths, the polarizabilities of ${:}A$ and ${:}C$ tend to make the reactions fast. In consequence, atoms with many electron shells are associated with fast reactions, whether their bonds are broken or whether they make bonds in the reaction.

43. THE STRENGTH OF THE PRODUCT ACID OR BASE (*A*)

According to the transition-state theory, the strength of the reactant and product bases of a three-center basic reaction affect the rate in opposite ways. The stronger the reacting base, the faster is the reaction; the stronger the base produced, the slower the reaction. A similar relationship holds for acidic reactions. In a complex reaction there is little doubt as to the identity of the reacting base, since the rate is determined by its concentration, but there is often considerable doubt as to the identity of the product base. For instance,

[26] Brönsted. J. N., Kilpatrick, Mary, and Kilpatrick, M., *J. Am. Chem. Soc.*, **51**. 428 (1929).

the rate of the basic hydrolysis of an ester varies with the concentration of hydroxide ion and the concentration of the ester. The former fact leaves no doubt that hydroxide ion is the reacting base, but the latter does not tell us what part of the ester molecule, $RCOOR'$, is the product base. The reaction may be determined by the base strength of

$$R\ddot{C}O\bar{O},\ \bar{O}{-}R',\ \text{or}\ R\overset{\bar{O}}{\overset{|}{\overset{+}{C}}}{-}OR'.$$

Again, when the three-center reaction is greatly perturbed by the Lowry effect of the solvent, there is, strictly speaking, no basic product. Instead of $A{:}B + {:}C \rightarrow A{:} + B{:}C$ we have

$$SH + A{:}B + {:}C \rightarrow SH{:}A + B{:}C,$$

where SH is the acid solvent. The basicity of ${:}A$ resists the reaction by preventing the combination of B with ${:}C$, but it also assists the reaction by combining with SH. For these reasons, the relationship between the strength of the product as a base or an acid and the rate of a basic or acidic reaction is not as clear-cut as the corresponding correlation of rate and basic or acidic strength of the reactant.

When the conditions are such that the group that functions as A in the reaction $A{-}B + C \rightarrow A + B{-}C$ can be definitely recognized, the expected correlation between the acidic or basic strength of the product and the reaction rate is found. This correlation can be expressed by equations corresponding to those of Brönsted, but with a change of sign. Thus for a basic reaction $\log k = \log G + x \log K_a$, and for an acidic reaction $\log k = \log G - x \log K_a$, where K_a is the dissociation constant of the acid conjugate to the base formed, or the dissociation constant of an acid formed.

There is no doubt that the reaction

$$RCOOCH_3 + N(CH_3)_3 \rightarrow RCOO^- + N(CH_3)_4{}^+$$

belongs to the type $A{:}B + {:}C \rightarrow A{:} + B{:}C$, and that $A{:}$ corresponds to $RCOO^-$. The rate of this reaction should vary directly with the strength of the acid $RCOOH$ when R is changed. This comparison has been made by Hammett and Pfluger[27] and they find that $\log k$ is a linear function of $\log K$, or

$$\log k = \log G + x \log K_a .$$

[27] Hammett, L. P., and Pfluger, H. L., *J. Am. Chem. Soc.*, **55**, 4079 (1933).

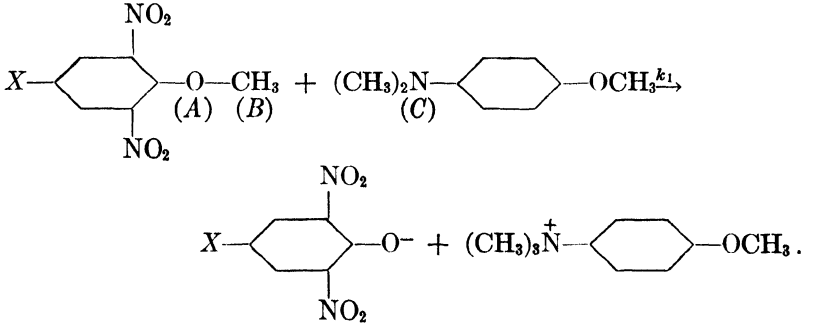
This relationship is shown in Table 47, where x has been taken as 0.8 and the accuracy of the relationship shown by the constancy of log G. The constancy is fairly good considering that aliphatic and ortho-substituted aromatic acids are included.

TABLE 47

THE LOGARITHMS OF THE RATE CONSTANT OF THE REACTION $RCOOCH_3 + N(CH_3)_3 \rightarrow RCOO^- + N(CH_3)_4^+$ AND THE DISSOCIATION CONSTANT OF RCOOH FOR VARIOUS R-GROUPS

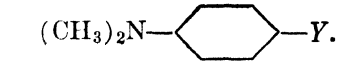
Acid	Logarithm of Rate Constant	Logarithm of Dissociation Constant	Log G
Acetic	−2.23	−4.74	1.55
p-Toluic	−1.91	−4.35	1.57
Benzoic	−1.79	−4.17	1.55
o-Toluic	−1.78	−3.87	1.32
Lactic	−1.45	−3.86	1.64
o-Chlorobenzoic	−1.14	−2.88	1.16
p-Nitrobenzoic	−0.95	−3.40	1.77
Phthalic	−0.91	−3.18	1.63
o-Nitrobenzoic	−0.5	−2.18	1.24

Another example in which there is a clear-cut relationship between the base strength of A and the rate is the following reaction:

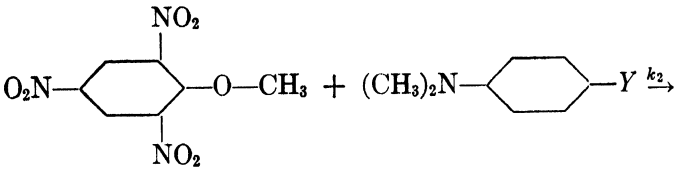


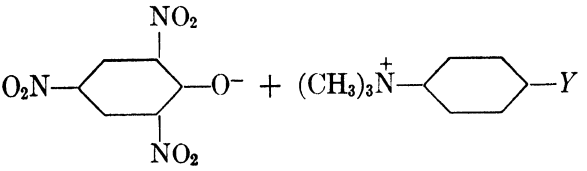
The rates of these reactions increase as the substituent, X, makes A: (i.e., $XC_6H_2(NO_2)_2O^-$) a weaker base. The ascending order of the effects of the groups is the normal order for para substituents, i.e. $N(CH_3)_2$, OCH_3, H, Cl, NO_2. The range of rate constants is 1.3×10^4 fold. This is greater than 2×10^3, the range of the dissociation constants of the corresponding monosubstituted phenols, XC_6H_5OH.

In striking contrast with the foregoing is the effect of change of the para substituent of the reacting base



The reactions





increase in speed as the substituent, Y, makes $:C$ (i.e. $YC_6H_4N(CH_3)_2$) a stronger base. The order of the effects of the Y groups is the reverse of that found when they are para substituents of the ether. These results are shown in Table 48.

TABLE 48

RELATIVE RATES OF QUATERNIZATION OF $(CH_3)_2NC_6H_4OCH_3$ WITH $XC_6H_2(NO_2)_2OCH_3$, AND OF $(CH_3)_2NC_6H_4Y$ WITH $O_2NC_6H_2(NO_2)_2OCH_3$ AT 35° IN ACETONE*

X or Y Group	X in Ether		Y in Amine	
	k_1†	Relative Rate	k_2†	Relative Rate
p-$N(CH_3)_2$	0.00005	1	0.7	5830
p-OCH_3	—	—	0.65	5410
p-CH_3	0.0004	8	0.272	2270
H	0.001	20	0.11	917
p-Cl	0.0055	110	0.025	208
p-NO_2	0.65	13000	0.00012	1

* Hertel, E., and Lührmann, H., *Z. Elektrochem.*, **45**, 405 (1939).

† Bimolecular constant in moles per liter and hours.

44. THE MIDDLE GROUP (*B*) IN THE THREE-CENTER REACTION

As we have seen, in its present very elementary form the transition-state theory gives an indeterminate answer to the question as to how a change of B in $A—B + C \rightarrow A + B—C$ affects the rate of an acidic or basic reaction. Hinshelwood, Laidler, and Timm[28] attempt an answer for the effect of these structural changes on the heat of activation. This answer would be applicable to the rates

[28] Hinshelwood, T. N., Laidler, K. J., and Timm, E. W., *J. Chem. Soc.*, 848 (1938).

also, as generally a decrease in the activation energy is accompanied by an increase in speed. They consider a change of structure in B as equivalent to a change in charge of the atom bonded to A, and the competition between A and C for this atom as a competition of two charges for the opposite charge on B. The change of charge on B produces a double change on the energy of the transition state, one for the effect of the interaction of A and B and the other for that of B and C. These are: $-\frac{e_A \delta e_B}{r_A}\left(\frac{r_A}{r_0} - 1\right)$, where e_A is the effective charge on A, δe_B is the change in the charge of B produced by the variation of structure, r_A is the distance between A and B in the transition state, and r_0 is the equilibrium bond distance of A—B; and $\frac{e_C \delta e_B}{r_C}$, where e_C is the effective charge on C and r_C is the B to C distance in the transition state.[29]

The signs of the effective charges on A and C are the same, so that the two potential-energy terms $\frac{e_A \delta e_B}{r_A}\left(\frac{r_A}{r_0} - 1\right)$ and $\frac{e_C \delta e_B}{r_C}$ have opposite effects on the activation energy. Thus in a basic reaction e_A and e_C are negative charges, and, if δe_C is positive, $\frac{e_A \delta e_B}{r_A}\left(\frac{r_A}{r_0} - 1\right)$ increases the activation energy, and $\frac{e_C \delta e_B}{r_C}$ decreases it. When δe_B is negative, the effects are reversed. In acidic reactions the relationship between the sign of δe_B and its two effects on the activation energy is the opposite of that for basic reactions. In general, the distance r_A is not much greater than r_0, and the interaction of δe_B with e_C is the predominant factor. Therefore, for basic reactions the heat of activation is decreased by a positive δe_B and increased by a negative one, and the reverse is true for acidic reactions. However, when the distances r_A and r_B are much larger than the bond distance r_0, $\frac{e_A \delta e_B}{r_A}\left(\frac{r_A}{r_0} - 1\right)$ is greater in magnitude than $\frac{e_C \delta e_B}{r_C}$, and consequently the effects of δe_B on the activation energies are reversed. The normal effect of a structural change that decreases the positive charge on B is to decrease the rate of a basic reaction and increase the rate of an acidic one; but when the transition state is diffuse (large separation of A, B, and C) the effect is reversed. However, in both cases there is a definite order for the effects of a series of groups.

[29] In the original paper, e_C and e_A have the opposite meanings, as the reaction is written $A + B—C \rightarrow A—B + C$.

A structural change that increases the positive charge of the central group is one that increases its strength as an acid, and decreases its strength as a base. In a basic reaction the central group is an acid and in an acidic reaction it is a base. There is therefore a correlation between the acidic or basic strength of the central group and the reaction rate. Normally, the stronger acid the central group is, the faster the basic reaction, but with a diffuse transition state the reverse is true.

The relationship between the strength of an aromatic central group and the reaction rate is given approximately by Hammett's equation. Normally, for a basic reaction ρ is positive, but with a diffuse transition state ρ is negative. Hammett cites sixteen cases of basic reactions in which the central group is aromatic and has been varied by meta and para substitutions. In all of these his equation is a fair approximation. In eleven of these ρ is positive. This confirms but does not prove that the majority of basic reactions have normal rather than diffuse transition states. That Hammett's equation holds suggests that an equation similar to Brönsted's equation would also give the relationship between the acidic or basic strength of the central group and the reaction rate. The equation for a basic reaction would be $\log k = \log G + x \log K_a$ for a normal transition state, or $\log k = \log G - x \log K_a$ for a diffuse transition state. The equations for acidic reactions would be $\log k = \log G - x \log K_a$ and $\log k = \log G + x \log K_a$ for normal and diffuse transition states, respectively. These equations have never been experimentally tested.

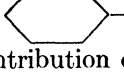
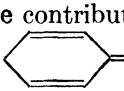
45. INDUCTIVE AND TAUTOMERIC EFFECTS

We have so far considered the effects of change of structure on reaction rate from the point of view of the thermodynamic properties of the transition state. Our deductions from the transition-state theory are, in the main, the same as those of Hinshelwood, although our approach has been somewhat different. In the paper quoted above, Hinshelwood notes that the deductions from the theory of the transition state are essentially the same as those made by the English school of chemists from a set of effects due to displacements of bond electrons from the midpoint of the bonds. We shall therefore give some account of these effects.

The effects are divided into two classes: inductive or I effects and tautomeric or T effects. Each class may be considered either as a permanent displacement of the electrons or as imposed on a molecule

by the approach of a reagent molecule. Thus, I effects are permanent or I_s, and dynamic or I_d, and are called, respectively, inductive and inductomeric effects. Similarly classified, the T effects become mesomeric or M and electromeric or E effects.

I effects of both kinds are represented by the symbol $\rightarrow$–, and T effects by the symbol $\curvearrowright$. In both cases the arrow points in the direction of the electron displacement.

An I_s effect is identical with what we have called a polar effect, and an M effect with what we have called a resonance effect, in considering the relationship between structure and equilibrium. The I_s effect arises from the uneven sharing of electrons in a bond between two atoms of different species or is transmitted to a bond between similar atoms from such a source, or from a formal charge of a neighboring atom. The M effect is a displacement due to the contribution of an alternative resonating structure in which atoms have formal charges. Thus we may represent methyl chloride by $H_3C\rightarrow$–Cl to show the electron displacement in the bond between carbon and chlorine, and aniline by  to show the electron displacement due to the contribution of the ortho and para quinoidal structures such as  .

When a bond with a marked I_s effect (e.g., $H_3C \rightarrow$ Cl) is broken, reactions in which the bond electrons are displaced in the direction of the arrow are assumed to be more rapid than those in which the electrons are displaced in the opposite direction. Thus CH_3Cl reacts with OH^- to form CH_3OH and Cl^- more rapidly than it would to form CH_4 and ClO^-.

In reactions of the type $A{:}B + {:}C \rightarrow A{:} + B{:}C$, any structural change of A that would reduce the potential of the negative charge on $A{:}$ has the I_s effect of increasing the rate, and similarly any structural change in ${:}C$ that has the opposite I_s effect increases the rate of the reaction. Similarly, structural changes producing the M effects on A and C shown by the curved arrows in $\overset{\frown}{A}{:}B + {:}\overset{\frown}{C} \rightarrow A{:} + B{:}C$ increase the reaction rate. These assumptions are quite natural. The correlation that exists between reaction rates and the strengths of reacting acids and bases is the experimental justification for them.

With respect to structural changes in B, it is generally assumed that an I_s effect that increases the positive charge on B accelerates the reaction $A{:}B + {:}C \rightarrow A{:} + B{:}C$. It is recognized that this

cannot be made a universal rule. When A: and B are separated with very little assistance from $:C$, this rule must be reversed.

The inductomeric effect is similar to the effect of polarizability which we have discussed in considering the deviation from the rule that the stronger the reacting base or acid, the faster the reaction. Thus the greater reactivity in three-centered basic reactions of both alkyl bromides and bromide ions than of the corresponding chlorine compounds is to be attributed to greater inductomeric possibilities of bromine atoms.

Later we shall consider the effect of resonance in the reactants and in the transition state on reaction rate. These correspond to the M and E effects.

46. THE EFFECT OF BRANCHING CHAINS

The rates of reaction of alkyl compounds vary with the degree of branching of the chain. The effect is most marked the nearer the branching is to the point of reaction. Hence in any general reaction of alkyl compounds the rate depends on whether the reactant is a primary, secondary, or tertiary alkyl compound. The relationship between the rates and the structure of the radicals changes with the type of reaction considered. In general, reactions of alkyl com-

Table 49

RELATIVE RATES OF ESTERIFICATION OF p-$O_2NC_6H_4COCl$ BY ALCOHOLS

Alcohol	Number Measured	Relative Rate	Per Cent Average Deviation
Methyl alcohol	1	2.40	—
Normal primary alcohols	6	1.0	8.7
2-Methyl-1-ols	3	0.44	5 3
3-Methyl-1-ols	3	0.97	2.7
Secondary alcohols	6	0.078	32
Tertiary alcohols	3	0.029	24
Aromatic primary alcohols	3	0.33	38
Aromatic secondary alcohols	3	0.0065	0

pounds can be divided into two classes: one in which tertiary alkyl compounds react faster than secondary and these in turn faster than primary, and the other in which this order is reversed. These orders are found not only when the alkyl radical is attached to a group that is removed in the reaction but also when its bond remains intact during the reaction. Thus the various alcohols react at different speeds with carboxylic acyl compounds, though in these processes the alkyl oxygen bond is not ruptured. The above table shows

the relative rates of reaction of some types of alcohols with *p*-nitrobenzoyl chloride taken from the work of Norris, Ashdown, and Cortese.[30]

Somewhat similar results are obtained by comparing the relative rates of acetal formation for acetaldehyde and various alcohols[31] as shown in Table 50.

TABLE 50
RELATIVE RATES OF FORMATION OF ACETALS USING ACETALDEHYDE AND VARIOUS ALCOHOLS

Alcohol	Relative Rate
Methyl alcohol	1.0
Ethyl alcohol	0.50
Propyl alcohol	0.46
n-Butyl alcohol	1.3
n-Heptyl alcohol	2.25
2-Propanol	0.042
2-Butanol	0.054
2-Pentanol	0.096
tert-Butyl alcohol	0.005

The acetal reaction is unusual in that, in a reaction that is faster for primary than for secondary alcohols, methyl alcohol is not the most reactive of the simple alcohols. The relative rates indicate that the rates tend to increase with the number of carbon atoms. The reason for this increase is that an acid catalyst is used and the alcohols are diluted only with the aldehyde. The activity of the catalyst increases as the per cent of oxygen in the solvent molecule diminishes, so that the catalyst is more active when an alcohol of high molecular weight than when one of low molecular weight is used.

Reactions of alkyl halides with hydroxide ion or amines (primary, secondary, or tertiary), the reaction of alkyl quaternary ammonium ions with hydroxide ion, and the reaction of trialkyl sulfonium ions with hydroxide ion are other instances in which the methyl compound reacts faster than the ethyl, the compounds of primary radicals faster than those of the secondary, and the latter faster than those of tertiary radicals. These reactions as a rule show a ratio of about 10 to 1 for the reaction rate of the methyl compound to that of the ethyl. The comparative reaction rates of ethyl and isopropyl or *tert*-butyl are often difficult to obtain, owing to the tendency

[30] Norris, J. F., and Ashdown, A. A., *J. Am. Chem. Soc.*, **47**, 837 (1925); Norris, J. F., and Cortese, F., *J. Am. Chem. Soc.*, **49**, 2640 (1927).

[31] Fehlandt, P. R., and Adkins, H., *J. Am. Chem. Soc.*, **57**, 193 (1935); and Hatch, G. B., and Adkins, H., *ibid.*, **59**, 1694 (1937).

for other reactions to occur with secondary and tertiary compounds. Hughes, Ingold, and Shapiro[32] have separated the reaction of isopropyl halides with aqueous alcoholic solutions of sodium hydroxide into its component parts and found that the bimolecular alkaline hydrolysis is only about $\frac{1}{25}$ as fast as the corresponding reaction of the ethyl halide.

On the other hand, the order of rates Tertiary > Secondary > Primary holds for a great number of reactions. A few examples are the hydrolyses and alcoholyses of alkyl halides without aid from hydroxide ion; the formation of alcohols from trialkyl sulfonium ions without the aid of strongly basic negative ions; the formation of ethylene derivatives from the halides and from the alkyl quaternary ammonium ions in basic solution, or from the alcohols in acid solution. In some of these the reaction rate of the tertiary compound is

Table 51

COMPARISON OF THE REACTIONS OF SOME ALKYL BROMIDES WITH PYRIDINE

Alkyl Bromide	Relative Rate of Alkene Formation	Relative Rate of Quaternary Ammonium Salt Formation
Ethyl bromide	1.5	2.1
n-Propyl bromide	1.5	1.4
n-Butyl bromide	1.0	1.0
iso-Butyl bromide	1.5	0.07*
sec-Propyl bromide	10.0	0.14
sec-Butyl bromide	13.5	0.09
tert-Butyl bromide	875	Not measurable

* This branched but primary bromide quaternizes at a rate characteristic of secondary rather than of primary bromides.

enormously greater than that of the secondary. Thus the work of Hughes, Ingold, and Gleave[33] has shown that *tert*-butyl and *sec*-propyl alcohols are eliminated from their trialkyl sulfonium ions without the aid of a basic negative ion, but the elimination of the tertiary alcohol is 2600 times as fast as that of the secondary. In the unimolecular hydrolysis[34] and alcoholysis this ratio can reach an order of magnitude of 10^4.

Table 51, from the work of Noller and Dinsmore,[35] shows the

[32] Hughes, E. D., Ingold, C. K., and Shapiro, U. G., *J. Chem. Soc.*, 225 (1936); 1177 (1937).

[33] Hughes, E. D., Ingold, C. K., and Gleave, J. L., *J. Chem. Soc.*, 1571 (1933); 236 (1935).

[34] Cooper, K. A., and Hughes, E. D., *J. Chem. Soc.*, 1183 (1937).

[35] Noller, C. R., and Dinsmore, R., *J. Am. Chem. Soc.*, **54**, 1025 (1932).

behavior of alkyl bromides with pyridine, with which they can react in two ways: to form an ethylene derivative or to form a quaternary ammonium salt. The former is a reaction where the order of rates is Tertiary > Secondary > Primary; in the latter, the order is reversed.

The differences in the reaction rates of primary, secondary, and tertiary alkyl compounds are generally attributed to the inductive effect. The replacement of a hydrogen atom by a methyl group is acid-weakening; i.e., it induces a negative charge on the atom on which the substitution has occurred, and also but to a less extent on the next atom. It therefore increases the ease of ionization of a halide ion from the molecule. This ease of separation can be more than compensated for by the smaller attraction for the reacting base. Consequently, the primary halides require a stronger basic reagent than the tertiary halides, but this order is reversed when the reagent acts as an ionizing rather than a basic reagent.

There seems little doubt that the inductive effect is responsible to a large extent for the relative rates of the reactions of primary, secondary, and tertiary alkyl compounds, but it is very doubtful that it is a complete explanation. The general reason for this skepticism is the insufficiency of the inductive effect to explain the results of alkyl for hydrogen substitution in static problems. Thus this substitution may produce increase instead of decrease in acidic strength, as in certain malonic acids, in aminoacetic acids, or in the change from secondary to tertiary ammonium ions. The primary, secondary, or tertiary character of carbon atoms produces strong effects on equilibria in which no definite difference in the polarities of reactants and products is apparent: e.g., in the reduction of ethylenes, in carbon bond energies, and in free radicals (see Chapter VII). Even the simplest inductive effect of this substitution, the production of an electric dipole in the change from benzene to toluene, is not explicable as a purely inductive effect; for, in the configuration obtained by using regular tetrahedra for the carbon atoms, the resultant of the three C—H dipoles of the methyl group is not balanced by that of the para C—H dipole. It would seem that there is no completely satisfactory explanation of all the effects resulting from the branching of the carbon chain.

Some specific objections can and have been raised to the explanation of the effects on the relative reaction rates of primary, secondary, and tertiary alkyl compounds as a simple inductive effect. Taylor[36]

[36] Taylor, W., *J. Chem. Soc.*, 992 (1937).

has shown that the order of velocities of the reactions of bromides with aqueous alcohol is *tert*-butyl ≫ methyl > *sec*-propyl > ethyl. The order of inductive effects is *tert*-butyl > *sec*-propyl > ethyl > methyl. This objection is probably not valid, as water or alcohol may have two independent actions on the bromide—as a base or as an ionizing agent—each reaction having its own transition state. Methyl bromide may react faster by the former reaction than propyl bromide does by the latter.

It is difficult to see how the relative inductive effects could result in the rule that, in alkene formation by the action of a base on an alkyl halide, the hydrogen from the least hydrogenated carbon atom adjacent to the halogenated carbon atom is removed. Thus CH_3—CHI—$CH(CH_3)_2$ forms CH_3—CH=$C(CH_3)_2$ rather than CH_2=CH—$CH(CH_3)_2$. If ionization of the chloride ion is preferred from R_3CCl rather than from RCH_2Cl, then $R_3\overset{+}{C}$ is a weaker acid than $R\overset{+}{C}H_2$, and $R_3\overset{-}{C}$: is a stronger base than $R\overset{-}{C}H_2$:. The removal of hydrogen ion by a base would be expected on these grounds to be faster from RCH_2H than from R_3CH. Hence the expected product would be CH_2=CH—$CH(CH_3)_2$.

The measurements shown in Table 49 are also difficult to explain on inductive effects alone. Without knowing more about the intimate mechanism of the reaction $ROH + O_2NC_6H_4COCl \rightarrow O_2NC_6H_4COOR + HCl$ than we do, it is not possible to predict the order to be expected from inductive effects. But the experiments show that the substitution of a methyl radical for a hydrogen atom in the *R* group decreases the rate of reaction, and this effect is more marked the nearer the substitution is to the point of reaction. However, the order of *I* effects is CH_3, H, C_6H_5, so that the introduction of a phenyl group instead of an alkyl one into the alcohol might be expected to have the opposite effect of that of a methyl group; or, if one allows for a certain amount of error in obtaining the relative *I* effects of groups, and assumes the order of *I* effects to be CH_3, C_6H_5, H, the phenyl group might, like the methyl group, decrease the rate, but to a much less extent. The actual values show that the introduction of the phenyl group decreases the reaction rate to a much greater extent than does the methyl group. The relative rates are 1 for RCH_2OH, and 0.078 for R_2CHOH, but 0.0065 for RArCHOH.

47. THE EFFECT OF RESONANCE ON REACTION RATE

It follows from the theory that the rate of a reaction is proportional to the free energy difference between the transition state and

the reactants. Therefore, resonance increases the rate of reaction when the resonance energy is greater for the transition state than for the reactants, and decreases the rate when the reverse is true. It is quite common to find that a compound which would give a highly resonating product if a certain bond were dissociated reacts rapidly with reagents that attack this bond. The high rate of reaction is a resonance effect. However, in these cases the activation energy is often not abnormally low. The rate appears to be more susceptible to resonance than does the activation energy. If we consider the transition state as the top of a ridge separating the valleys (reactants and products), resonance reduces the height of the entire ridge. The higher parts of this ridge can be more favorable for resonance than the lower, and the proportion of the reacting molecules that pass through these higher energy configurations is increased by resonance. In consequence, though the height of the transition barrier as a whole is lowered and the number of molecules per second passing across it is increased, the average height across which the molecules pass (activation energy) need not be decreased.

47a. Effect of resonance in a reacting or product base. Let us consider a reaction of the type $A{:}B + {:}C \rightarrow A{:} + B{:}C$ in which ${:}C$ is the resonating structure $({:}M{-}P{=}Q,\ M{=}P{-}Q{:})$. The interaction of ${:}M$ and $P{=}Q$ is greater in the reactant, $:M{-}P{=}Q$, than it is in the transition state, $A{:}B{:}M{-}P{=}Q$, since in the latter the basicity of $:M$ is to some extent neutralized by B. From our fundamental axiom, the resonance $({:}M{-}P{=}Q,\ M{=}P{-}Q{:})$ here decreases the reaction rate.

Were we to assume that this resonance were absent in the transition state, the resonance term in the free energy of the base would apply equally to the equilibrium constant for the addition of a proton and to that for the formation of the transition state. The magnitude of the resonance effect **R** would be the same in the expressions for the dissociation constant of the acid and the rate of the reaction; i.e., $\log K_a = \log K_0 + \mathbf{R}$ and $\log k_a = \log k_0 - \mathbf{R}$, where K_0 and k_0 are the values that the dissociation constant of the acid and the rate constant for a reaction of its base would have if there were no resonance at all. By Brönsted's equation, $\log k_0 = \log G - x \log K_0$, so that $\log k_a = \log G - x \log K_a + (x - 1)\mathbf{R}$. Hence Brönsted's equation, $\log k_a = \log G - x \log K_a$, would not apply to a resonating base unless x were nearly equal to one. However, experimentally it seems to apply equally well to resonating and nonresonating bases; hence we may assume the resonance is in part retained in the transition state. The molecular conditions arranged

in ascending order of the degree to which the electron pair of a base partakes of resonance with an adjacent double bond can be given (1) as in stable combination, (2) as in a transition state, and (3) as the free base. If this is so, then in the reaction $A{:}B + {:}C \rightarrow A{:} + B{:}C$, if $A{:}$ is ${:}M{-}P{=}Q$, there is more interaction between ${:}M$ and $P{=}Q$ in the transition state than there is in the reactant ($Q{=}P{-}M{:}B$). Hence the resonance increases the rate of reaction. We then have the rule that ${:}M{-}P{=}Q$ is a slowly reacting base, but its compound ($Q{=}P{-}M{:}B$) reacts rapidly with bases. This rule is illustrated by the effects of the resonance of a para nitro group on the reaction

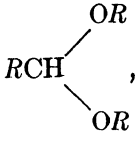
$$XC_6H_2(NO_2)_2OCH_3 + (CH_3)_2NC_6H_4Y \rightarrow XC_6H_2(NO_2)_2O^- + (CH_3)_3\overset{+}{N}C_6H_4Y$$

(see Table 48); when Y is the p-nitro group in the reacting base the reaction is very slow, but when X is the p-nitro group of the methoxy compound the reaction with the base is very fast.

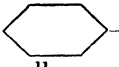
47b. Resonance of the middle group of the transition state. Apparently in the transition state of $A{:}B + {:}C \rightarrow A{:} + B{:}C$, and of other three-center reactions, resonance occurs not only with groups in A and C as we have shown above but also with groups in B, for we find that structural changes in B that produce a greater resonance in B than in $A{:}B$ increase the rate of reaction. The most important of these structural changes are the introduction of a double bond so that B becomes a group of the type $M{-}P{=}Q$, with M either lacking or having unshared electrons, and the introduction of an atom of markedly basic character so that B becomes a group of the type $M{-}P{:}$ in which M is acidic and P basic.

We have seen that when the structural form of a reactant is such that its resonance is decreased when it combines, the reaction rate is retarded but when it is such that the breaking of a bond would increase the resonance, a reaction in which that bond is broken is accelerated. This is expressing certain well-known generalizations in terms of a theory. The first generalization is that when the combining atom of a base is attached to a pair of doubly bonded atoms (i.e., is alpha to the double bond) it is a less reactive base than one in which this relationship is not present. For example, the negatively charged oxygen atom of a carboxylate ion or of a phenolate ion is alpha to a double bond, and these ions react much less rapidly in general than do alcoholate ions. The second generalization is that a reaction that breaks the bond of an atom alpha to a double bond is abnormally fast. The third generalization is that if the products

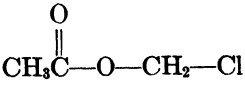
of the reaction are such that it appears that the electrons move away from an atom attached to a basic atom (one having unshared electrons of appreciable combining power), the reaction is abnormally fast. For example, in the hydrolysis of an ether the electrons of the C—O bond would be removed from the carbon. Hence by this rule an acetal,



since it has another basic oxygen atom attached to the carbon atom, is an abnormally rapidly hydrolyzed ether. The first of these rules applies to C in $A—B + C \rightarrow A + B—C$; the second and third apply to $A—B$, irrespective of whether the structural peculiarity mentioned in the rule is situated in A or in B.

Table 52 taken from the work of Conant, Kirner and Hussey[37] shows an application of the last two of the above rules. The reaction is between organic chlorides and potassium iodide in acetone solution. It is probably a three-center basic reaction with iodide ion attacking the organic radical and releasing chloride ion. The relative rates of similar halides reacting with tertiary amines or negative ions are very similar and show the same phenomenon. The compounds having as part of their structures C=C—C—Cl,  —C—Cl, O=C—C—Cl, N≡C—C—Cl, and O—C—Cl, all react much more rapidly than saturated alkyl compounds. These two rules must be qualified by the proviso that the bond in $A—B$ is not of such a character as to permit a strong resonance interaction with the unsaturated group, for in that case the resonance could be greater in the reactant than in the transition state. This proviso would be applicable if the bond between A and B were a double one, or if the contribution of an ionic component to the A—B bond were great.

The relative rates shown in Table 52 and those of similar reactions that might have been used to illustrate the rules also have some other characteristics in common. Thus, when an oxygen atom is alpha to a carbonyl group, the interaction between them diminishes the basicity of the oxygen atom and the unsaturated character of the carbonyl group. Consequently the reaction of



[37] Conant, J. B., Kirner, W. R., and Hussey, R. E., *J. Am. Chem. Soc.*, **46**, 232 (1924); **47**, 476, 488 (1925).

is slower than that of $CH_3O—CH_2—Cl$, and the reaction of an α-chloro ester is slower than that of an α-chloro ketone. The latter phenomenon is due to the same causes which make the dissociations and enolizations of β-ketonic esters smaller than those of 1,3-diketones. While these relationships are to be expected from the resonance theory, another peculiarity of the relative rates is shown in Table 52, and by other cases of high reactivity of alpha halogen atoms, which is not in accord with a simple resonance explanation of the phenomena. This relationship is that C—Cl bonds alpha to a carbonyl group are much more reactive than those alpha

TABLE 52

RELATIVE RATES OF REACTION OF *R*Cl WITH KI IN ACETONE

No Direct Interaction		Direct Interaction	
Compound	Relative Rate[a]	Compound	Relative Rate[b]
n-C_4H_9Cl	1.00	$C_6H_5COCH_2Cl$	105000
C_2H_5Cl	1.94	CH_3COCH_2Cl	35700
n-$C_5H_{11}Cl$	1.26	$N{\equiv}C—CH_2Cl$	3070
		$CH_3C(=O)—O—CH_2Cl$	270
iso-$C_5H_{11}Cl$	0.65		
		$C_2H_5OC(=O)—CH_2Cl$	1720
$CH_3CHClCH_3$	0.015		
		$(C_2H_5OC(=O))_2CHCl$	60200
n-$C_3H_7CHClCH_3$	0.048	$CH_2{=}CH—CH_2Cl$	79
$(CH_3)_3CCl$	0.018	$C_6H_5CH_2Cl$	197
cyclo-$C_6H_{11}Cl$	0.0001	$(C_6H_5)_3CCl$	38000
$C_6H_5(CH_2)_3Cl$	1.35	$CH_3O—CH_2Cl$	918
$C_6H_5CO(CH_2)_3Cl$	230[b]		

[a] At 60°C. [b] At 50°C.

to an aromatic nucleus or to an ethylenic double bond. Assuming the resonance to be between a positively charged atom and the double bond, there seems to be no reason why it should be more effective in the carbonyl than in the allyl or benzyl compounds. The transition state of the reaction of α-chloroacetone with iodide ion might be

$$\bar{I}:\overset{+}{Cl}:\overset{-}{C}H_2—\overset{O}{\overset{\|}{C}}—CH_3,$$

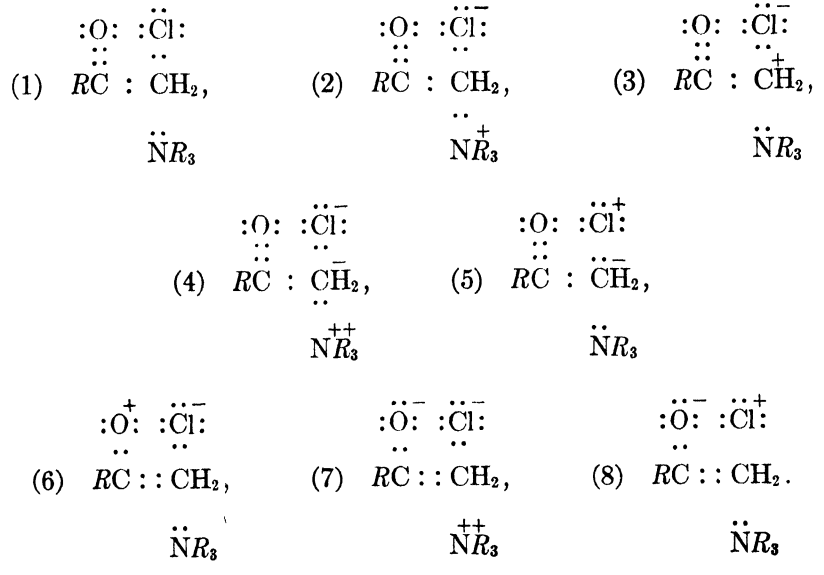
in which case a very strong interaction between $:C^-$ and $C{=}O$ would occur. Reactions of this type can actually occur. Thus

Olson[38] considers that it can be definitely shown that, in the rearrangement

$$CH_3COCHBrCOOC_2H_5 \rightarrow CH_2BrCOCH_2COOC_2H_5$$

catalyzed by HBr, bromine is formed as an intermediate. However, this theory of the high reactivity of bromine alpha to C=O compared to that of bromine alpha to C=C does not account for the fact that this higher reactivity is also found in reactions with tertiary amines and alcoholate ions. The reaction of a tertiary amine or an alcoholate ion with an organic halide produces a Walden inversion. The amine or other base must therefore be attached to the carbon and not to the halogen atom in the transition state.

A better and more general explanation of the high reactivity of a halogen attached to a carbon atom alpha to a carbonyl group can be obtained by considering all the resonating electronic distributions of the transition state. For the transition state of the reaction $RCOCH_2Cl + NR_3 \rightarrow RCOCH_2\overset{+}{N}R_3 + Cl^-$, the resonance is between the following electronic distributions:



Distributions (1) to (5) involve no interaction with the double bond. Distribution (6) is more stable in allyl and benzyl compounds than in carbonyl ones; but distribution (7) and (8) are more stable

[38] Olson, A. R., private communication.

in carbonyl than in allyl and benzyl compounds. Were the resonance effect of the double bond on the transition state due only to distribution (6), the α-halogen ketones would not be as reactive as the allyl and benzyl halides; but distributions (7) and (8) contribute strongly when and only when the double bond is one to an atom that can readily become negatively charged. This is especially the case with C=O and C≡N, and halogens on carbon atoms alpha to these groups are exceedingly reactive.

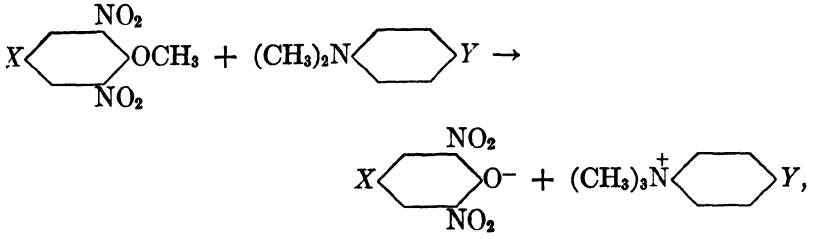
The activation of the alpha C—Cl bond by a carbonyl group is small compared to the corresponding activation of an alpha C—H bond. This activation can lead to a new path for the reaction, for it permits an acid- or base-catalyzed enolization to be the master reaction. This occurs in the halogenation of ketones and aldehydes at the alpha position. The rate of the reaction is then independent of the concentration and nature of the halogen. The important transition state (that for the master reaction) does not include the halogen. In other cases an ionization may be involved in the mechanism, but is not the master reaction. The important transition state then includes the other reactant but not the alpha hydrogen atom. Finally there may be no preliminary enolization, and both reactants and the α-hydrogen atom are included in the transition state. In all these cases the rate is increased by resonance, for there is little resonance in the reactants but more resonance in the transition state.

47c. Resonance effects of para substituents. Substitution changes a property of a compound not only through the direct action of the polarity and resonance of the introduced group, but also because by induction, resonance, or steric hindrance it alters the resonance and inductive effects which were present in the original compound. The effect of a substituent group therefore depends on the compound in which it is introduced. This generalization is as applicable to the rate of a reaction as it is to any other property. In aromatic compounds the effects of substituent groups are generally complicated in this way. Often the group resonates with the benzene ring and so changes the polarity of the ring or its resonance with other parts of the molecule. Further, the benzene nucleus often has large resonance effects on reaction velocities, and these resonances arise from forms that have formal charges in the ring and are therefore profoundly affected by the polar character of a substituent group. Nevertheless, we have seen in discussing the strengths of aromatic acids that the relative effects of meta and para substitutions are to a

great extent invariant to a change in the parent acid, though the effect of any one group depends greatly on the parent acid. Hammett has shown that this invariance of the effect of a substitution in a benzene ring is also largely true of reaction rates as well as acid strength. That is, the equation $ln\ k = ln\ k_0 + \sigma\rho$ holds both for rate and for equilibrium constants.

We have seen that in the acid strengths this invariance is found in meta substitutions and in para substitutions only when the group has no great resonance interaction with the basic atom produced by the dissociation of a proton. But groups such as NO_2, $B(OH)_2$, $C{\equiv}N$, etc., when in the para position, resonate strongly with the basic atom of phenolate ions and anilines, and their para σ values, calculated from the dissociation constants of phenylboric and aromatic carboxylic acids, cannot be used to calculate the strengths of phenols and anilines with these groups in the para position. Special σ values can be assigned for these groups in the para position of phenols and anilines, or a term could be added to log K_σ to correct for the extra resonance.

This extra resonance effect must also exist in the reaction rates of such para substituted phenols and anilines, when the resonance is markedly affected by the change from reactant to transition state. Thus in the reaction



when $X = NO_2$ there is more resonance of this type in the transition state than in the reactants; but when $Y = NO_2$ this resonance is greater in the reactants than in the transition state. Consequently the use of $\sigma(p\text{-}NO_2)$ as obtained from benzoic acids to calculate the rate gives too low a value when $X = NO_2$ and too high a value when $Y = NO_2$. If the values of $\sigma(p\text{-Cl})$ and $\sigma(p\text{-}NO_2\text{-benzoic})$ given in Table 46, and the values of the reaction rates when $X = Cl$, $Y = OCH_3$, and $X = H$, $Y = OCH_3$ (see Table 48) are used, then the value of log k for $X = NO_2$, $Y = OCH_3$ can be calculated. Similarly, log k for $X = NO_2$, $Y = NO_2$ can be calculated from $X = NO_2$, $Y = Cl$, and $X = NO_2$, $Y = H$. A comparison of

calculated and observed values confirms the prediction. The calculated values of log k for $X = NO_2$, $Y = OCH_3$ is less than that observed: -0.47 and -0.18, respectively; and the calculated value for $X = NO_2$, $Y = NO_2$ is greater than that observed: -3.16 and -3.92, respectively.

The basic groups—amino, hydroxyl, and alkoxyl—can also produce extra resonance when they are para to a group that readily accepts electrons. When this resonance is markedly greater in the transition state than in the ground state, the reaction will be anomalously fast. This rapidity is to be expected in the replacement of a negative ion from an atom para to the basic group when ρ for the reaction is negative, for a negative value of ρ indicates that the atom at which

Table 53

THE CALCULATED AND OBSERVED VALUES OF THE RELATIVE RATES OF THE ALCOHOLYSES OF PARA DERIVATIVES OF BENZOYLCHLORIDE AND TRIPHENYLMETHYL CHLORIDE

		$XC_6H_4COCl + C_2H_5OH$ $\rho = 1.38$		$XC_6H_4CCl(C_6H_5)_2 + C_2H_5OH$ $\rho = -2.38$	
X Group	σ	Log $\frac{k}{k_0}$	Log $\frac{k}{k_0}$ (Calc.)	Log $\frac{k}{k_0}$	Log $\frac{k}{k_0}$ (Calc.)
p-NO_2	0.778	1.28	1.08	−1.96	−1.85
p-I	0.276	0.279	0.359	−0.461	−0.657
p-Br	0.232	0.322	(0.322)	−0.553	−(0.553)
p-Cl	0.227	0.279	0.316	−0.495	−0.539
p-F	0.062	0.040	0.080	−0.120	−0.167
p-CH_3	−0.170	−0.222	−0.237	0.613	0.405
p-OCH_3	−0.268	−0.310	−0.372	>1.95	0.638

one base is being replaced by another lacks electrons in the transition state.

The foregoing has been illustrated in Table 53, taken from the work of Nixon and Branch.[39] The relative rates of the alcoholyses of two types of p-substituted aromatic compounds, benzoyl chlorides and trityl chlorides, have been calculated from the rates for the p-bromo derivatives, using Hammett's values for σ, and compared with the observed values. The alcoholysis of the benzoyl chlorides has a positive value of ρ, and the calculated and observed values agree as closely as can be expected. The alcoholysis of the trityl chloride has a negative value of ρ, and here the calculated and observed values agree as closely as can be expected except that of

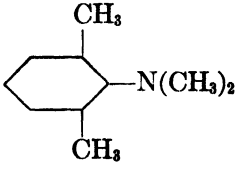
[39] Nixon, A. C., and Branch, G. E. K., *J. Am. Chem. Soc.*, **58**, 492 (1936); Branch, G. E. K., and Nixon, A. C., *J. Am. Chem. Soc.*, **58**, 2499 (1936).

p-methoxytriphenylmethyl chloride. The rate constant for the alcoholysis of this substance is more than twenty times as great as the calculated value.

48. STERIC EFFECTS

The equilibrium between reactants and the transition state, like other equilibria, is affected by the repulsions between atoms that are brought near to each other as a result of the steric requirements of bond distances and angles. When the effects of these repulsions are to increase the free energy of the reactants more than that of the transition state, these steric requirements increase the reaction rate, and when the reverse is the case the reaction is retarded. As we have seen in discussing equilibria, the steric factor acts in various ways. The simple repulsion between groups can be different in the two systems. The steric factor can impose a configuration in which the directly transmitted effects of the polarities of substituent groups is either at a maximum or at a minimum. The repulsions between groups can interfere with configurations favorable to resonance. The steric factor also determines the formation of chelate rings. In view of this complexity, we do not know very much about steric effects on reaction rates. Their existence was demonstrated many years ago, and they were called steric hindrances. It was assumed that groups prevented reactions by getting in the way of the approach of the reactive parts of the reactants. However, steric effects can result in an increase as well as a decrease of reaction rates.

Substitution in the ortho position is one of the commonest causes of steric effects. The earliest observation of the steric effect of ortho groups was made by Hofmann,[40] who found that



and related dimethylanilines with both ortho positions occupied form quaternary salts very slowly when heated with methyl iodide at 150°.

The theory of a steric effect was first advanced by V. Meyer to account for the slow esterification of ortho-substituted benzoic acids. Goldschmidt[41] and Kellas[42] found that ortho-substituted methyl-,

[40] Hofmann, A. W., *Ber.*, **5**, 713, 718 (1872).
[41] Goldschmidt, H., *Ber.*, **28**, 3218 (1895).
[42] Kellas, A. M., *Z. physik. Chem.*, **24**, 221 (1897).

chloro-, bromo-, iodo-, and nitrobenzoic acids are all esterified more slowly than benzoic acid. Thus after two hours at 51°, using the same concentration of hydrochloric acid, the percentages esterified were 82.5 for benzoic acid, 50.9 for *o*-chlorobenzoic acid, 48.3 for *o*-methylbenzoic acid, 20.5 for *o*-iodobenzoic acid, and 8.6 for *o*-nitrobenzoic acid. These differences are not due to the steric factor alone, but the existence of the steric factor is shown by the similar behavior of methyl and nitro groups, which in general have opposite effects. In the base-catalyzed hydrolyses of ortho-substituted esters, the nitro derivative is more active than the methyl one. In fact, the ester of *o*-nitrobenzoic acid hydrolyzes faster than that of benzoic acid in an alcoholic solution of potassium hydroxide. Even here steric hindrance is apparent, for *o*-nitrobenzoic ester hydrolyzes only a little faster than benzoic ester, but *o*-toluic ester hydrolyzes very much slower than benzoic ester. Should we extend the rule—that the relative effects of groups on the dissociation constant of a benzoic acid are the same as those on the rate of a reaction of an aromatic compound—to include ortho substituents, we would assume that *o*-toluic ester hydrolyzes a little faster than benzoic ester, and *o*-nitrobenzoic ester hydrolyzes very much faster. The alkaline hydrolysis of an ester of an aromatic acid is a reaction whose rate increases with the strength of the corresponding acid (ρ is positive) and the order of strengths of the acids are $o\text{-}O_2NC_6H_4COOH \gg o\text{-}CH_3C_6H_4COOH > C_6H_5COOH$.

The steric effects of ortho substituents are greatly enhanced when both ortho hydrogen atoms have been replaced. Meyer[43] based his theory largely on a study of the esterification of di-ortho-substituted benzoic acids. When CH_3, OH, and F are the substituents in the two ortho positions, benzoic acids do not esterify appreciably in twelve hours at 0° when their alcoholic solutions are saturated with hydrochloric acid. They do, however, esterify when hydrochloric acid gas is passed through their boiling alcoholic solutions. Even if the latter method is used, there is practically no esterification when both ortho positions are occupied by such groups as Cl, Br, I, and NO_2.

Countless examples of the steric effects of ortho substitution can be cited, but we shall content ourselves with the exceedingly interesting example of the reactions of ortho-substituted benzoyl chlorides with alcohol. These have been studied by Norris and his co-

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[43] Meyer, V., *Ber.*, **28**, 1254 (1895); also van Loon, J., and Meyer, V., *Ber.*, **29**, 839 (1896).

workers.[44] The rate of alcoholysis of benzoyl chloride is increased by para substitution of nitro and chloro groups, but decreased by para substitution of methyl and methoxy groups. A single *o*-nitro group increases the rate of reaction, but not nearly as much as a *p*-nitro group. A single *o*-chlorine also increases the rate and indeed more than that of a *p*-chlorine. The para chloro compound reacts about twice as fast as benzoyl chloride and the ortho isomer about three and a half times as fast. If one considers that the strength of benzoic acid is increased much more by an ortho than by a para nitro group, and is increased only 50 per cent by a *p*-chlorine but twenty fold by an *o*-chlorine, the *o*-nitro group and *o*-chlorine atoms either have a marked steric effect on the alcoholysis rate of benzoyl chlorides or have marked acid-strengthening steric effects on the strength of benzoic acid.

The methyl and methoxyl groups which decrease the rate in the para position increase the rate in the ortho position. Their steric effects in the ortho position are not hindrances, but strong assistances to the alcoholysis of the benzoyl chloride.

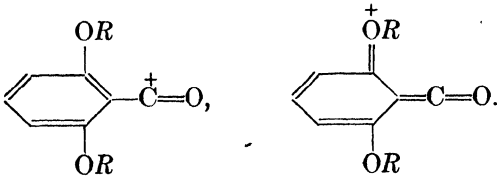
The alcoholysis of a 2,6-dinitro- or 2,6-dichlorobenzoyl chloride is so slow at 0° that it cannot be measured. That is, the rates must be less than one hundredth as fast as the alcoholysis of benzoyl chloride. The alcoholysis of a 2,6-dimethyl- or 2,6-dimethoxybenzoyl chloride at 0° is so fast that it cannot be measured. That is, it must be greater than a hundred times as fast as the alcoholysis of benzoyl chloride. In all these instances the ortho effect is greatly enhanced by having both ortho positions substituted. Two of the groups show steric hindrances, and the other two have steric effects that increase the reaction rate.

To understand these peculiar steric effects it is necessary to consider the difference between the reactions of $XC_6H_4CCl(C_6H_5)_2$ and of XC_6H_4COCl with alcohol. In the transition state of the former reaction, the unpaired electrons of the alcohol and of the chloride ion are distant from the methyl carbon atom. This carbon atom behaves as a positively charged carbon atom and resonates strongly with the benzene nuclei. Any substitution in a nucleus that stabilizes a positive charge by induction or resonance decreases the free energy of the transition state and increases the speed of the reaction. Hence a *p*-methoxy group increases the speed and a *p*-nitro group decreases

[44] Norris, J. F., Fasce, E. V., and Staud, C. J., *J. Am. Chem. Soc.*, **57**, 1415 (1935); Norris, J. F., and Young, H. H., Jr., *ibid.*, **57**, 1420 (1935); Norris, J. F., and Ware, V. W., *ibid.*, **61**, 1418 (1939).

it. On the other hand, in the alcoholysis of a benzoyl chloride the alcohol is close to the aliphatic carbon atom (there is probably a preliminary addition of alcohol to the carbonyl group) and this atom does not behave as a positively charged one. In the reactant, a benzoyl chloride, the carbonyl group has a large ionic component $(\overset{+}{C}—\overset{-}{O})$. Any substitution in the benzene nucleus that stabilizes a positive charge by induction or resonance decreases the free energy of the reactants and decreases the reaction rate. The *p*-nitro group increases the speed and the *p*-methoxy group decreases it. The effects of substitution on these two alcoholyses are shown in Table 53.

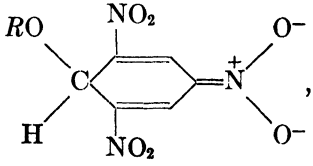
The steric effect of two ortho groups prevents the close approach of alcohol to the carbonyl group in the transition state for the alcoholysis of a benzoyl chloride. The reaction goes over to the same type as the alcoholysis of the trityl chlorides, i.e. one in which incoming and outgoing groups are loosely bonded in the transition state. The effects of halogens and nitro groups on the one hand and of methyl and methoxy groups on the other are reversed. The effect of the methoxy group is predominantly through its resonance. It should be noted that, in the normal molecule of 2,6-dimethoxybenzoyl chloride, the steric hindrance reduces the stabilizing resonance to a minimum by preventing the oxygen and chlorine atoms getting into the plane of the ring; but in the transition state the chlorine atom is further away and the resonance is not prevented, just as it would not be in the ion:



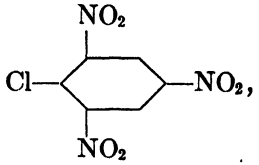
Steric effects are not limited to aromatic compounds. Sudborough and his co-workers[45] attributed the slower rate of esterification of alpha-substituted acetic acids ($k_{CH_3COOH}/k_{(CH_3)_3CCOOH} = 40$), the slower rate of esterification of *cis* acids than of *trans*, and the slower rate of esterification of unsaturated than of saturated acids, to steric hindrance. In general, however, an aliphatic compound has a greater number of configurations than an aromatic one, and steric hindrance is as a rule more complex and less striking in aliphatic than in ortho-substituted aromatic compounds.

[45] Sudborough, J. J., and Lloyd, L. L., *J. Chem. Soc.*, **73**, 81 (1898); Sudborough, J. J., and Lloyd, L. L., *ibid.*, **75**, 467 (1899); Sudborough, J. J., and Roberts, D. J., *ibid.*, **87**, 1840 (1905).

In the transition state of $A—B + C \rightarrow A + B—C$ there is a linear configuration of A, B, and C, so that a steric hindrance will result if the arrangement of atoms around B is such as to make it difficult to obtain this linear configuration. Thus, if a chlorine atom in C_6H_5Cl were replaced by such a reaction, it would be necessary to put a group inside the benzene ring to obtain a linear configuration with the carbon and chlorine atoms. It is therefore not surprising that the chlorine in aromatic chlorides is unreactive. When an aromatic halogen is replaced by a basic group, the mechanism is probably not a simple three-center reaction in which the halogen and the base are equally bonded in the transition state. Thus the base may first add to the nucleus, and the removal of the halide ion may be a follow reaction. This is rather suggested by the fact that groups that allow a ready replacement of a nuclear halogen by a base—e.g., ortho and para nitro groups—also permit the addition of a base to the nucleus. Thus 1,3,5-trinitrobenzene adds alcoholate ion to form

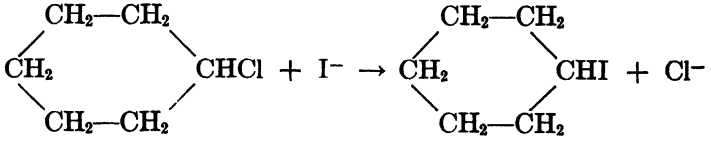


, and picryl chloride,

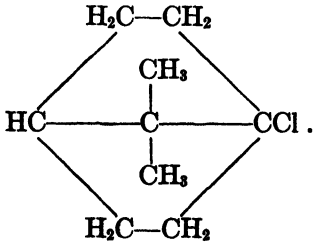


reacts at speeds comparable to those of carboxylic acid chlorides.

The cyclohexane ring also produces steric difficulties to a three-center linear reaction. Thus the reaction

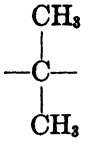


is very slow (see Table 52). Lately an interesting example of this type of steric hindrance has been found by Bartlett and Knox.[46] It is very difficult to remove chlorine from 1-chloroapocamphane:



[46] Bartlett, P. D., and Knox, L. H., *J. Am. Chem. Soc.*, **61**, 3184 (1939).

The bridge



increases the difficulty of obtaining a linear configuration of Cl, C, and the entering group over that which exists in chlorocyclohexane.

Chapter X

REACTIONS OF THE DOUBLE BOND

Substances containing double or triple bonds often react rapidly with reagents in such a way that two reacting molecules combine to form a single molecule. As this is what happens when two substances each containing an atom with incompletely saturated valences are brought together, compounds with multiple bonds have been classed as unsaturated compounds. So much has this been the case that unsaturation has come to connote a multiple bond rather than an unsatisfied valence.

The appearance of unsaturation of multiple bonds has led to the assumption that the reactivity of these bonds is due to an incomplete neutralization of the valences of the connected atoms. However, this unsaturation is apparent only under special circumstances. For instance, addition to a double bond is not an instantaneous process but needs energy for activation in the same way that reactions of saturated compounds do. It has become more common to think of the unsaturation of the atoms attached by multiple bonds as latent. It is then assumed that activation to form valence-unsaturated atoms precedes the reaction. Two types of activation can be assumed. For instance, in the case of ethylene, $CH_2::CH_2 \rightarrow \dot{C}H_2{:}\dot{C}H_2$ and $CH_2::CH_2 \rightarrow \overset{+}{C}H_2{:}\overset{\cdot\cdot\,-}{C}H_2$. In the first type the unsaturation is similar to that of free radicals, and in the second to that of acids and bases. When one uses the transition state theory, there is no significance to a preliminary activation of the double bond, unless this is the rate-determining step. A purely electronic shift as a rate-determining step is not usual, and can be recognized from a kinetic study, since in that case the rate would be independent of the concentration and nature of the addend. The rate depends only upon those molecular species which appear in the transition state and the properties of the transition state, independent of the particular path by which it was formed.

The equation for an addition to a double bond, $R{-}S + P{=}Q \rightarrow$

$R—P—Q—S$, would suggest that the transition state has a planar cyclic configuration:

$$\begin{matrix} R & \cdots & P \\ \vdots & & \vdots \\ S & \cdots & Q \end{matrix}.$$

We do not think that this is true in general, and we shall assume that in most reactions of the double bond the transition state of the master reaction is linear, involving either three centers or four centers in a Lowry mechanism. When a preliminary dissociation of the addend, $R—S$, occurs, and it is not the rate-determining step, either R or S is not included in the linear transition state, unless the reaction goes by a Lowry mechanism.

The linear transition state is an idealization. With only three atoms the lowest energy transition configuration is actually linear, and this would be true also for the transition state for $A—B + C \rightarrow A + B—C$ when B is a central atom with other groups that are alike or interact equally with both A and C. When the ideal conditions do not obtain, as for instance when there is a resonance interaction between a group in B and other bonds of B, the perturbation can affect the spatial relations of the atoms just as resonance affects the shape of a molecule. When $A—B$ is a double-bonded system (e.g., $P{=}Q$), the extra bond will be a perturbing factor. Thus, if a linear arrangement is the most stable for the phase $P{=}Q\ \ C$, it need not be so for the phase $—P—Q—C$. For instance, if Q is a carbon atom, tetrahedral angles are favored in the latter phase. We do not know the actual shape of this transition state. Presumably the angle PQC is between 180° and 110°. When we assume a linear transition state for an addition reaction, we mean that the chief bonds are between P and Q and between Q and C, with no appreciable interactions between P and C or between the groups bonded to these atoms. Thus, if C is $R—S$, the linear transition state is $P—Q—R—S$ with no bond between P and S. In the other type of transition state there are such additional bonds. The two types differ from each other in essentially the same sense that a chain compound differs from a cyclic one.

There are, however, reactions of multiple bonds that are best considered as forming cyclic planar transition states. In general, we do not know definitely which reactions have planar and which have linear transition states. We shall assume that most of the addition reactions have linear transition states, and only at the end of this

chapter briefly discuss a few reactions for which we have assumed planar cyclic transition states.

The multiple bonds found in organic compounds are either between two very similar atoms or between atoms that have very different attractions for electrons. The latter type of multiple bond is very polar, and has a very large contribution from an ionic form, $P^+—Q^-$. The best and commonest examples of these two types are the non-polar double bond, C=C, and the polar one, C=O. We shall discuss only these two multiple bonds, and their combinations. Even these discussions will be limited to what is necessary to exemplify general principles.

49. THE ETHYLENIC DOUBLE BOND

The ethylenic double bond does not appear to be very reactive to basic reagents. In homogeneous solution it reacts with strongly acidic compounds (hydrogen halides, sulfuric acid, etc.), and with compounds of two strongly electronegative elements (halogens, ClOH, etc.). It appears to be quite active towards radicals, as it takes part in many chain reactions where, presumably, radicals constitute the chain. For instance, the photochemical addition of halogen is probably a chain reaction involving radicals. The ethylenes are rapidly oxidized by many reagents, for instance, MnO_4^-. Additions to ethylenes are often catalyzed by surfaces, and in this way they can be reduced with hydrogen.

49a. Ethylenes as bases or pseudo-bases. It has been suggested[1] that, when a halogen adds to an ethylenic double bond, one of the halogen atoms accepts a pair of electrons from the double bond, and halide ion dissociates and finds its way to the positively charged atom of the ethylene. The mechanism can be represented schematically by the following equations:

$$CH_2::CH_2 + Br:Br \rightarrow \overset{+}{C}H_2:CH_2:Br + :Br^- \rightarrow Br:CH_2:CH_2:Br$$

In this mechanism the ethylene acts as a pseudo-basic reagent (a substance that is a base after activation). The transition state is then similar to those of basic reactions. It would be a linear configuration, $CH_2{=}{=}CH_2$ --- Br --- Br, in which the main resonance forms are $CH_2::CH_2\,Br:\,Br$ and $CH_2:CH_2:Br\,Br:$. This mechanism is supported by the following facts. The addition of bromine to ethylenes in carbon tetrachloride is strongly catalyzed by traces of

[1] Burton, H., and Ingold, C. K., *J. Chem. Soc.*, 912 (1938).

water.[2] This is suggestive of a Lowry mechanism in which the acidic transition state is stabilized by the basic catalyst. When ethylene is brominated in water solution in the presence of chloride and nitrate ions, CH_2BrCH_2Cl and $CH_2BrCH_2ONO_2$ are formed as well as the dibromide.[3] The polar effects of substituent groups also agree with this mechanism. A substituent group of positive polarity (e.g., Br) would reduce the stability of a transition state in which $R\overset{+}{C}H—CH_2—Br\ Br^-$ is a more important component than $R\overset{-}{C}H—CH_2—Br\ Br^+$, and hence decrease the reaction rate. A group with negative polarity (e.g., CH_3) would have the opposite effects. The Ingolds[4] give 0.04 and 5.5 for the relative rates of bromination of $BrCH{=}CH_2$ and $(CH_3)_2C{=}CH_2$, respectively, taking the rate of bromination of ethylene as unity.

The foregoing discussion does not necessitate the formation of the free ion $R\overset{+}{C}H—CH_2—Br$. The transition state $RCHCH_2Br_2$ is solvated by basic or acidic molecules present in the solution. The ion $R\overset{+}{C}HCH_2Br$ can be considered as having a definite existence only when there are especially strong resonances stabilizing it.

Although it seems probable that the mechanism suggested above for additions of halogens to ethylenes is effective under some conditions, it is not likely to be applicable to all. The chain reactions involving radicals would have to be assumed under certain conditions. Stewart and his co-workers[5] have shown that the addition of halogens can induce substitution reactions. Such complexities are more characteristic of chain reactions involving radicals than of mechanisms involving ions.

The mechanism suggested by the Ingolds is probably correct for the addition of strong acids to olefins. The transition state, $\overset{+}{C}H_2{=}CH_2 \cdots H \cdots Cl^-$, corresponding to this mechanism, is the normal one for an acidic reaction.

The best-known rule concerning the relative rates of addition reactions to ethylenes is Markownikoff's.[6] This rule states that when a halogen acid adds to an ethylene, the halogen adds to the carbon

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[2] Davis, H. S., *J. Am. Chem. Soc.*, **50**, 2769 (1928).
[3] Francis, A. W., *J. Am. Chem. Soc.*, **47**, 2344 (1925).
[4] Ingold, C. K., and Ingold, E. H., *J. Chem. Soc.*, 2354 (1931).
[5] Stewart, T. D., and Smith, D. M., *J. Am. Chem. Soc.*, **51**, 3082 (1929); **52**, 2869 (1930).
[6] Markownikoff, W. B., *Ann.*, **153**, 256 (1870).

atom with the fewer number of hydrogen atoms. This phenomenon is due to the relative rates of the alternative additions. In terms of rate, the rule is that the reaction $R\text{CH}{=}\text{CH}_2 + \text{H}X \rightarrow R\text{CH}X{-}\text{CH}_3$ is faster than the reaction $R\text{CH}{=}\text{CH}_2 + \text{H}X \rightarrow R\text{CH}_2{-}\text{CH}_2X$. The rule is sometimes explained on the basis of the induction effect of R, which makes $R\overset{+}{\text{C}}\text{H}{-}\overset{..-}{\text{C}}\text{H}_2$ more stable than $R\overset{..-}{\text{C}}\text{H}{-}\overset{+}{\text{C}}\text{H}_2$. However, this rule is also valid when R is a chlorine atom; in that case a pure inductive effect cannot explain the phenomenon. It is probably better to class this phenomenon with the large number of dubiously explained or unexplained differences in the reactions of primary, secondary, and tertiary carbon compounds. Markownikoff's rule also applies to addends other than halogen acids (e.g., sulfuric acid, HO—Cl, I—Cl, etc.). In general, one or the other pole of an unsymmetrical addend goes preferentially to the less hydrogenated carbon atom. Where one pole is known to be more basic than the other, it is that pole that adds to the less hydrogenated carbon atom. The rule can therefore be used to determine the more basic pole of the addend. Thus HO—Cl adds as HO and Cl, and the hydroxyl group goes to the less hydrogenated carbon atom. This has been taken as evidence that in hypochlorous acid the electrons of the O—Cl bond are shifted towards the oxygen atom. However, the oxygen may add to the less hydrogenated carbon atom because its unshared electrons are more basic than those of the chlorine atom.

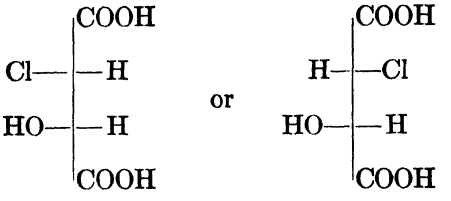
Markownikoff's rule can be inverted by groups that have a high affinity for electrons, such as NO_2. It is also inverted in additions to unsaturated carbonyl compounds. For instance, $\text{CH}_2{=}\text{CHCOOH} + \text{HBr}$ forms $\text{CH}_2\text{BrCH}_2\text{COOH}$ rather than $\text{CH}_3\text{CHBrCOOH}$. The structure $\text{C}{=}\text{C}{-}\text{C}{=}\text{O}$ is a resonating one ($\text{C}{=}\text{C}{-}\text{C}{=}\text{O}$, $\overset{+}{\text{C}}{-}\text{C}{=}\text{C}{-}\text{O}^-$), and this resonance may account for the product.

Kharasch and Mayo[7] have shown that peroxides catalyze the addition of halogen acids to ethylenes. The catalysis increases the speed of the reaction $R\text{CH}{=}\text{CH}_2 + \text{H}X \rightarrow R\text{CH}_2{-}\text{CH}_2X$ more than that of the reaction $R\text{CH}{=}\text{CH}_2 + \text{H}X \rightarrow R\text{CH}X{-}\text{CH}_3$. In consequence, Markownikoff's rule can fail in the presence of peroxides. Since peroxides often exist in organic liquids that are exposed to air, much of the previous work on the proportions of the alternative products of addition is erroneous. However, the discovery of the

[7] Kharasch, M. S., and Mayo, F. R., *J. Am. Chem. Soc.*, **55**, 2468 (1933).

peroxide effect confirms and indeed strengthens the validity of Markownikoff's rule for reactions carried out in the absence of peroxides.

49b. Stereochemistry of addition reactions. The mechanism of an addition to a double bond could determine the configuration of the product when more than one spatial configuration is possible for it. Thus, if the ethylene can exist in *cis* and *trans* configurations and the addend has no group in common with the ethylene, the product can have one of two configurations other than enantiomorphic forms. If bromine is added to maleic acid, the product might be a racemic mixture of *d*- and *l*-dibromosuccinic acids or the meso isomer. If ClOH is added, the products might be racemic mixtures of



which may be distinguished as the meso and racemic types, respectively, since in the former the carboxyls and hydrogens are related to each other in the same way as they are related in meso-tartaric or meso-dichlorosuccinic acid. If, however, HCl is added, a racemic mixture of *d*- and *l*-chlorosuccinic acids is obtained by any mechanism.

A four-center quadrilateral transition state would always lead to the formation of a meso type from a *cis* compound and a racemic type from the *trans* isomer. This type of addition was at first thought to be the rule, for when maleic acid (the *cis* compound) is oxidized with aqueous permanganate ion, meso tartaric acid is formed. Michael[8] has shown that this is exceptional rather than general, and his findings have been confirmed by later work. Thus, in the addition of HOCl to malcic acid, the racemic type of compound is formed, but the addition to fumaric yields the meso type. This is just the reverse of the older theory. When chlorine is added to an aqueous solution of maleic acid in the dark, the meso compound is formed, but this is also obtained as the major product with fumaric acid.[9] Again, in an addition to a triple bond, the *cis* product expected from a quadrilateral configuration of the transition state is

[8] Michael, A., *J. Prakt. Chem.*, **46**, 402 (1892).

[9] Kuhn, R., and Ebel, F., *Ber.*, **58**, 919 (1925); Kuhn, R., and Wagner-Jauregg, T., *Ber.*, **61**, 520 (1928); Lossen, W., *Ann.*, **348**, 273 (1906).

not obtained as the major product, but instead the more stable of the geometric isomers is the major product. Thus Michael found that HCl + HOOCC≡CCOOH → HOOCCCl=CHCOOH gives forty-five times as much chlorofumaric as chloromaleic acid.

If the transition state for an addition has a linear three-center configuration, an inversion at one of the poles is to be expected. This corresponds to the Walden inversion in a substitution reaction. To complete the addition, the other pole must also be attacked. If this attack also corresponds to a Walden inversion reaction, as for instance by a simultaneous attack on both poles, the *cis* compound yields the meso type of addition product and the *trans* isomer yields the racemic type. If the second pole adds directly at the point freed by the three-center reaction before the trivalent carbon atom has had time to become coplanar, the *cis* compound forms the racemic addition product and the *trans* forms the meso. If time to achieve coplanarity is allowed, both isomers yield the same product, which presumably is the more stable of the two. The experiments cited above show that all these possible results occur, and they confirm the theory that the common additions to double bonds are linear reactions.

Michael also studied the formation of double-bonded compounds from stereoisomers. In general, the more stable *trans* isomer is obtained. Thus, both meso and racemic $(CHClCOOH)_2$ give chlorofumaric acid with alcoholic potassium hydroxide, and both meso and racemic $C_2H_5OOCCHBrCHBrCOOC_2H_5$ form *trans*-$C_2H_5OOCCH{=}CHCOOC_2H_5$ when treated with zinc. Michael assumes that the general rule is the preferential formation of the more stable isomer. In the formation of a triple bond from a double bond, Michael found that the geometric isomer that is formed more readily from the acetylene derivative is that one which more rapidly reverts to the acetylene.[10] Thus *trans* HOOCCH=CClCOOH is the principal product of the addition of HCl to HOOCC≡CCOOH. It reverts to HOOCC≡CCOOH much more rapidly than does the *cis* isomer.

49c. Macropolymerization. When two double-bond groups in different molecules collide so as to form a linear transition state, $\begin{matrix} R_2 & R_2 & R_2 & R_2 \\ C{=}C & \cdots & C{=}C \end{matrix}$, only two of the four atoms involved have satisfied valences. Either each of the other two has an odd electron, or one is

[10] Michael, A., *J. Prakt. Chem.*, **66**, 291 (1899); *Ber.*, **34**, 4215 (1901).

positively and the other negatively charged. The two unsaturated atoms are distant from each other, and exceedingly reactive towards a double bond. The unsaturated atom is more likely to react with one of the many double bonds than with one of the few other atoms with unsatisfied valences. This will be especially the case when the unsaturation is due to an unpaired electron rather than to a lack or excess of electrons, for a radical is, in general, more reactive towards saturated compounds than are acids or bases. Moreover, the forces by which the radicals attract each other are less effective at long distances than the electrostatic attractions between the oppositely charged atoms which would result from the alternative mode of reaction. The result of the combination between the product of the linear reaction of two ethylene molecules and a third one,

$$\begin{matrix} & R_2 & R_2 & R_2 & R_2 & & R_2 & R_2 \\ \text{---} & \text{C} & \text{—C} & \text{—C} & \text{—C} & \text{---} & \text{C} & \text{=C} \end{matrix} ,$$

also has two unsaturated atoms, and it also is more apt to react with another ethylene molecule without losing its activity than to combine with loss of its unsaturation. The process can go on so as to form a great chain of combined molecules—a macropolymer.[11] This mechanism can be shown for the macropolymerization of styrene by the following equations:

$$C_6H_5CH{::}CH_2 + C_6H_5CH{::}CH_2 \rightarrow \cdot CH(C_6H_5){:}CH_2{:}CH(C_6H_5){:}CH_2\cdot ,$$

$$\cdot CH(C_6H_5){:}CH_2{:}CH(C_6H_5){:}CH_2\cdot + C_6H_5CH{::}CH_2 \rightarrow$$

$$\cdot CH(C_6H_5){:}CH_2{:}CH(C_6H_5){:}CH_2{:}CH(C_6H_5){:}CH_2\cdot ,$$

and so on to

$$\cdot CH(C_6H_5)—CH_2—\left(CH(C_6H_5)—CH_2—\right)_n CH(C_6H_5)—CH_2\cdot$$

[11] Staudinger, H., *Trans. Faraday Soc.*, **32**, 97 (1936); Staudinger, H., *Die Hochmolekularen Organischen Verbindungen* (Julius Springer, Berlin, 1932); A. C. S. Monograph No. 75, *Polymerization*, by Burke, R. E., Thompson, H. E., Weith, A. J., and Williams, I. (Reinhold Publishing Corp., New York, 1937).

It has been suggested by Evans[12] that the combination with phenyl groups most widely separated,

$$\cdot CH(C_6H_5):CH_2:CH_2:CH(C_6H_5)\cdot,$$

is favored because it allows the maximum resonance between the trivalent carbon atoms and the benzene rings. But in that case it would also be necessary to have the adjacent form

$$\cdot H_2C:CH(C_6H_5) : CH(C_6H_5) : CH_2\cdot$$

as well, in order to maintain a polymerizing chain involving the 1,4-diphenyl units.

Macropolymerization is a variant of the chain mechanism. Instead of each preliminary step leading to many units of a reaction, each preliminary step leads to a single reaction between many units of reactant. Like chain reactions, macropolymerization can be retarded by traces of inhibitors, which no doubt introduce chain-terminating reactions. The nature of these chain-terminating steps in inhibited macropolymerizations is not known.

50. THE CARBONYL DOUBLE BOND

The highly polar carbonyl group reacts rapidly with any substance with basic properties, or with any bond that would be rapidly broken by an acid. These reagents have been called nucleophilic, and the opposite type electrophilic. Thus, electrophilic reagents add preferentially to C=C bonds and nucleophilic reagents to C=O bonds. The product of an addition to a carbonyl compound is often a substance that would undergo the reverse reaction rapidly. The reactivity of these compounds is therefore a rate rather than an equilibrium phenomenon. In fact, in many cases the addition product is an intermediate in a reaction and is not actually isolated. That this should be so is due to the stability of the carbon-oxygen double bond. The contribution of the ionic component $\overset{+}{C}—O^-$ is great. The bond energy of the carbon-oxygen double bond is more than twice that of the carbon-oxygen single bond, while the energy of the carbon-carbon double bond is less than twice that of the carbon-carbon single bond.

[12] Evans, M. G., *Trans. Faraday Soc.*, **35**, 824 (1939).

The transition state for the addition of bases to carbonyl compounds is almost certainly linear. However, in this transition state the oxygen atom would be definitely basic and its stability would be enhanced by the presence of an acid. Lowry mechanisms are presumably common in additions to carbonyl compounds, though the effects of the acid must often be hidden by the neutralization of the reacting base by the acid catalyst.

50a. Addition of bisulfite ion. One of the simplest additions to a carbonyl group is that of bisulfite ion to an aldehyde or ketone. We shall therefore use this reaction as an example of a simple addition without any complicating factors other than the achievement of the equilibrium distribution of hydrogen ion among the various bases present. The rate of addition of bisulfite ion depends to a great ex-

TABLE 54
EFFECT OF BRANCHING OF THE CARBON CHAIN ON THE REACTIVITY OF CARBONYL COMPOUNDS*

Compound	Per Cent Reaction		
	$KHSO_3$	NH_2OH	$C_6H_5NHNH_2$
Aldehyde	70–90	85 (C_6H_5CHO)	—
CH_3COCH_3	22	82	66
$CH_3COCH_2CH_3$	14	75	52
$CH_3COCH(CH_3)_2$	3	33	15

* See Petrenko-Kritschenko, P., and Kantscheff, W., *Ber.*, **39**, 1452 (1906); Stewart, A. W., *J. Chem. Soc.*, **87**, 186 (1905). For more extended tables, see the section by S. Goldschmidt, p. 501, in *Stereochemie*, K. Freudenberg, editor (Franz Deuticke, Leipzig u. Wien, 1932), and the section by C. F. H. Allen and A. H. Blatt, vol. I, p. 555, in *Organic Chemistry*, H. Gilman, editor (John Wiley & Sons, New York, 1938).

tent on the degree of hydrogenation of the carbon atoms in the region of the bond. The more hydrogenated these carbon atoms are, the faster the addition; and the nearer the hydrogenated atoms are to the oxygen atom, the greater is the effect. Thus aldehydes add faster than ketones. Acetone adds more rapidly than other noncyclic unsubstituted aliphatic ketones. Methyl *n*-propyl ketone adds faster than methyl isopropyl ketone. Although the addition to methyl *n*-alkyl ketones is retarded as the number of carbon atoms in the alkyl radical is increased, the effect becomes small beyond three carbon atom radicals. On the other hand, increasing the size of both the radicals of acetone greatly retards the reaction. Di-*tert*-butyl ketone is therefore very unreactive. Table 54 shows the relative rates of addition to some of these alkyl compounds in the form of per cent reaction under identical conditions.

The differences in the rates of addition of bisulfite ion to aldehydes and the various alkyl ketones have been attributed to steric hindrance. They could also be attributed to the inductive effects of the alkyl groups. If the effects are to be attributed to induction, the direction of the effect corresponds to a close approach of the addend and small separations of the oxygen atom in the transition state; i.e., the induced charge has a greater action on the entering base than on the electrons that are separated when the double bond to the oxygen atom changes to a single one. However, at the present time it is best to consider the phenomenon as another example of the unexplained effects of the degree of hydrogenation of carbon atoms.

50b. Oximes, hydrazones, and semicarbazones. There are many reactions of aldehydes and ketones in which the doubly bonded oxygen atom is replaced by a doubly bonded nitrogen atom with the elimination of water; e.g.:

$$R_2CO + H_2NOH \rightarrow R_2C{=}NOH + H_2O,$$

$$R_2CO + H_2NNHC_6H_5 \rightarrow R_2C{=}NNHC_6H_5 + H_2O,$$

$$R_2CO + H_2NNHCONH_2 \rightarrow R_2C{=}NNHCONH_2 + H_2O.$$

The rates of these reactions vary with a change in the carbonyl compounds in a way very similar to that of the bisulfite additions. It is likely that the rates of these reactions are governed by a preliminary addition of the base:

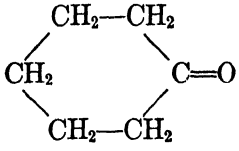
$$R_2CO + H_2NOH \xrightarrow{\text{slow}} R_2C\begin{matrix}\diagup\,O^- \\ \\ \diagdown\,{}^+NH_2OH\end{matrix} \xrightarrow{\text{fast}} R_2C{=}NOH + H_2O.$$

The relative rates of oxime and hydrazone formation parallel those of the addition of bisulfite. This comparison is shown in Table 54.

The work of Conant and Bartlett[13] on the rate of formation of semicarbazones with various aldehydes and ketones ($RCOR' + H_2NNHCONH_2 \rightarrow RR'C{=}NNHCONH_2$) shows that the rate of this reaction is affected by substituent groups in much the same way as the rate of addition of bisulfite ion. Acetaldehyde reacts sixty times as fast as acetone. In both aldehydes and ketones the replacement of a methyl group by a more branched alkyl group decreases the rate. For instance CH_3CHO reacts eighteen times as fast as

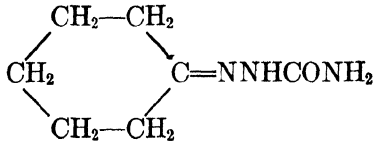
[13] Conant, J. B., and Bartlett, P. D., *J. Am. Chem. Soc.*, **54**, 2881 (1932).

$(CH_3)_3CCHO$, and CH_3COCH_3 nearly a hundred times as fast as $(CH_3)_3CCOCH_3$. An aromatic nucleus conjugate with the carbonyl group decreases the rate, acetaldehyde reacting a hundred and eighty times as fast as benzaldehyde. This effect can be attributed to the resonance, and is found in most reactions of carbonyl compounds. Cyclohexanone



is very reactive towards both the formation of a carbazone and the addition of bisulfite ion. This is of interest, since cyclohexyl chloride is unreactive, probably owing to the steric hindrance of the Walden inversion. As far as the steric factor is concerned, the chloride and the ketone differ in that, in the transition state for the removal of halogen from the former, there are five groups attached to the carbon atom, but in the transition state of the reaction of the carbonyl group there are only four groups (the two parts of the ring, the oxygen atom and the reacting base) attached to the carbon. While this would explain the difference in the steric factor, it does not account for the high reactivity of the ketone.

Conant and Bartlett also measured the rates for the reverse reaction. With one exception these rates show the same peculiarities. The phenyl group decreases the rate. In both aldehydes and ketones, the tertiary butyl compound reacts slower than the corresponding methyl compound. The cyclohexane derivative



hydrolyzes more rapidly than the acetone semicarbazone. The exception is that the ketonic semicarbazones are more reactive than the corresponding aldehyde derivatives, whereas the aldehydes form the semicarbazones much more rapidly than the ketones.

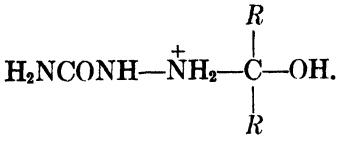
To understand this phenomenon, one must consider the direction of the dipole of $H_2C{=}CHR$. This direction, as obtained from that of the dipole of C_6H_5R and the fact that $C_6H_5CH{=}CH_2$ has little or no dipole, is primary carbon atom *minus* and secondary carbon atom

plus. In a double bond to carbon, C=*D*, the contribution of $\overset{+}{C}—D^-$ is greater for the less hydrogenated than for the more hydrogenated carbon atoms, and the component $\overset{-}{C}—D^+$ is greater for the more hydrogenated carbon atoms. In C=O the important ionic component is $\overset{+}{C}—O^-$, and the bond is more stable for ketones than for aldehydes. But in C=N—N: the component $\overset{-}{C}—\overset{+}{N}—\ddot{N}$ must be relatively more important than its analogue in C=O, and probably it is the most important ionic component of the C=N—N: system because of the resonance ($\overset{-}{C}—\overset{+}{N}—\ddot{N}$, $C—N=N^+$). The effects of the ionic components of the double bonds are greater in the reactants than in the transition states, so that if the above analysis of them is granted, it follows that the aldehydes are more reactive than the ketones but the semicarbazones of ketones are more reactive than those of aldehydes. Branching the chain at the alpha or more distant positions has the same effect on the reactivities of carbonyl compounds and of semicarbazones, but branching the chain at the carbon pole of the double bond has opposite effects on the reactivities of these compounds. Hence it is impossible to use only the same set of inductive effects to account for both phenomena.

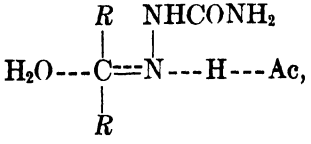
The rate of formation of a semicarbazone varies in two opposing ways with the concentration of acid. Acid combines with the semicarbazide removing a reactant, and it catalyzes the reaction between ketone and semicarbazide. The first effect depends on the hydrogen ion concentration, but the second is a general acid catalysis and depends on the concentrations and strengths of all the acids present. With a fixed concentration of hydrogen ion, the speed can be increased by increasing the concentration of the buffer acid and its salt. The transition state for the master reaction includes the ketone, the semicarbazide, which is a base, and a catalytic acid or mixture of acids. This is best explained by Lowry's theory of the combined action of a base and acid causing a shift of the electronic structure. The transition state would be

$$H_2NCONH—NH_2---\begin{matrix} & R & \\ & | & \\ C & = & O \\ & | & \\ & R & \end{matrix}---H---Ac,$$

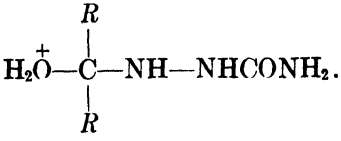
and the product of this step would be the intermediate



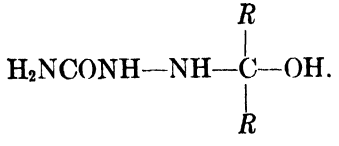
The transition state for the reverse reaction may be formulated as



and the intermediate product as



These two intermediate products would be in rapid equilibrium with themselves and with



The mechanism of oxime and hydrazone formation probably is similar.

50c. Addition of organometallic compounds. The ethylenic double bond reacts with acids rather than bases and the carbonyl double bonds with bases rather than acids. Hence they react with saturated molecules as pseudo-bases and pseudo-acids, respectively. Just as the ethylenic double bond reacts with a compound of a weak base (e.g., chlorine, which is a compound of the weak base chloride ion), so the carbonyl double bond reacts with a compound of a weak acid, such as the ion of an electropositive metal; hence the reactivity of carbonyl compounds towards organometallic compounds, especially those of highly electropositive metals, and the inertness of ethylenes to the same reagents. The most important of these reagents are the Grignard reagents and the lithium alkyls. Their superiority lies in the fact that, though the metals are strongly electropositive and

therefore show rapid reactions, their organometallic compounds are easy to prepare and handle.

50d. The aldol condensation. Normally an organo-hydrogen compound does not add to a carbonyl group. One may attribute this fact to the great strength of hydrogen ion as an acid. The hydrogen ion here referred to is not that found in solutions of strong acids in water (hydronium ion), but the proton itself. However, when there is a sufficiently strong positive polar effect in the organic radical and some base to assist the neutralization of the proton in the transition state, a sufficient separation of the proton can be obtained to permit an addition of the organic radical to a carbonyl group. Thus chloroform reacts with some carbonyl compounds. Much more rapid reactions can be obtained when the organic radical is such that it would resonate were the proton removed. Then whether the proton is removed before the addition reaction or merely partially separated in the transition state, resonance is greater in the transition state than in the reactants. This is true whether the master reaction is the removal of the proton or the addition to the carbonyl group. The best-known examples of this type of reaction are those in which both reactants are carbonyl compounds, the addend being an alpha-hydrogen compound of a radical containing a carbonyl group

$$\left(\text{e.g., } \overset{\displaystyle O}{\overset{\|}{R\text{C}}}\text{—C}R_2\text{—}\right).$$

Some examples of the addition of one carbonyl compound to another are the aldol condensation; the formation of acetoacetic ester; the condensation of benzaldehyde with one of the components of a mixture of an acid anhydride and a carboxylate salt; the formation of mesityl oxide, phorone, and mesitylene from acetone; and the condensations of aromatic aldehydes and ketones. Acids and bases are generally catalysts for these reactions. They have sufficient in common to warrant their being classed together as the aldol type of condensation.

One of the steps of an aldol type of condensation forms a C—C bond in which one carbon is alpha to a carbonyl group and the other is attached to a basic atom (oxygen). Both the alpha rule and the rule of reactivity of a bond from an atom attached to a basic atom indicate that this bond is active towards a fission in which the electron pair is retained by the carbon atom alpha to the carbonyl group, and the resulting lack of electrons on the other carbon atom

is reduced by those of the basic atom. Such a fission of this bond leads to a reversal of the reaction

$$R\overset{\overset{O}{\|}}{C}—CH_2—H + \overset{\overset{O}{\|}}{C}R_2 \rightleftarrows R\overset{\overset{O}{\|}}{C}—CH_2—\overset{\overset{OH}{|}}{C}R_2.$$

Consequently, aldol-type condensations generally need some follow step to stabilize the product. These follow reactions are often the loss of water or alcohol. Thus

$$CH_3\overset{\overset{O}{\|}}{C}—CH_3 + \overset{\overset{O}{\|}}{C}(CH_3)_2 \rightarrow$$

$$CH_3\overset{\overset{O}{\|}}{C}—CH_2—\overset{\overset{OH}{|}}{C}(CH_3)_2 \rightarrow CH_3\overset{\overset{O}{\|}}{C}—CH=C(CH_3)_2 + H_2O.$$

Diacetone alcohol — Mesityl oxide

In the aldol condensation, the aldol itself can be obtained with proper precautions but readily decomposes to the unsaturated compound.

The intimate mechanisms of the aldol-type condensations are not known, but it is probable that in every case the carbonyl group is involved in the resonance of the transition state. That is, one of the resonating electronic distributions is

$$\begin{matrix} :\ddot{O}:^- & & :\ddot{O}:^- \\ R\ddot{C}::CH_2 & & \ddot{C}R_2^+ \end{matrix}.$$

The basic catalyst stabilizes the transition state by helping to neutralize the proton or the acidic carbon of

$$\begin{matrix} O^{-\prime} \\ +| \\ CR_2, \end{matrix}$$

or even both. This base may be assumed to remove a proton from one of the carbonyl molecules, or to add to the carbonyl group of another before the collision, or to function during the collision.

There are two suggested mechanisms for aldol-type condensations. According to one of these the alpha hydrogen is removed by the action of the basic catalyst; the resulting ion then acts as a base and adds to the carbonyl group of another molecule. From this point on, the follow reactions depend on the particular reactants. According to the other suggestion, the basic catalyst adds to a carbonyl

group. Using $\bar{O}R'$ as the base and RCOCH$_3$ as the carbonyl compound, the reaction is

$$R\text{COCH}_3 + \bar{O}R' \xrightarrow{\text{fast}} R\text{—}\underset{\displaystyle O^-}{\underset{|}{\overset{|}{C}}}\text{—CH}_3.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{\displaystyle R'}{\underset{|}{O}}$$

This compound then reacts with the alpha hydrogen of another molecule:

$$\underset{\displaystyle CH_3}{\underset{|}{\overset{|}{R\text{C}}}}\text{—}\underset{\displaystyle O^-}{\underset{|}{O}}R' + H_3\text{C}\overset{\displaystyle O}{\overset{\|}{\text{C}}}R \xrightarrow{\text{slow}}$$

$$HOR' + \underset{\displaystyle CH_3}{\underset{|}{\overset{|}{R\text{C}}}}\text{—CH}_2\overset{\displaystyle O}{\overset{\|}{\text{C}}}R \xrightarrow{\text{fast}} \text{follow reactions.}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{\displaystyle O^-}{\underset{|}{\overset{|}{}}}$$

Both of these feasible mechanisms have transition states with resonance between a negatively charged alpha carbon atom and a carbonyl group, and with the acidity of the transition state neutralized by the basic catalyst. In one, the acidity is assumed to reside in a hydrogen atom and the product of the neutralization is assumed to be removed before the formation of the transition state. In the other, the acidity is assumed to reside on a carbon atom and the basic catalyst is included in the transition state. If the solvent is R'OH, solvation of the intermediate ion and the transition state can remove the differences between the two mechanisms.

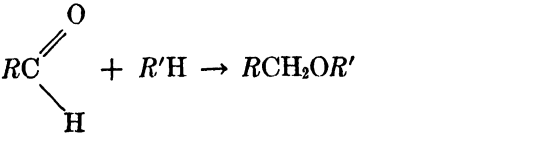
The electron distribution

$$\begin{array}{l} :\ddot{O}:^- \; H^+ \; :\ddot{O}:^- \\ R\ddot{C}::CH_2 \; \dot{C}R_2 \end{array}$$

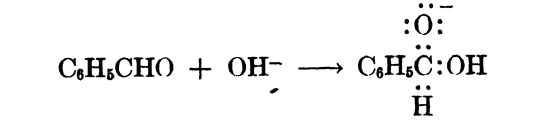
which we have assumed to be one of the phases of the transition state of aldol-type condensations, is more basic as well as more acidic than the ground states. Aldol-type condensations may then be expected to be catalyzed by acids as well as by bases. Although bases are as a rule more efficient condensing reagents than acids, many aldol-type condensations are effected with the aid of acidic

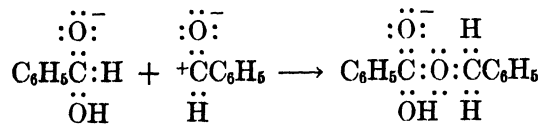
compounds. The amphoteric character of the transition state permits the formation of chelate structures when the catalytic base is conjugate to an acid having more than one acidic proton. A secondary amine is, therefore, a more effective catalyst than a tertiary amine of the same basic strength, when the solvent is not sufficiently acidic to make this difference between secondary and tertiary atoms inconsequential.

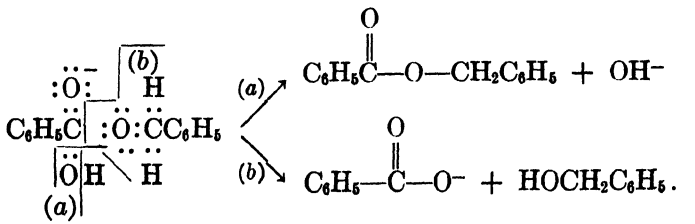
50e. The Cannizzaro reaction. The acid R^+ is normally too strong for its compounds to add to carbonyl groups at appreciable speed. A reaction of the type



is normally not obtainable at moderate temperatures, but strongly basic atoms attached to a carbon atom can make a hydrogen atom attached to the same carbon active. Since the basic atom only supplies electrons, the active C—H bond behaves as if it were $\overset{+-}{C}H$. If it reacts with a carbonyl group, the hydrogen goes to the carbon and the carbon to the oxygen of the carbonyl group. When hydroxide ion or another base adds to an aldehyde, a negatively charged oxygen results and the aldehydic bond becomes active towards a carbonyl group, but as $\overset{+-}{C}H$ rather than $\overset{-+}{C}H$. Thus the following series of steps can symbolize the Cannizzaro reaction:

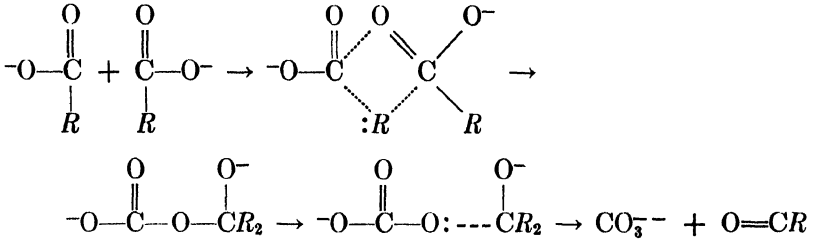






As this reaction is slower than the aldol condensation, it occurs to an appreciable extent only when there is no alpha C—H bond.

Similarly, an alkyl group can react as R^- under the influence of a negatively charged oxygen atom attached to the same carbon atom as it is. Thus the scheme



can be used to indicate the tautomeric (resonance) effects assisting the formation of ketones from the salts of carboxylic acids.

51. CONJUGATE SYSTEMS

Two pairs of double-bonded atoms joined by a single bond are called a conjugate system of double bonds. The type formula is $M{=}N{-}Q{=}P$. Such a system is capable of an addition to the extreme atoms with an accompanying doubling of the bond between the central atoms. This type of addition can be represented by the general equation $R{-}S + M{=}N{-}Q{=}P \rightarrow R{-}M{-}N{=}Q{-}P{-}S$. It is usual to number the atoms in the conjugate system and to describe the type of addition by the numbers on the atoms to which the parts of the addend are attached in the product. Thus the general equation given above is that for a 1,4 addition.

The theory that additions usually occur through linear transition states readily explains 1,4 and other types of conjugate addition. The transition state can be represented as

$$(S{-}R\ M{=}N{-}Q{=}P,\ \overset{*}{S}\ R{-}M{-}\overset{*}{N}{-}Q{=}P,\ \overset{*}{S}\ R{-}M{-}N{=}Q{-}\overset{*}{P}),$$

where the asterisks indicate unsaturated atoms. The final product can then be one in which S has satisfied the unsaturated valence of either N or P, forming

$$R{-}M{-}\underset{\displaystyle S}{\underset{|}{N}}{-}Q{=}P \quad \text{or} \quad R{-}M{-}N{=}Q{-}P{-}S.$$

In general, a conjugate system adds 1,2 or 1,4, depending on the nature of the addend and the conditions of the experiment. The

products of addition to a conjugate system are not always determined by the relative rates or competing reactions. In some instances equilibrium among the products is established during the reaction. But it has been shown that the 1,4 product is often obtained under conditions for which the rearrangement of the 1,2 to the 1,4 product is too slow to occur.

We have seen that the greater speed of addition of bases and organometallic compounds to carbonyl than to ethylenic double bonds can be attributed to the greater ease of obtaining a negative charge on an oxygen atom than on a carbon atom. This factor would not be operative in conjugate systems of ethylenic and carbonyl double bonds ($\underset{(1)}{C}=\underset{(2)}{C}-\underset{(3)}{C}=\underset{(4)}{O}$); for it would not be necessary to charge a carbon negatively in the transition state for the addition of a basic atom to the ethylenic carbon atom (1). The transition state for a base, $\ddot{B}$, adding to this type of conjugate system can be written

$$(B\colon C{=}C{-}C{=}O, \quad B{-}C{-}\bar{C}{-}C{=}O, \quad B{-}C{-}C{=}C{-}O^{-}).$$

In consequence, addition to the ethylenic carbon atom (1) often occurs in these conjugate systems with reagents that do not usually add to ethylenic double bonds. Thus the cyanide ion of HCN, the sulfite ion of bisulfites, the nitrogen of hydroxylamine and of ammonia, and the alkyl group of organometallic compounds are all known to add to atom (1) of the system $\underset{(1)}{C}=\underset{(2)}{C}-\underset{(3)}{C}=\underset{(4)}{O}$. The rest of the addend is found on atoms (2) or (4), depending on where it is most stable. These reactions are all in competition with the 3,4 additions. Similarly, the ethylenic bond, when conjugated with a carbonyl group, can function like a carbonyl group in an aldol-type condensation (reactions between ălpha C—H and C=O bonds). Thus

$$C_6H_5CH{=}CH\overset{O}{\overset{\|}{C}}C_6H_5 + CH_2(\overset{O}{\overset{\|}{C}}{-}OC_2H_5)_2 \rightarrow C_6H_5CH(\overset{O}{\overset{\|}{C}}{-}OC_2H_5)_2{-}CH_2\overset{O}{\overset{\|}{C}}C_6H_5.$$

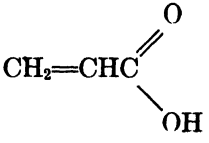
The reaction can also be written as a 1,4 addition to form the enol,

$$CH(COOC_2H_5)_2CH(C_6H_5)CH{=}C(OH)C_6H_5.$$

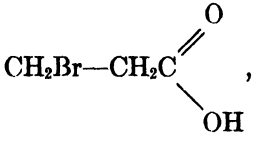
Unlike simple aldol-type condensations, these reactions are not completed by loss of water or alcohol to form an unsaturated compound. The analogous stabilization for this type of reaction is the loss of water or alcohol to form a ring.

Whether a simple carbonyl reaction or an ethylenic addition occurs with a conjugate system of C=C and C=O bonds depends on the substituent groups in the conjugate system, the reagent, and the conditions of the reaction. The substituents in the conjugate system seem to be more important than the reagent. That is, certain compounds seem to be more liable to 1,4 addition than others with all types of reagents. The most noteworthy example is that unsaturated aldehydes almost invariably yield the products to be expected from a simple aldehyde, while unsaturated ketones add chiefly at the 1,4 positions.

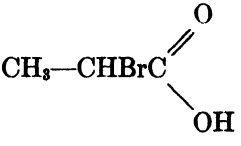
The effect of conjugation of a C=C with a C=O bond is also noticed in reactions that normally occur with ethylenes, because the product is not what would be expected from Markownikoff's rule. Thus



adds hydrogen bromide to form



whereas



is to be expected from Markownikoff's rule. The reaction can be represented as a 1,4 addition forming the enol $CH_2BrCH{=}C(OH)_2$.

While the C=O bond activates the C=C bond when conjugate with it, the reverse is not true. Carbonyl groups conjugated with ethylenic bonds or phenyl groups, as a rule, are less reactive towards bases than are simple carbonyl compounds. When a base adds to

the system $\underset{(1)}{C}=\underset{(2)}{C}-\underset{(3)}{C}=\underset{(4)}{O}$, the transition state for the addition to atom (1), (B: $C=C-C=O$, $B-\overset{-}{C}-C-C=O$, $B-C-C=C-O^-$), has more resonance than the reactant, since atom (2) has more negative charge in the transition state than in the ground state. On the other hand, the transition state for addition to atom (3),

$$B\colon\ \begin{matrix} C=O \\ | \\ C=C \end{matrix}\ , \qquad \begin{matrix} B-C-O^- \\ | \\ C=C \end{matrix}\ ,$$

has less resonance than the ground state, unless the C—O distance is very much greater than the equilibrium bond distance. The resonance effect accelerates addition to atom (1) but retards addition to atom (3). However, atom (1) is less charged than atom (3) and, without the resonance effect, addition to atom (3) would be faster than addition to atom (1). The system $\underset{(1)}{C}=\underset{(2)}{C}-\underset{(3)}{C}=\underset{(4)}{O}$ adds bases faster than the ethylenic double bond but slower than the carbonyl one. The base adds either at atom (1) or at atom (3). The former alternative results in 1,2 or 1,4 addition products, and the latter in 3,4 addition products.

52. SUBSTITUTION REACTIONS OF BENZENE

The benzene ring is a special type of conjugate system. There would seem little doubt that resonance would decrease the energy of the ground state of benzene more than it does that of the transition state of an addition reaction, and would therefore retard the reaction. However, the Kekule resonance would be absent in the product, so the addition compound would be unstable with respect to the reactants. The direct comparison of the relative rates of simple addition to benzene and ethylene is not possible. Since rapid reactions yielding stable products would result from the formation of a transition state for a benzene addition, one can assume that, if these reactions were as fast as additions to ethylene, benzene would react as rapidly as ethylene, even though the final products were not those expected from addition. In general, benzene does react with substances that add to ethylene, but these reactions are slower than those of ethylene, and are not additions.

The transition state for addition to benzene, like that for addition to ethylene, belongs to the linear type in the sense that only one part of the addend is bonded to the benzene molecule. Addition along the axis in the plane of the ring would be opposed by the hydrogen

atom. Both the hydrogen atom and the incoming group are probably displaced from this axis. Actually we have no evidence as to the shape of the transition state.

Benzene reacts with a large number of reagents in such a way that part of the reagent replaces a hydrogen atom of the benzene ring. The chief reagents employed are nitric acid, sulfuric acid, chlorine, bromine, and a mixture of alkyl or acyl halide and aluminum chloride. The reactions are called nitrations, sulfonations, chlorinations, brominations, and alkylations or acylations of benzene. In these reactions, the replaced hydrogen appears as hydrogen ion or one of its compounds. For the present we shall mean a reaction of this type when we refer to a substitution reaction of benzene or of one of its derivatives.

52a. The directing influence of substituents. When a substituted benzene is treated with one of these reagents, a mixture of isomeric products is formed. Thus nitration of a monosubstituted benzene produces a mixture of ortho, meta, and para nitro compounds. The proportion of these isomers in the mixture varies with the derivative of benzene used and with the conditions of the reaction. In general, the conditions necessary to obtain the substitution are such that the isomeric products would not change from one to another at a speed comparable with their rate of formation. The proportion of the isomers is therefore governed by the rates of formation of the products rather than by their relative free energies. The mole fraction of any one of the isomers in the mixture is therefore given by the equation $N = \frac{k}{k_o + k_m + k_p}$, where N is the required mole fraction, k the rate constant of the reaction forming the required isomer, and k_o, k_m, and k_p are the rate constants of the reactions forming the ortho, meta, and para isomers, one of which is k.

Early in the study of the isomers formed in substitution reactions of benzene derivatives, two approximate generalizations were observed: (1) the proportion of ortho, meta, and para products depends chiefly on the group present in the reacting benzene derivative, and only to a lesser degree on the reagent and conditions of the reaction; (2) groups could be divided into two main classes, those favoring the formation of meta isomers and those favoring the formation of ortho and para isomers. These two classes are called respectively meta-directing and ortho-para-directing. When more than one group is present, each retains its directing influence, so that if both groups belong to the same class and are meta to each other, or if they belong

to opposite classes and are ortho or para to each other, the proportion of the favored isomers is increased; whereas if the groups are of opposite classes and are meta to each other, or if they belong to the same class and are ortho or para to each other, the directing influences of the group are opposed and the isomers are formed in more nearly equal proportions. The foregoing rules are not exact laws. The proportions of isomers obtained in nitrations and sulfonations are not exactly the same, and vary with the temperature. Again, the division into *m*- and *o-p*-directing groups is not the only one possible. Thus the carboxyl group might be classed as a meta-ortho-directing group, for, although the major product is the meta isomer,

TABLE 55

DIRECTING INFLUENCE OF GROUPS

Group	Directing Influence	Group	Directing Influence
NR_2	*o-p*	CH_2Br	*o-p*
NH_2	*o-p*	N=NAr	*o-p*
OR	*o-p*	HC=O	*m*
OH	*o-p*	RC=O	*m*
SH	*o-p*	ROC=O	*m*
F	*o-p*	HOC=O	*m*
Cl	*o-p*	ClC=O	*m*
Br	*o-p*	H_2NC=O	*m*
I	*o-p*	C≡N	*m*
NHCO*R*	*o-p*	CF_3	*m*
Ar	*o-p*	CCl_3	*m*
CH=CH_2	*o-p*	SO_3H	*m*
R	*o-p*	SO_2R	*m*
CH_2OH	*o-p*	NO_2	*m*
CH_2F	*o-p*	$\overset{+}{N}R_3$	*m*
CH_2Cl	*o-p*		

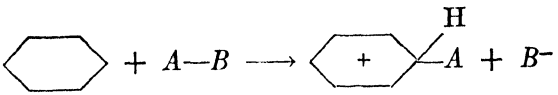
a considerable amount of the ortho isomer is always formed, while the para isomer is almost absent from the products. Further, there is no sharp distinction between *m*- and *o-p*-directing groups. By varying a group, we can pass gradually from one class to another. Thus CH_2Cl directs very little to the meta position; $CHCl_2$ produces about 40 per cent of the meta isomer, which is the proportion to be expected on equal chances, since only 40 per cent of the five hydrogen atoms in the ring are meta; and CCl_3 is definitely meta-directing.

The directing power of substituent groups has long intrigued the imagination of chemists. Correlations have been made between the directing influence and other characteristics of the groups. One of

the earliest of these is the Crum-Brown Gibson rule that groups whose hydrogen compounds are easily oxidized by oxygen are meta-orienting while those whose hydrogen compounds resist oxidation are ortho-para-orienting. The correlation is not exact. One of the most recently noted correlations is that when the dipole moment of an alkyl compound of the group is greater than that of its aryl compound the group is *o-p*-directing, while *m*-orienting groups show the reverse relationship between the dipole moments of their alkyl and aryl compounds.[14] Very recently the "Sutton rule" has been given a quantitative interpretation by Ri and Eyring,[15] who were able to calculate the dipole moments of certain monosubstituted benzenes from the relative amounts of the *o*, *m*, and *p* isomers obtained on nitration.

Explanations of the directing influence of groups based on electronic configurations abound in the literature.[16] All these explanations are based on the assumptions (1) of an electronic configuration of benzene, (2) of a way in which a group changes this configuration, and (3) of a way in which these changes affect the substitution of ortho, meta, and para hydrogen atoms. The result is that quite different assumptions can lead to the same conclusions. We shall consider the problem from the standpoint of the free energy change in forming a transition state. This approach may appear quite different but will include the above three assumptions, and will be in essence similar to Ingold's theory.

We shall assume that the substitution reactions occur through a linear transition state leading to the ionization of the reagent, *A*—*B*, and the combination of a group with a carbon of the benzene ring. There are two reactions[17] of this type:



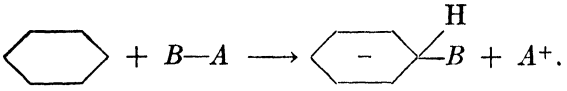
[14] Sutton, L. E., *Proc. Roy. Soc.*, **133A**, 668 (1931).

[15] Ri, T., and Eyring, H., *J. Chem. Phys.*, **8**, 433 (1940).

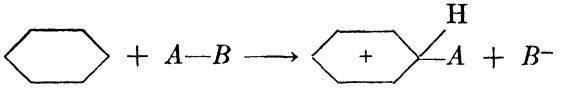
[16] Flürscheim, B., *J. prakt. Chem.*, **66**, 445 (1922); Fry, S. F., *J. Am. Chem. Soc.*, **38**, 1323 (1916); Lapworth, A., and Shoesmith, J. B., *J. Chem. Soc.*, **121**, 1391 (1922); Stieglitz, J., *J. Am. Chem. Soc.*, **44**, 1299 (1922); Holleman, A. F., *Chem. Rev.*, **1**, 187 (1925); Eastman, E. D., *J. Am. Chem. Soc.*, **44**, 445 (1922); Ingold, C. K., *Annual Reports Chem. Soc.*, **23**, 134 (1926); *Rec. trav. chim.*, **48**, 805 (1929); Latimer, W. M., and Porter, C. W., *J. Am. Chem. Soc.*, **52**, 206 (1930).

[17] Reactions of this type probably have Lowry mechanisms; i.e., in the first *B* is attacked by an acid and in the second *A* is attacked by a base, during the dissociation of *A*—*B*.

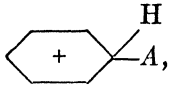
and



In the transition state for the former of these reactions, the ring is charged positively, and in that for the latter the ring is charged negatively. A positively charged group present in the nucleus must increase the free energy of the transition state by the former mechanism and hence decrease the rate of reaction. The effect of the group $-\overset{+}{N}(CH_3)_3$ is the nearest approach we can get to that of a positive charge. The substitution reactions of $C_6H_5\overset{+}{N}(CH_3)_3$ are slower than those of benzene, and consequently we shall assume

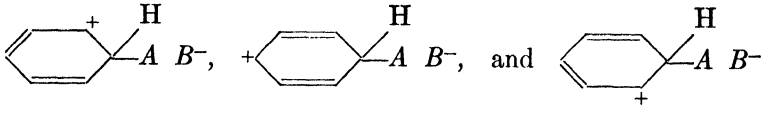


as the rate-governing step of the reaction. The follow step is the loss of hydrogen ion from

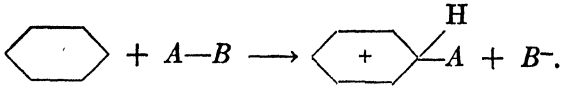


forming C_6H_5A. There are other lines of reasoning that lead to the same conclusion. If the reaction is a linear addition of $A—B$ to benzene, the final product must be formed by the loss of a hydrogen atom. This is more likely to be lost as H^+ than as H^-, and hence the intermediate is more likely to be $C_6H_6A^+$ than $C_6H_6B^-$. Again, since benzene contains double bonds, it is probably a nucleophilic reagent, and its combination with $A—B$ would be $C_6H_6A^+$ rather than $C_6H_6B^-$.

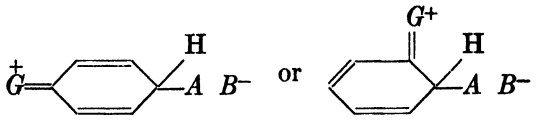
The electron arrangements

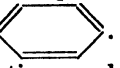


are included in the resonating phases of the transition state of the reaction

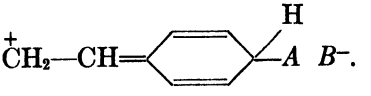


If an atom attached para or ortho to A has an unshared pair of electrons, the additional form



is included in the resonating phases of the transition state. This additional phase would not exist were the substitution occurring meta to G. The transition states for the ortho and para substitutions therefore have lower free energies than that for the meta substitution, and ortho and para substitutions are faster than meta ones when the substituent group (G) has an unshared pair of electrons on the atom attached to the ring. The outstanding examples of this rule are the *o-p*-directing powers of the hydroxyl, alkoxyl, and amino groups. Further, since the combination of A—B with the ring tends to liberate a positive charge on the ortho and para positions, the conjugation of the basic group, $\ddot{G}$, with the ring is more complete in the transition state than in the normal molecule $\ddot{G}$—  . Consequently, this resonance increases the rate of the reaction, and the substitution reactions of $\ddot{G}$—C_6H_5 are faster than those of benzene. This rule holds very exactly when the most prominent character of $\ddot{G}$ is its basicity. The rates of substitution reactions of anilines and phenols are of a much higher order of magnitude than those of benzene.

If the substituent group in the benzene is a non-polar double-bonded group, such as CH=CH_2 ,[18] C_6H_5 , or N=N—Ar, resonance is also increased in the transition state of the substitution reaction when the substitution is ortho or para. The new contributing form is



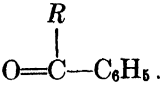
Such groups are therefore *o-p*-orienting and increase the speed of reaction.

The condition is changed when the directing group is one with a

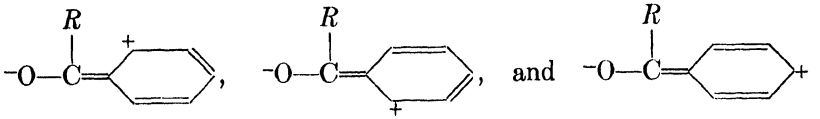
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[18] The directing influence of CH=CH_2 has not been determined for styrene itself, but for its less reactive derivatives.

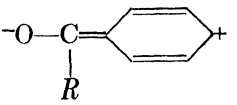
polar double bond with its less readily negatively charged atom attached to the benzene ring; e.g.,



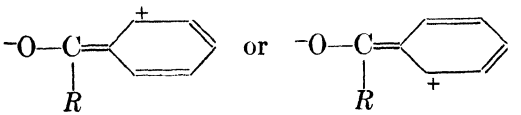
Such a group resonates with the benzene ring, the forms



contributing to the structure. This resonance tends to charge the ring positively, and hence occurs more readily in the ground state than in the transition state, in which the ring is already positively charged. Groups of this type therefore decrease the rate of substitution. However, the interference between the carbonyl and the transition-state resonances are least when the substitution occurs at the meta position. Thus in the para quinoidal form



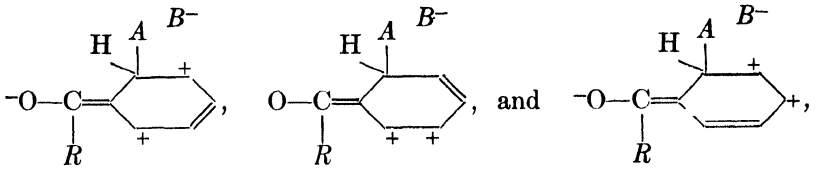
no double bond is available for the formation of the transition state for a para substitution, and in the ortho quinoidal forms



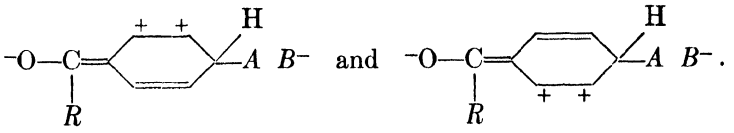
there are no double bonds for 2- or 6- substitutions, respectively. All forms, however, have double bonds available for 3- and 5- (meta) substitutions. Hence polar double bonds of this type are meta-directing. One reaches the same conclusion by considering the resonance in the transition state. When *A*—*B* is para or ortho to *R*C=O, one of the forms has no double bond to resonate with the carbonyl group. But when *A*—*B* and *R*C=O are meta to each other, there is always a double bond conjugated with the carbonyl group. Resonance is therefore greater in the transition state for the meta substitutions than in those for ortho and para substitutions.

There is a difference in the interference of the carbonyl resonance with the transition states of ortho and of para substitutions. The

phases that allow positive charges in the ring from the carbonyl and transition-state resonances at the same time are, for ortho substitution,



while for para substitution they are



There are, therefore, three forms for ortho substitutions but only two for para substitutions. Furthermore, the wider separation of the positive charges makes the first-mentioned form for ortho substitutions more stable than any form for para substitution. For this reason ortho substitution is favored over para substitution. This is in general true of carbonyl derivatives. For instance, the proportions obtained on nitrating benzoic acid are 18.5 per cent ortho, 80.2 per cent meta, and 1.3 per cent para. The nitro group is similar to the carbonyl group, except that it is more completely meta-directing. The proportions obtained in the nitration of nitrobenzene are 6.4 per cent ortho, 93.2 per cent meta, and 0.25 per cent para.

When an atom lacking electrons is attached to the benzene ring, its conjugation with the ring puts a positive charge on the nucleus. This resonance is analogous to that of the conjugation of a carbonyl or nitro group with the ring, and favors meta and ortho over para substitution. The group $B(OH)_2$ is an example of a group with an atom lacking electrons attached to the benzene ring. The nitration of phenylboric acid, $C_6H_5B(OH)_2$, produces appreciable yields of *m*- and *o*-nitrophenylboric acids, but only traces of the para isomer. The proportion of the meta and ortho isomers varies markedly with the conditions of the nitration.

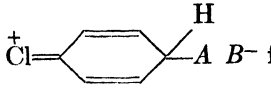
A group can charge the benzene ring positively or negatively by its inductive effect. As we have seen already, the inductive effect corresponding to a positive charge decreases the stability of the transition state and decreases the rate of the reaction. An inductive effect of the opposite kind has the reverse effect. The inductive

effect of a group acts on the atom to which the group is attached more strongly than on the other atoms of the ring. The charge imposed on the ring by the formation of the transition state is located chiefly on the atoms ortho and para to the point of substitution. Hence the inductive effect of a substituent group affects the rate of ortho and para more than it does that of meta substitutions. Groups with positive polarity will be meta-directing, for the rate of meta substitution is greater than that of ortho and para substitutions, though less than the rate of reaction with benzene. The opposite type of group is *o-p*-directing and tends to increase the reaction rate. The facts do not quite confirm this deduction. Although groups of strongly positive polar character, $-\overset{+}{N}R_3$, SO_3H, NO_2, are in general meta-orienting and produce slow reactions, all positively polar groups are not meta-orienting. The halogens represent such an exception, but this is not a serious objection to the reasoning given above, since the halogens are *o-p*-directing by virtue of their unshared electron pairs. The real difficulty is that, although for a series of saturated groups, meta orientation increases with acid-strengthening character, they are definitely acid-strengthening long before they are meta-orienting. The following results with groups that are usually assumed not to resonate with the benzene ring illustrate this point. The percentages of meta obtained on nitration are[19] 4 per cent for $C_6H_5CH_3$, 7 per cent for $C_6H_5CH_2Br$, 12 per cent for $C_6H_5CH_2Cl$, 19 per cent for $C_6H_5CH_2F$, and 48 per cent for $C_6H_5CH_2NO_2$. There is a steady increase in the per cent of meta corresponding to the increase in the positive polarity of the groups, but only the first of these groups (CH_3) is acid-weakening, and only the last can be classed as meta-directing. Again, in the following series nitration yields 100 per cent meta for $C_6H_5\overset{+}{N}(CH_3)_3$, 88 per cent meta for $C_6H_5CH_2\overset{+}{N}(CH_3)_3$, 19 per cent meta for $C_6H_5CH_2CH_2\overset{+}{N}(CH_3)_3$, and 5 per cent meta for $C_6H_5CH_2CH_2CH_2\overset{+}{N}(CH_3)_3$. The percentage of meta falls off with the insertion of methylene groups as an inductive effect should, but the groups $CH_2CH_2\overset{+}{N}(CH_3)_3$ and $CH_2CH_2CH_2\overset{+}{N}(CH_3)_3$ are definitely *o-p*-directing, though they would increase the strength of an acid. It would appear that there is some other factor besides those that are natural consequences of the theories of resonance and inductive effect. Apparently the

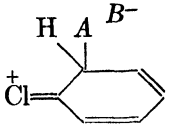
[19] Ingold, C. K, *Annual Reports, Chem. Soc.*, **23**, 134 (1926); and *Rev. trav. chim.*, **48**, 805 (1929).

change of a carbon atom from the secondary to the primary condition is an *o-p*-directing substitution. This is in accordance with the direction of the dipole moment of toluene. Such a moment stabilizes the transition state, but no moment should be obtained from the vector sum of C—H bond moments in toluene unless we assume some esoteric change in the electron distribution of carbon bonds as we pass from primary to secondary to tertiary carbon.[20]

The theory that the directing influence of a group arises from the inductive, resonance and other effects tending to charge the phenyl nucleus electrically, or to take care of charges imposed by the reaction, suggests a correlation between fast and ortho-para substitutions, and slow and meta substitutions. In general there is such a correlation, but it is not required to be perfect, nor is it so in fact. The halogens are *o-p*-directing groups, but the substitution reactions of halogenated benzenes are generally slower than those of benzene. The carbon atom of the C—Cl bond dipole is its positive pole. In the normal molecule the carbon atom attached to the chlorine atom is the most positively charged one in the benzene nucleus. Were this the only effect of the halogen, it would be meta-directing and the substitution would be slow. However, in the transition state for ortho and para substitutions there is a phase in which this atom lacks electrons and can form an extra bond with the chlorine atom, using the unshared pair of electrons for this purpose. If this form,

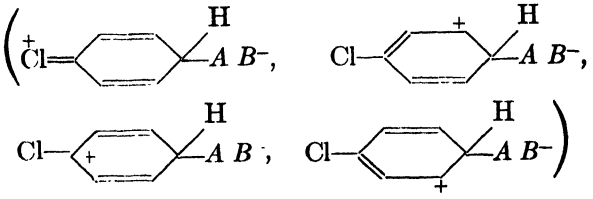


for a para substitution, or



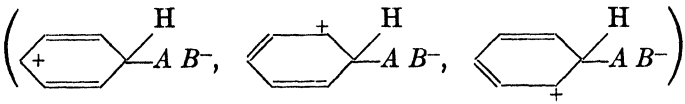
for an ortho one,

is more stable than any other phase in which the bonding of *A* to the ring opposes a positive charge to the C—Cl dipole, then the chlorine atom is *o-p*-directing. This does not necessitate that the complex



[20] See section 30a, Chapter VII.

be more stable with respect to the reactants than



is with respect to its reactants. The reason is that except in the para quinoidal phase, the chlorine atom reduces the stability of the transition-state quinoidal phases, on account of the high positive polarity of the halogen. Consequently the substitution of chlorobenzene can be slower than that of benzene.

The fact that under highly acid conditions the nitration of aniline yields *m*-nitroaniline has often been cited as an objection to theories of the orienting effects of groups. C. K. Ingold has pointed out that this objection to any theory that classes $\overset{+}{N}H_3$ as a *m*- and NH_2 as an *o*-*p*-directing group cannot be valid. In acid, aniline is in equilibrium with its positive ion. The former substitutes rapidly at the ortho and para positions, the latter slowly at the meta position. When the concentration of the base is reduced sufficiently, the slow meta substitution of the ion becomes the predominant reaction.

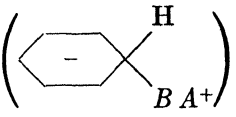
52b. Application of Hammett's equation to para and meta substitution. The suggested master step for substitution reactions of benzene is analogous to the basic three-center reaction

$$A{:}B + {:}C \rightarrow {:}A + B{:}C.$$

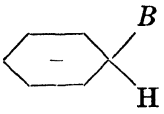
The benzene nucleus functions as the base $:C$. It may be called a pseudo-basic three-center reaction. Hammett's work has shown an appreciable degree of regularity in the relative effects of meta and para substitution on the rates of the basic reactions of aromatic compounds, and in Table 46 the constants (σ values) for various substitutions are found. Since the aromatic compound is the base in the substitutions, the ρ values for the reactions are negative; i.e., the more negative the σ value for the substitution, the faster will be the reaction. If then the σ value for the para substitution of a group is more negative, or less positive, than the constant for its meta substitution, the group is para-directing. Groups with the reverse relationship of para and meta σ values are meta-orienting. This correlation is valid to the extent that variations from Hammett's equation, $\log k = \log k_0 + \sigma\rho$, are not large enough to change the order of meta and para substitution. The correlation is valid for most of the common groups; e.g., amino, hydroxyl, alkyl, halogen, acyl, cyanide, and nitro groups. Incidentally, the groups which for

para substitution have negative σ values increase the speed of substitution, and those for which para-substitution σ values are positive decrease it. Thus, though chlorine is *o-p*-directing, it has a positive σ value and decreases the rate. Hammett's values of σ for *p*- and *m*-dimethylamino make this group meta-orienting according to this rule. We think this anomaly is due to erroneous values of σ assigned to this group.

52c. The reaction of benzene as a pseudo-acid. Just as the benzene nucleus acts as a pseudo-base in reactions, it could also act as a pseudo-acid. In this case the formation of a transition state



would give the nucleus a negative charge, and the value of ρ in the equation $\log k = \log k_0 + \sigma\rho$ is positive. From this it follows that *m*-directing groups produce faster reactions at the ortho and para positions, and *o-p*-directing groups favor reactions at the meta positions. The products of a transition state of this type are



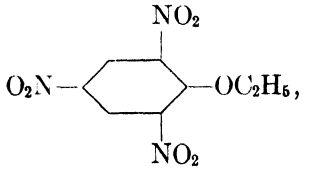
and A^+.

Stable products can be obtained only if the conditions are such that H^- can be removed, or better, if the aromatic compound already contains a group that can readily be removed as a negative ion. The reaction is then not the replacement of a hydrogen atom but the replacement of the more negative group.

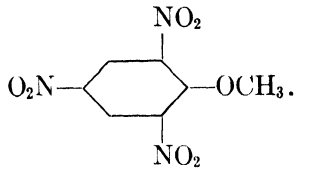
The replacement of negative groups from the benzene nucleus by bases has been studied by Schöpff, Kenner, Holleman, and Borsche.[21] The expected reversal of the directing power of the groups is found. When the benzene ring contains several groups that stabilize negative charges (nitro groups), the salts of the intermediate ion $(Ar—B)^-$ can be obtained. That these ions have the expected structure has

[21] Schöpff, M., *Ber.*, **24**, 3771 (1891); Fischer, Paul, *Ber.*, **24**, 3785 (1891); Grohmann, A., *Ber.*, **24**, 3808 (1891); Kenner, J., *J. Chem. Soc.*, **105**, 2717 (1914); Holleman, A. F., *Rec. trav. chim.*, **35**, 1 (1915); **39**, 435 (1920); Holleman, A. F., den Hollander, I., and van Haeften, F. E., *Rec. trav. chim.*, **40**, 323 (1921); Borsche, W., *Ann.*, **386**, 356 (1912); Borsche, W., and Bahr, H., *Ann.*, **402**, 81 (1914).

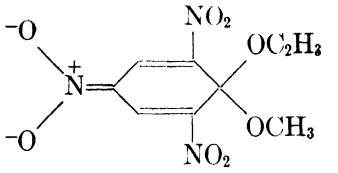
been shown by the identity of the products obtained from methylate ion and



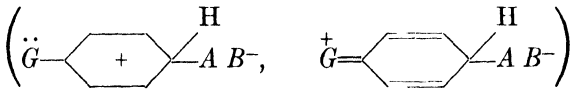
and from ethylate ion and



This shows the structure to be

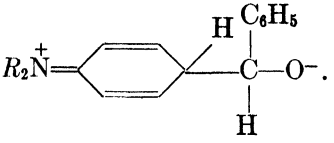


52d. The reaction of carbonyl compounds with phenols and anilines. As we have seen, the resonance

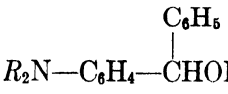


greatly enhances the stability of the transition state when $\ddot{G}$ is a strongly basic group such as NH_2, NR_2, or OH. In consequence anilines and phenols react with substituting reagents that are almost inert to other types of benzene derivatives. This leads to the possibility of forming carbon-to-carbon bonds by combining carbonyl compounds with anilines and phenols. The ortho and para positions of phenols and anilines, like the α position of a carbonyl compound, are reactive towards the C=O group. The products of these condensations are *p*- or *o*-hydroxy- and aminoarylmethane derivatives. These reactions as a rule do not stop with the addition of one phenol or aniline. The resulting hydroxy or aminoaryl carbinols are also substituting reagents for phenols and anilines. The activity of the carbinol hydroxy group is due to a resonance involving the phenol

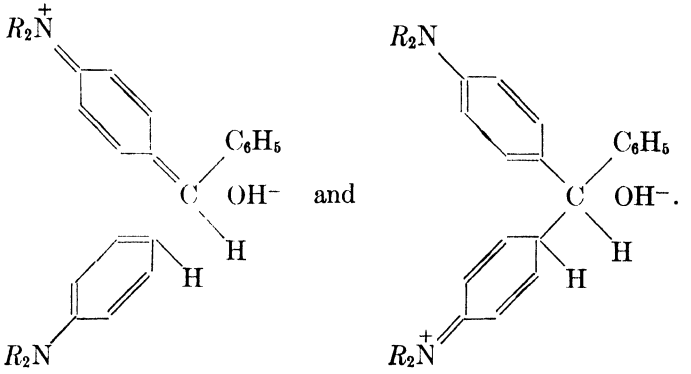
or aniline already present in the carbinol, as well as to the resonance of the entering phenol or aniline. These resonance effects can be illustrated by the condensation of dimethylaniline and benzaldehyde to form the leucobase of malachite green. The transition state of the first step is stabilized by the phase



By transfer of a hydrogen ion, the product of the first step forms



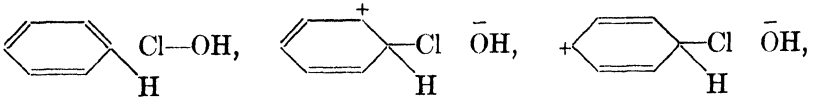
The transition state of the reaction between this and another molecule of dimethylaniline has two quinoidal phases:



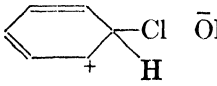
When the hydroxide ion moves away, it combines with hydrogen ion from the positive ion. The final products are therefore $(R_2NC_6H_4)_2CHC_6H_5 + H_2O$. It seems to be impossible to obtain tetra-arylmethanes by this type of reaction. Thus phenol and carbon dioxide form $(HOC_6H_4)_3C—OH$, but not $(HOC_6H_4)_4C$. This is probably due to steric hindrance.

52e. The relationship between addition to ethylene and substitution in benzene. We have assumed that the transition states of the substitution reactions of benzene are linear, just as we did for the

more common addition reactions of an ethylene. The difference between a substitution reaction of benzene and an acidic addition to an ethylene lies essentially in the follow reactions, or further complication of the transition state. In $C_2H_4 + ClOH \rightarrow HOC_2H_4Cl$ the transition state includes the two forms $CH_2{=}CH_2$ Cl—OH and $\overset{+}{C}H_2—CH_2—Cl$ $\bar{O}H$. In the transition state for the reaction of benzene and HOCl, the forms would be



and



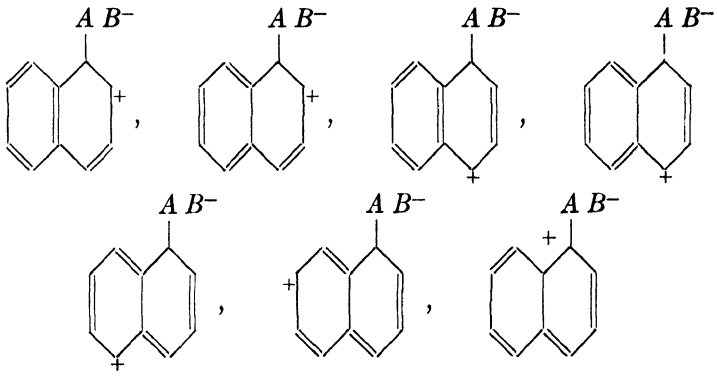
In the former, when Cl is not bonded to OH, the resulting positive charge is located on a single atom, whereas in the latter it is distributed among three atoms. Again, in the latter the proton indicated by H in the formula is readily removed, owing to the consequent restoration of the powerful benzene resonance. These two factors tend to produce addition reactions with ethylenes and substitution reactions with benzenes, whether follow reactions or further complication of the transition states (Lowry mechanisms) are assumed. A substituent group in an ethylene directs the positions taken by the two parts of a polar addend, in the same way as a substituent group in benzene directs the position taken by a group replacing hydrogen. Markownikoff's rule corresponds to *o-p* substitution.

The assumption of very similar transition states for substitution of benzenes and addition to ethylenes gives the foregoing theory some of the characteristics of those theories that assume preliminary addition.[22] Except for the assumption of an *o-p*-directing effect from the dehydrogenation of a nuclear carbon atom, we have closely followed Ingold's theories of the inductive and tautomeric (resonance) effects of groups on the favored positions of substitution.

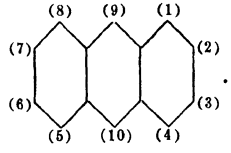
52f. Condensed-ring systems. The hydrogen atoms of aromatic hydrocarbons other than benzene are not equivalent. The resonance factor in the relative reactivities of the different positions of these hydrocarbons towards substitution can be judged by the number of

[22] Holleman, A. F., *Die direkte Einführung von Substituenten in den Benzolkern.* Veit, Leipzig, 1910.

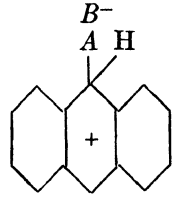
forms of the quinoidal states with a positive charge in the nucleus. For the alpha position of naphthalene there are seven forms with A not bonded to B:



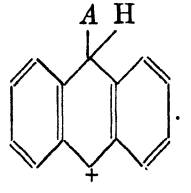
For the beta position there are only six such forms. The resonance factor favors alpha substitution. The main product of the nitration of naphthalene is α-nitronaphthalene. The difference between positions is still more marked in anthracene,



There are sixteen forms of the transition state of the type



for reaction at (9), twelve for reaction at (1), and only ten for reaction at (2). The product of the transition state for the reaction at (9) is

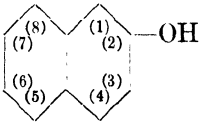


Equal resonances are obtained from this by loss of hydrogen ion or neutralization of the charge by addition of a negative ion to the (10) position (four Kekule forms in each case). Anthracene should therefore behave like ethylene and undergo an addition rather than a substitution. The addition has to be 9,10 (corresponding to 1,4 addition), as this type of addition interferes with the resonance less than any other.

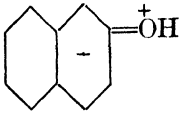
In cold carbon disulfide solution, chlorine adds to anthracene; at 100° it substitutes, forming 9-chloroanthracene and 9,10-dichloroanthracene. Presumably the addition reaction is faster than the substitution, and occurs first. The mono substitution product can be obtained from the addition product by loss of HCl.

A theoretical comparison of the rate of substitution of one aromatic hydrocarbon with another is not easy. Such rates depend not only on the resonance in transition states but also that in the reactants, and the resonating forms of the transition states are not comparable with the Kekule forms of the hydrocarbons. However, there is little doubt that, with sixteen quinoidal forms of the transition state and four Kekule forms of the hydrocarbon, anthracene should be more reactive than benzene, which has two Kekule forms for the reactant and three quinoidal phases of the transition state.

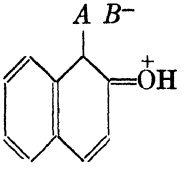
Substituent groups in compound aromatic nuclei retain their *o-p-* and *m*-directing characters. Certain non-equivalences of position occur in the compound nuclei. Thus the two positions ortho to the hydroxyl group are not equivalent in β-naphthol,



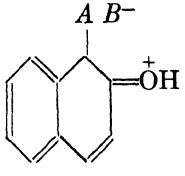
The number of forms of the type



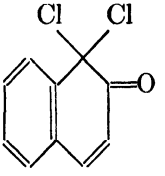
differ for various positions of substitution. There are two for substitution at position (1),



and

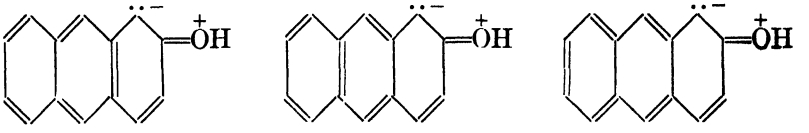


but only one each for substitutions at (3), (6), and (8), and none for substitutions at (4), (5), and (7). Substitution occurs very rapidly and predominantly at position (1). The much greater reactivity of position (1) than of any other position in β-naphthol will lead to reaction at this position even if it is already occupied, provided a stable product can be obtained by a follow reaction, such as the loss of hydrogen ion from the hydroxyl group. With chlorine, α-chloro-β-naphthol gives



in preference to a dichloronaphthol. Other substituting reagents and other α-substituted β-naphthols have been found to yield similar ketones.[23]

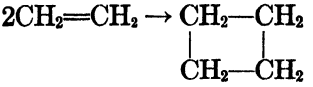
By considerations exactly analogous to those used on the naphthols, it may be seen that β-anthrol should substitute almost exclusively in the α position. There are three forms in which the negative charge is on carbon atom (1):



There are two forms in which the negative charge is on carbon atom (9), one each with the negative charge on carbon atoms (3), (6), or (8), and none with the negative charge on atoms (4), (5), (7), or (10). Fries[24] has found that 2,6-dihydroxyanthracene brominates exclusively in the (1) and (5) positions.

53. FOUR-CENTER REACTIONS

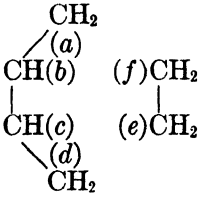
In the reaction



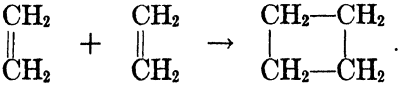
[23] Zincke, Th., *Ber.*, **21**, 3378, 3540 (1888); Fries, K., and Hübner, E., *Ber.*, **39**, 435 (1906); Fries, K., and Hempelmann, E., *Ber.*, **41**, 2614 (1908); Fries, K., and Schimmelschmidt, K., *Ann.*, **484**, 245 (1930).

[24] Fries, K., Walter, R., and Schilling, K., *Ann.*, **516**, 248 (1935).

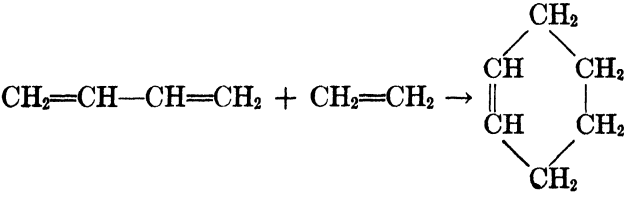
the transition state almost certainly has the four carbons in a plane quadrilateral figure. A linear combination would leave the very reactive bi-radical $\cdot CH_2—CH_2—CH_2—CH_2\cdot$, which would form a macropolymer. However, in simple cases the energy barrier to these four-center reactions would be high. The polymerization of ethylenes to cyclobutanes is slow and occurs only at high temperatures, with heats of activation in the neighborhood of 40 kcal. However, if the six carbon atoms of an ethylene and a conjugate system of four atoms are arranged in a ring, there would be considerable resonance in the transition state. Thus for $CH_2=CH—CH=CH_2$ and $CH_2=CH_2$ we could have the hexagonal arrangement



with six electrons left to form three more bonds: *af*, *bc*, and *de*; or *ab*, *cd*, and *ef*; as well as the less stable combinations *ad*, *bc*, *ef*; *ab*, *cf*, *de*; and *af*, *be*, and *cd*. The resonance is similar to that in a benzene ring, except that the molecules that make up the system repel each other while in benzene all the parts are held together by bonds. Also, this system would need more energy than does benzene to make all the distances between carbon atoms the same, and so the resonance of the six-electron system would not be so good in this transition state as it is in benzene. But, though less than the full benzene resonance energy is to be expected from this transition state, very much more would be obtained than in the quadrilateral transition state for the reaction.



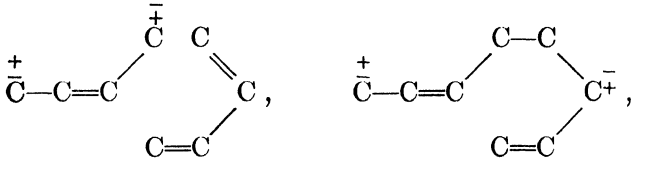
In consequence, the activation energy of the reaction



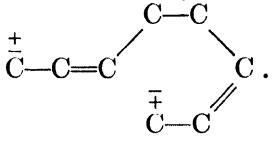
should be much less than 40 kcal. and the reaction should be possible at moderate temperatures. This type of reaction has been discovered. It is known as the Diels-Alder diene condensation.

Evans and Warhurst[25] have calculated the energy of formation of the transition state for the dimerization of simple ethylenes as 36 kcal. They calculate the energy obtained by the six-electron resonance in the diene condensation as 18 kcal. and the energy needed to form the transition state for this reaction as 18 kcal. The heat of activation for the dimerization of simple ethylenes is fairly constant and averages 39 kcal.[26] Evans and Warhurst give 26.3 kcal. as the average heat of activation of the dimerization into six-membered rings of aliphatic chain dienes. The agreement between calculated and actual values is not very good, but the predicted qualitative effect is found.

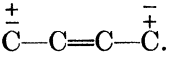
In the condensation between two dienes, further resonance arises. This extra resonance exists in both the reactant and the transition state, but is a combination of more forms in the latter than in the former, and would be expected to increase the reaction rate. The ionic forms that allow conjugation between the unsaturated side chain and the ring in the transition state are



and



The resonance in the reactant is increased by the ionic forms

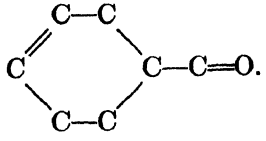


The condensation between an ethylene and a diene is therefore difficult to obtain because of the more rapid condensation of the diene with itself. The carbonyl group gives even better ionic resonance

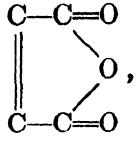
[25] Evans, M. G., and Warhurst, E., *Trans. Faraday Soc.*, **34**, 614 (1938).

[26] Krauze, M. V., Nemtzov, M. S., and Soskina, E. A., *Compt. Rend. U.R.S.S.*, **3**, 262 (1934).

than the ethylenic double bond. In consequence, in the diene condensation of a mixture of compounds having the skeleton structures C=C—C=C and C=C—C=O, the former supplies four atoms to the six-membered ring and the latter two carbon atoms. The product is



These reactions are faster and have lower activation energies than those between two dienes. The conjugated system, maleic anhydride



is a very efficient reagent in diene condensations. It supplies two carbon atoms to the six-carbon ring formed, the other four coming from a conjugated diene.

53a. Aromatic rings in the diene condensation. The diene condensation between benzene and maleic anhydride does not occur. This can be attributed to the large energy of the resonance between the Kekule forms of benzene. This resonance tends to be lost in the transition state, and only resonance between ionic forms replaces it. When, however, the process of saturating a ring in a polynuclear aromatic compound does not decrease the number of Kekule forms, the diene condensation occurs so as to saturate this ring. For instance, maleic anhydride adds to the central nucleus of anthracene at the (9) and (10) positions. Taking n_d and n_r as the number of Kekule forms of the diene condensation product and of the reacting aromatic hydrocarbon, respectively, the ease of diene condensation increases as the quantity $\frac{n_d - n_r}{n_d + n_r}$ increases.[27] Therefore tetracene and pentacene are very reactive.[28] In a complex polynuclear aromatic hydrocarbon, the reaction occurs at that point for which $\frac{n_d - n_r}{n_d + n_r}$ is greatest.

[27] See section 32a, Chapter VII. Note that the sign of the difference here is the reverse of what it is in the case of the quinones of Chapter VII.

[28] Clar, E., *Ber.*, **73**, 81 (1940); *Ber.*, **72**, 1817 (1939). See also Kon, G. A. R., *Annual Reports Chem. Soc.*, 1932, p. 163.