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ORGANIC ELECTRODE  
PROCESSES



# ORGANIC ELECTRODE PROCESSES



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London: Chapman & Hall Ltd.

REINHOLD PUBLISHING CORPORATION  
NEW YORK

1958

FIRST PUBLISHED 1958

PRINTED IN GREAT BRITAIN BY THE WHITEFRIARS PRESS LTD  
LONDON AND TONBRIDGE

*To*

**JODY**

*whose tenderness and thoughtfulness  
illuminated the period of this endeavour*



## FOREWORD

**I**N INORGANIC CHEMISTRY the electrochemical method is both well understood and widely used, but in organic chemistry the reverse is true. This is a strange anomaly, the reasons for which are obscure, but whatever they may be there is no doubt of the desire of many organic chemists to know more about the principles and practice of organic electrochemistry. As Dr. Allen points out in his preface, this book is his response to many requests for information and instruction. The enthusiasm which he shows for the subject will do much to advance interest in the field. It will do much also to dispel a certain mystery which surrounds the subject, and which seems, in part, to originate in a shyness which many organic chemists have towards subjects of a physical chemical nature.

The author is well equipped for the task, having spent the greater portion of his research career in investigations of experimental electro-organic chemistry, and in this book he carefully balances the sifting of knowledge with the application of principles to practice.

The future of the subject may merit speculation. There seems at the present time to be a growing interest in radical reactions at the anode, with all that that may imply for modern technology. On the other hand, the steady inflation which is occurring in the cost of conventional reducing metals may well initiate a resurgence in the importance of cathodic reduction. In any event, Dr. Allen's book seems to have made a timely appearance to inspire thought, interest, and experiment.

CHRISTOPHOR L. WILSON

University of Notre Dame,  
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*March 1957.*



## AUTHOR'S PREFACE

**D**URING the last few years I have been privileged to deliver lectures here and abroad on the various aspects of electro-organic chemistry. Many members of my audiences have suggested that if there were available a comprehensive monograph which would enable the novice to obtain a complete picture of the techniques involved, and of the results one might anticipate when undertaking an organic electrochemical investigation, they would be much more desirous of attempting to utilize the technique. Although a number of excellent books have been written on the subject, each suffers from inadequacy in one or more of the necessary aspects of this science. Further, some of the better books have been out of print for some time. Therefore, in view of the steadily increasing interest in organic electrochemistry, I have attempted to present as complete a picture as possible of the various phases with which the potential investigator need be acquainted. There are many subjects, especially those involving the theoretical aspects, which could have been presented in a more elaborate form, but I felt this complexity might discourage the reader. If I have erred in omission of facts which may be deemed vital by some readers I sincerely beg forgiveness, and take refuge in the word "oversight."

In closing I wish to express my sincere appreciation to Dr. A. H. Corwin, whose initial stimulus led me into this most fascinating field; to Drs. J. Bockris and A. Hickling for their moral support; to Drs. J. Marsh and R. Mizzoni for their helpful suggestions; to Mr. R. Wolf and Miss R. Cole for their artistic and photographic contributions; and last, but not least, to three wonderful girls, Misses P. McGovern, V. Powell, and J. Siragusa, whose efforts helped bring this manuscript to its final form.

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*March 1957.*

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## INTRODUCTION

*For out of olde fildes, as men seith,  
Cometh al this newe corn fro yeer to yeer  
And out of old bokes, in good feith,  
Cometh al this newe science that men lere.*

CHAUCER.

TODAY in the field of electrochemical processes we discuss subjects such as overpotential, effects of medium, temperature, concentration, etc., on the progress of an electrolysis as if they were new conceptions. But the literature indicates that investigators of the previous century were well acquainted with these phenomena, although perhaps not to the point of creating definite terms for their observations. Therefore, our present-day knowledge in the field of electrolytic processes is a result, in part, of rediscovery and elaboration.

The fact that electricity is a potential oxidizing or reducing agent was realized very early in the nineteenth century by Rheinold and Erman (1) who electrolysed dilute aqueous solutions of alcohol. Grutthus made the interesting observations that indigo-white, upon electrolysis in a basic medium, gave a blue precipitate at the anode. This precipitate disappeared upon reversal of the current. Lüdersdorff in 1830 was the first to undertake a detailed study of the products obtained using different electrodes in the oxidation of alcohol. It was Faraday who first realized the potentialities of using electric currents to bring about the synthesis or degradation of a compound. However, in spite of Faraday's extensive researches, it was not until the time of Kolbe's important discoveries that the principles of electrolytic oxidation and reduction were established. In 1845, by electrolytic means, he completely replaced the chlorine with hydrogen in chloromethylsulphonic acid. He also observed that trichloromethylsulphonic acid was completely decomposed in an aqueous solution at a platinum electrode. Concerning this he stated: "This acid, which is stable to the strongest oxidizing media, breaks down with little difficulty at a platinum anode." Kolbe now turned his attention to the anodic

oxidation of organic substances from which resulted the synthesis of hydrocarbons by electrolysis of salts of monobasic aliphatic acids. These discoveries led to extended studies on the effects of electrolysis on aromatic hydrocarbons and their derivatives. Toward the closing years of the last century, investigators such as Gattermann, Haber, Löb, Tafel and others made tremendous contributions to the knowledge of the quantitative effects of electrolytic oxidation and reduction on organic compounds.

Fritz Haber laid a sound foundation for the methodical study of electro-organic processes by introducing the concept of controlled electrode potential. In 1898 there appeared a paper by Haber (2) on the stepwise reduction of nitrobenzene. He showed, for example, that by variation of the cathodic potential he could obtain either azoxybenzene or hydrazobenzene. In his discussion he stated that: "The electric current up to this time has been regarded in organic electrochemistry as a means of reaction whose effects are determined through current density, current duration and occasionally through the material of the electrode. This view is incomplete, for oxidation and reduction processes depend mainly on the potential of the electrode at which they take place. The current density, current duration and electrode material are important only in so far as they determine the electrode potential and its changes in the process of electrolysis." This fact seems to have been overlooked to a great extent by subsequent workers in the field, with the result that only empirical information has been forthcoming. However, of late there has been renewed interest in controlled potential electrolysis, and it is now possible to anticipate more quantitative information as a result of the rediscovery of Fritz Haber's work.

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- (2) Haber, *Z. Elektrochem.*, 1898, 4, 506.

## GENERAL CONSIDERATIONS

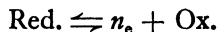
### (1) POLARIZATION

THE passage of an electric current tends to displace the potentials of the electrodes in the system concerned. As a result, during an electrolytic oxidation or reduction the electrodes are not in a state of equilibrium. Under such conditions the electrodes are considered to be polarized. Therefore, any pair of electrodes which comprise a cell, and are connected to an outside source of voltage so as to permit the passage of current, are considered to be polarized. Substances which tend to re-establish the equilibrium state are referred to as depolarizers. Thus if an electrolytic oxidation or reduction is performed on a compound which is susceptible to oxidation or reduction, this substance will tend to return the electrode to its state of equilibrium.

### (2) REVERSIBLE ELECTRODE PROCESSES

Our prime concern will be with organic electrode processes which are mainly irreversible, therefore we shall touch only lightly on reversible processes.

As reduction involves the increase in negative charge or the gain of electrons, and oxidation the decrease in negative charge or the loss of electrons, one can create a system wherein there is a state of equilibrium between the oxidized and the reduced forms represented by



where Red. and Ox. represent the reduced and the oxidized form and  $n$  the number of electrons involved in this change of state.

In order to have a reversible oxidation-reduction process it is necessary that both species be present in the system, and also that minute changes in potential result in the change of one form to another, depending on the extent of the potential change. In other words, if

the potential is made more positive, then oxidation with loss of electrons should tend to compensate for this positive change in potential. A more negative potential should be compensated for by addition of electrons to the oxidized form. Therefore, the equilibrium potential for any reversible system as indicated by the above equation can be given by the following expression:

$$E = E_0 - \frac{RT}{nF} \ln \frac{(\text{Ox.})}{(\text{Red.})}$$

where  $E_0$  is the standard oxidation-reduction potential, Ox. and Red. the concentrations of oxidized and reduced forms, and  $n$  the number of electrons involved in the transformation.

### (3) IRREVERSIBLE ELECTRODE PROCESSES

As mentioned previously, most processes involving the electrolytic oxidation or reduction of organic compounds are irreversible. There are, however, some noteworthy exceptions such as quinone  $\rightleftharpoons$  hydroquinone, leuco base  $\rightleftharpoons$  coloured form of the triphenylmethane dyes, etc. However, these systems are rare and in general we must be content with empirical data. An irreversible system does not give a definite potential which varies according to the amount of oxidized and reduced form in the system, as is obtained by application of the thermodynamic expression for the reversible system. As the potential of the systems depends more on the nature of the medium, its degree of acidity or alkalinity, the electrode and its history, than on the concentrations of oxidized and reduced forms, it is not possible to apply the simple principles which hold for reversible electrode processes. It must be remembered that there is a distinct difference between chemical reversibility and thermodynamic reversibility. A ketone  $\rightleftharpoons$  secondary alcohol may be reversible chemically, but it certainly does not generally give a definite thermodynamically reversible potential. That does not mean to imply that once the ketone is electrolytically reduced to the alcohol it cannot be again oxidized electrolytically back to the ketone. Such is possible, but it requires totally different conditions of potential, medium, pH and electrode material, to achieve this transformation.

If we may take licence from Fritz Haber and assume from his statement that an oxidation or reduction process depends mainly on the potential of the electrode at which it occurs, then there is a focal point

for a beginning. However, it must be remembered that without consideration of the medium in which the electrolysis is performed, acidity or alkalinity of this medium, concentration of depolarizer, electrode material, etc., electrode potential becomes an abstract and meaningless term. Therefore, at this point, electrode potential and each of the various factors which control and contribute to this potential at the electrode surface will be discussed.

#### (4) ELECTRODE POTENTIAL

If a ketone is reduced with tin and hydrochloric acid one usually obtains an alcohol. If the synthetic chemist thinks further about the matter he realizes that a two electron change has taken place with the addition of hydrogen to form the alcohol. He may not extend his thoughts to the fact that this particular reaction has a definite E.M.F. Therefore, if this reaction were carried out electrolytically at the same E.M.F. in a suitable medium the electrode would contribute the two electrons and the medium the hydrogen necessary for the reduction.

We may refer to this E.M.F. of the reaction as the electrode potential or as a reference potential  $v$ , a standard reference electrode (e.g. saturated calomel electrode). There are two methods by which one can attain the desired electrode potential. The first is in the use of electrode material of proper overpotential. By overpotential is meant the difference between potential at which gas evolution is first observed, and the theoretical reversible potential of the electrode in the same solution (1). The higher the hydrogen overpotential of the electrode generally the more powerful its reducing ability, or the greater the energy content of the hydrogen liberated. The oxidizing ability and the energy content of the oxygen liberated at the anode is similarly dependent on the oxygen overpotential. We may therefore regard the potential as being a measure of the potential energy of the hydrogen or oxygen liberated.

It has been shown by LeBlanc (2) that aqueous solutions of acids and bases, in general, have a "decomposition potential" in the vicinity of 1.7 volts at a smooth platinum electrode (Table 1: 1).

The term "decomposition potential" refers to that potential at which appreciable current begins to flow through the solution, accompanied by hydrogen evolution at the cathode and oxygen evolution at the anode. The reason given by LeBlanc for the "decomposition potential" being the same in different solutions is that the hydrolysis

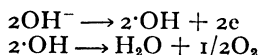
ORGANIC ELECTRODE PROCESSES

TABLE 1: 1

*Decomposition Potentials of Acids and Bases in Aqueous Solutions*

<i>Acids</i>	<i>Volts</i>	<i>Bases</i>	<i>Volts</i>
Nitric acid . . .	1·69	Ammonium hydroxide . . .	1·74
Sulphuric acid . . .	1·67	Sodium hydroxide . . .	1·69
Phosphoric acid . . .	1·70	Trimethylammonium hydroxide	1·74
Trichloroacetic acid . . .	1·66	Diethylammonium hydroxide . . .	1·62
Perchloric acid . . .	1·65	Potassium hydroxide . . .	1·67

of water is common to all cases, with the discharge of hydrogen ions at the cathode and hydroxyl ions at the anode, the hydroxyl ions forming oxygen according to the following scheme:



The fact that aqueous solutions of halogen acids have lower decomposition potentials (Table 1: 2) is explained by the fact that the discharge potential of the halogen is lower than that required for hydroxyl ion discharge.

TABLE 1: 2

*Decomposition Potentials of Aqueous Halogen Acid Solutions*

Hydriodic acid . . . . .	0·52 volts
Hydrobromic acid . . . . .	0·94 volts
Hydrochloric acid . . . . .	1·31 volts

As previously mentioned, the decomposition potential of aqueous acid or base solution is about 1·7 volts. This is only true if smooth platinum electrodes are used. Other electrodes in the same medium will give different decomposition potentials.

An indication of the relative ability of a metal to reduce or oxidize can be obtained from the Table 1: 3.

From the table it can be seen that mercury, zinc, lead and tin should be the most desirable electrodes to use for difficult reductions, and nickel, platinum and copper for compounds easily reduced.

This is in general agreement with observations that have been made in the past. The reduction of nitro compounds in acid media at a high overpotential electrode such as lead, mercury, tin or zinc yields the

GENERAL CONSIDERATIONS

TABLE I: 3  
*Cathodic and Anodic Electrode Overpotentials*

	<i>Hydrogen Overpotentials (In N.H<sub>2</sub>SO<sub>4</sub>)</i>	<i>Oxygen Overpotentials (In N.KOH)</i>
Palladium . . . . .	0·00	0·43
Gold . . . . .	0·02	0·53
Iron . . . . .	0·08	0·25
Smooth Platinum . . . . .	0·09	0·45
Silver . . . . .	0·15	0·41
Nickel . . . . .	0·21	0·06
Copper . . . . .	0·23	—
Cadmium . . . . .	0·48	0·43
Tin . . . . .	0·53	—
Lead . . . . .	0·64	0·31
Zinc . . . . .	0·70	—
Mercury . . . . .	0·78	—

amine ; a low overpotential metal such as nickel or platinum yields intermediate reduction products such as phenylhydroxylamines or azoxy- and hydrazo- compounds derived from phenylhydroxylamines (3).

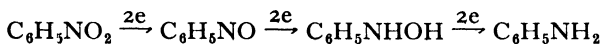
The electrodes used for electrolytic oxidations are somewhat more limited because it is difficult to obtain a stable anode potential with many electrodes in the presence of a depolarizer. The potential generally rises rapidly from the low value, at which the anode dissolves, to the high value for passivity and oxygen evolution. However, since platinum and sometimes gold are nearly always passive it is possible to obtain graded potentials with these metals.

It is difficult to give definite rules concerning the efficiency of an electrode for anodic oxidation. If the oxidative process is due to the presence of oxygen in an active form it might be anticipated that a high anode potential would indicate a more effective oxidizing power. This does not seem to hold in all instances, for, as will be seen later, there are processes which appear to be independent of the anode potential. In these cases it is possible that the effective oxidizing agent may be something other than oxygen, perhaps hydrogen peroxide. The prime prerequisite for a metal to be used as an anode is that it be essentially passive in the electrolytes used. In the absence of halogens, metals such as platinum or gold are usually not attacked and therefore are suitable. These may on occasion be used with chloride providing the

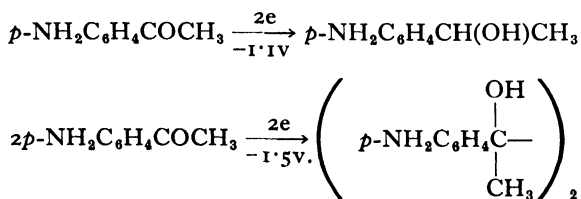
amount is low. This also holds for anodes of cobalt and nickel provided high current densities are used. At still higher current densities iron can be utilized. However, once this metal has become passive it is then possible to use the electrode at low current densities. Lead can also be used in acid solutions of moderate concentration. In a sulphuric acid medium lead first forms a sulphate coating which is converted into an oxide coating. With an alkaline medium it is necessary to use metals whose oxides are insoluble. Lead even behaves as an insoluble electrode at high current densities in this medium, although at low current densities it is not passive and will go into solution. In this type medium platinum is as suitable as it is in an acid medium.

The second method, whereby the desired electrode potential may be attained at the working electrode, is to utilize a high hydrogen overpotential metal (mercury) for reductions, or a high oxygen overpotential metal (platinum) for oxidations, and to control the applied voltage across the cell so as to obtain the desired electrode potential. The potential at the working electrode is measured against that of a standard reference electrode with a vacuum tube voltmeter. This will be discussed further in Chapter II.

Often by utilizing the same electrode, the same medium and the same temperature, it is possible to obtain different products from the same starting material by merely changing the electrode potential. This fact has been demonstrated by Haber (4) in his studies on the reduction of nitrobenzene, in which it was shown that the first step is the formation of nitrosobenzene, followed by the hydroxylamine and finally aniline:

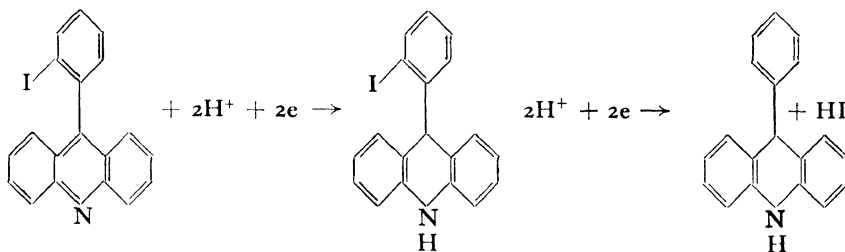


Each of these steps is controlled by the potential at the cathode surface. It has also been demonstrated that *p*-aminoacetophenone can be reduced at a mercury cathode to either the hydrol or the pinacol, depending upon the potential at the mercury cathode (5), thus:



## GENERAL CONSIDERATIONS

The stepwise reduction of 9-(*o*-iodophenyl) acridine (6) is another example of the use of controlled potential to obtain desired partially reduced compounds. This reduction proceeds according to the following scheme:



The fact that the electrode potential is probably the most important factor in determining the reaction occurring during electrolytic reduction is not difficult to comprehend. It is known, for instance, that in a reduction at a constant current density the initial potential will increase as the reduction proceeds, as illustrated by the reduction of *p*-methoxyacetophenone (Table I: 4) (7). This means that if one

TABLE I: 4

*Reduction of p-Methoxyacetophenone to its Pinacol in an Aqueous-Methanolic Potassium Acetate Medium*

Time (min.)	Ref Pot. v. S.C.E.	c.d. amp./cm. <sup>2</sup>
0	2.40	0.288
2	2.46	
3	2.48	
5	2.50	
7	2.58	
9	2.60	
11	2.79	
13	2.86	
14.6	3.00	0.288

desires to attack the more easily reduced centre in a compound having two reducible centres, under constant current density conditions, one should choose an electrode of proper overpotential to prevent possible reduction of both centres. In other

words electrolysis at a specific potential is equivalent to using one reducing or oxidizing reagent, whereas constant current density electrolysis is comparable to using a number of reducing or oxidizing reagents in the same reaction vessel. The maximum potential obtainable would of course depend on the electrode material used.

It is not meant to imply by the above that constant current density electrolysis is of no value. If one has a compound with one or more reducible centres and a complete reduction is desired, it is usually of no consequence what the electrode potential is, so long as it is greater than the minimum potential required for the desired reaction. In these cases constant current density electrolysis will give satisfactory results with possible sacrifice in current efficiency.

### (5) VOLTAMMETRIC CURVES

If an increasing potential is applied on a cathode in a medium which does not contain a depolarizer, there will be a relatively small flow of current ( $a$ ), which can possibly be attributed to diffusion of hydrogen from the electrode, or the presence of a trace of reducible material in solution. When the potential reaches a certain voltage ( $b$ ) the evolution of hydrogen gas bubbles will be observed from the cathode, and the current will increase rapidly ( $A$  in Fig. 1:1).

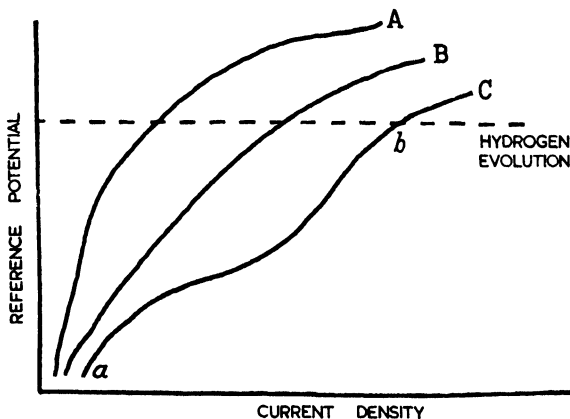


FIG. 1:1. *Reference Potentials in Cathodic Reductions.*

In the presence of a depolarizer which reduces relatively slowly as many organic compounds do, a voltammetric curve such as  $B$  will be

obtained. A compound which is rapidly reduced will give a curve as illustrated by *C*. From curves *B* and *C* it can be seen that by controlling the potential at a particular point, one can control the reducing power of the electrode. It is not enough to set the current density at a particular value, for, as it was shown previously, removal of depolarizer due to its reaction with hydrogen will cause the potential to increase, with resultant hydrogen evolution. However, the current density can be regulated so as to maintain a constant electrode potential.

#### (6) CATALYTIC EFFECT OF ELECTRODES

In general the overpotential of the electrode is a suitable indication of its reducing ability. There are, however, occasions in which the nature of the electrode material exerts a pronounced catalytic effect on the reaction. In these instances a low overpotential electrode may be as effective as, or perhaps more effective than a higher overpotential electrode. As an example we might consider the cathodic reduction of nitric acid to ammonia. If a relatively high overpotential cathode such as amalgamated lead is used, a small percentage of ammonia is obtained together with a large amount of hydroxylamine, whereas spongy copper, which has a low overpotential, will give very high yields of ammonia (8).

Similarly, when ketones are reduced at cathodes of relatively high overpotentials, the pinacol is generally obtained. If a cadmium electrode, which has a relatively lower potential, is used, the more highly reduced form, the hydrocarbon, is obtained (9). The ability of high overpotential electrodes to reduce resistant compounds can also be hindered by the presence of catalytic quantities of other metals such as copper, platinum or silver in the medium or electrode. Therefore, it is essential that the electrode be absolutely pure. This is the reason mercury is usually suitable for reductions and platinum for oxidations, since these metals can be obtained in an extremely pure state.

In some instances the catalytic effect of the anode metal may overshadow the consideration of potential. In the oxidation of iodate in alkaline medium at a smooth platinum electrode, increase in electrode potential results in increased yield of periodate. However, use of a lead dioxide electrode results in a still better yield, even though the anode potential of this electrode is somewhat lower (10). Therefore, it is difficult to say in this case that the potential is the governing factor in the process. Methyl alcohol, when subjected to anodic oxidation in a dilute sulphuric acid medium at a smooth platinum anode, yields

formaldehyde with an 80 per cent efficiency. When platinized platinum or lead dioxide anodes are used, the decrease in yield of formaldehyde is accompanied by increased quantities of the more highly oxidized products, formic acid and carbon dioxide (11). In many oxidations better results can be obtained with platinized platinum or lead dioxide. This is especially so in the oxidation of benzene derivatives.

#### (7) ALLOY ELECTRODES

As has been suggested previously, the use of certain electrodes, though of lower potential, may reduce a compound to a greater degree than that of a higher overpotential electrode. It has also been found that alloy electrodes may be more efficient in certain instances.

The reduction efficiency of nitrobenzene in an alcoholic-alkaline solution is increased from 58 to 72 per cent by the addition of 12 per cent iron to a nickel cathode (12). The yield of pinacol from the electrolytic reduction of acetone is tremendously improved by the use of a lead-tin or lead-copper electrode (13).

#### (8) CATALYTIC EFFECTS OF ADDED SUBSTANCES

In addition to the catalytic effect of a particular electrode material or an alloy electrode on the reaction, the addition of various salts to the electrolyte may have an effect on the products obtained from an electrolytic reduction. The addition of salts of lead and mercury to low overpotential electrodes, such as nickel, will increase the efficiency of the electrode. Also, certain metals may be deposited on the cathode, react with the depolarizer, and then be redeposited from solution. The reduction of nitro-compounds to their hydrazo-derivatives in a basic medium is facilitated by zinc, lead or tin hydroxide dissolved in the catholyte (14). The lead probably causes an increase in the overpotential of the cathode, but with the zinc or tin salts the effects may be partly due to the chemical action of the metal (15). Indigo is reduced to indigo-white at a zinc cathode. This will also occur at other cathodes in the presence of zinc salts (16). The same reduction can be accomplished chemically with zinc. Similarly, in the synthesis of methyl anthranilate from the methyl ester of *o*-nitrobenzoic acid, a 40 per cent yield is obtained using a lead cathode. Addition of a catalytic amount of stannous chloride to the electrolysis medium will increase the yield to 90 per cent (17).

Electrolytic reductions performed at a mercury cathode in an

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alkaline medium, or in the presence of an alkali salt, may be a result of chemical reduction by the amalgam. Benzoic acid in an alkaline medium can be reduced to the tetrahydro compound (18). The same reaction can be accomplished chemically with sodium amalgam. L6b and Moore (19), in their experiments on the controlled potential reduction of nitrobenzene in an alkaline medium, reported that the addition of copper powder increased the efficiency for the formation of aniline from 33.2 to 52.6 per cent. In this case it is doubtful if chemical action can account for the reduction, even though phenylhydroxylamine can be reduced to aniline with copper powder. Some German patents (20) claim the addition of powdered metals, particularly copper when used with a copper cathode, have facilitated the reduction of nitro-compounds to their respective amines. Thus it has been possible to achieve the difficult reduction of some azoxy compounds such as *o*-azoxychlorobenzene to their respective amines.

Another type of catalytic effect which can, in some cases, produce increased reduction efficiency is obtained by the addition of ions capable of existing in two stages of oxidation; e.g. titanium, vanadium, chromium, iron and cerium. These are sometimes referred to as "hydrogen carriers." As an example  $Ti^{+4}$  is reduced at the cathode to  $Ti^{+3}$ , which, being a strong reducing agent, reacts with the substance present in the solution and in so doing is reoxidized to  $Ti^{+4}$ . The resultant ions are once more reduced cathodically, and the process goes continuously.

An acid solution of chlorate is reduced much more effectively at a platinum cathode if a small quantity of vanadic acid is present to facilitate conversion to the chloride. The reduction of nitro compounds to their respective amines is often facilitated by the addition of a tin salt (21). The addition of antimonous or arsenious oxides to the sulphuric acid medium used in the reduction of *N,N*-dimethylphenylacetamide results in a considerable increase in yield of the phenyl ethyl amine (22). The yield at a lead cathode increased from 41 to 80 per cent as a result of using the oxide catalysts. The addition of iodine has been reported to increase the speed of reduction of certain nitro compounds to the amine (23).

There have been some reports on anti-catalytic effects of certain substances. Ordinarily, use of a lead cathode will result in an excellent yield of aniline from nitrobenzene. If it is desired to stop the reduction at *p*-aminophenol, the efficiency of the lead cathode can be advan-

tageously diminished by the addition of arsenic or bismuth powder or copper sulphate to the catholyte (24).

Many electrolytic oxidations are also facilitated by the presence of ions capable of existing in two valence states, and the action of these "oxygen carriers" is comparable to that of the "hydrogen carriers" previously mentioned. Potassium permanganate has been used as a catalyst for the manufacture of saccharin by electrolysis of toluene sulphonamide (25). The oxidation of anthracene to anthraquinone in an acetone-sulphuric acid solution at a platinum anode takes place with a 55 per cent efficiency. The addition of a cerium, chromium or manganese salt results in an increase to an 80 per cent efficiency (26). Similarly acetic acid has been obtained by oxidation of paraldehyde in a dilute sulphuric acid medium, in the presence of salts of cerium, manganese, molybdenum, or vanadium (27).

The effectiveness of various catalysts varies. In the oxidation of naphthalene to naphthoquinone the catalytic effect increases in the following order: manganous sulphate, dichromate and ferrocyanide, potassium chlorate, vanadic acid, ceric nitrate (28). There have been reported instances wherein the use of different catalysts has resulted in different oxidation products. If a chromium salt is used as a catalyst in the oxidation of toluene in a sulphuric acid medium, benzoic acid is obtained. If a manganous salt is used the product obtained is benzaldehyde (29).

It has been reported that fluorides in the electrolyte have the effect of increasing the overpotential at platinum, gold, silver and carbon anodes (30). Therefore, their use has a pronounced effect on the reaction process. Thus Skirrow (31) reportedly obtained a more efficient oxidation of naphthalene and benzene in an aqueous hydrofluoric acid solution than in a medium containing a comparable quantity of sulphuric acid. On occasion, perchlorates have been found to have an effect similar to that of fluorides.

### (9) NATURE OF MEDIUM

The products obtained as a result of anodic or cathodic electrolysis are influenced to a marked degree by the nature of the electrolyte used. In the bimolecular reduction of *p*-dimethylaminoacetophenone an acid medium favours the high melting form, whereas a basic medium favours the lower melting pinacol (32). It has also been reported that when benzophenone is reduced in an aqueous-acidic medium the

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pinacone, a rearrangement product of the benzophenone pinacol, is obtained. In a basic medium the pinacol is obtained (33).

In an acid solution, acetaldehyde, when oxidized yields acetic acid; in an alkaline medium formic acid is obtained (34). Aniline in a dilute acid medium is oxidized to aniline black or quinone, whereas in an alkaline medium, azobenzene is obtained (35). The use of a concentrated sulphuric acid medium results in a formation of *p*-aminophenol.

In general there are a limited number of solvents that may be used for anodic or cathodic processes. In most cases water alone cannot be used because of the low solubility of the organic compound in this medium. However, in many instances it is possible to obtain satisfactory concentration of depolarizer by mixing with other solvents. Electrolytic oxidations can generally be performed in aqueous solutions of methanol or acetic acid, absolute methanol, glacial acetic acid, and mixtures in varying proportions of acetic acid and ethylene dichloride or pyridine. Reductions of compounds not too soluble in water can be performed in such media as methanol, ethanol, acetic acid, acetic acid-benzene mixtures, dimethylformamide and dioxane. It should be remembered that if it is possible to have some water in the solvent system the resistance of the needed solution will be diminished, effecting a saving in the power required to accomplish the reaction and in the power dissipated as heat. If the latter is excessive, it may in some cases cause undesirable chemical side reactions. If it is necessary to use a non-aqueous medium for an oxidation or reduction, it is possible, by utilizing proper membranes to separate the anolyte from the catholyte, to use either an aqueous catholyte or anolyte respectively. This aspect will be discussed in Chapter II.

There are many electrolytes which can be used in an aqueous medium. In the nonaqueous media mentioned above salts such as lithium chloride, lithium nitrate, potassium acetate have been found most suitable. Acids, such as sulphuric, are generally as satisfactory in nonaqueous media as they are in an aqueous medium. In addition to potassium hydroxide there are organic bases, such as tetramethylammonium hydroxide, which are suitable for basic electrolysis in nonaqueous media. McKee and Brockman have developed a novel method for increasing the solubility of organic compounds (36). They obtain the desired solubility by "salting-in" the organic compound with saturated solutions of sodium *p*-toluene-sulphonate or sodium cymene-

sulphonate. In addition to these saturated salt solutions being good solvents they are also excellent conductors.

Wetting agents, such as the "aerosols," have on occasion been found satisfactory for solubilizing the organic compound in an aqueous medium. The use of nonaqueous solvents may be avoided by utilizing a vigorously agitated suspension of the organic compound. Although satisfactory results can be obtained in many instances, the efficiency of this method is considerably lower than that employing a solution of the substance.

#### (10) CONCENTRATION OF DEPolarizer

In general the concentration of the depolarizer does not affect the nature of the products obtained. However, one would anticipate that the formation of bimolecularly reduced compounds would be favoured by high concentration, as the chance of collision between the reactive specie would be increased. The reaction rate is affected by increasing the concentration of depolarizer. In this manner a higher current density can be maintained with good process efficiency. In a reversible process the "limiting current density" at which one attains 100 per cent efficiency is directly proportional to the concentration of the depolarizer. For an irreversible process this can only be considered as an approximation, a guide in deciding on the concentration of depolarizer to use for a given current density, in order to try to approach a maximum efficiency.

In order to further understand the evaluation of "limiting current density" for a reaction at a particular concentration, it might be desirable to briefly describe the so-called "diffusion layer" which exists at the electrode surface. The concentration of depolarizer which is being oxidized or reduced at the electrode surface differs from that in the bulk of the medium. There will be, therefore, a concentration gradient in passing from the electrode to the electrolyte. The so-called "diffusion layer," then, is the surface layer in which most of the concentration change occurs.

As mentioned previously, it is possible to obtain an approximate "limiting current density" for irreversible reactions if certain assumptions are made. The first is that the thickness of the diffusion layer is 0.05 cm. thick (37), bearing in mind that this will decrease with increased temperature and agitation. The second assumption is that the diffusion coefficient of the depolarizer is 0.6 to 0.8 cm.<sup>2</sup> day<sup>-1</sup>, which is a value

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obtained for nonelectrolytes capable of reversible oxidation or reduction, e.g. quinone  $\rightleftharpoons$  hydroquinone. With this information we can utilize the equation developed by Nernst (38) from Fick's Law

$$\delta = \frac{ADcn}{0.895 i}$$

where  $\delta$  is the thickness of the diffusion layer,  $A$  the area of the electrode,  $D$  the diffusion coefficient,  $i$  the current,  $c$  the concentration of depolarizer, and  $n$  the difference in charge between the oxidized and reduced form. Substitution of 0.05 cm. for  $\delta$  and expression of  $i/A$  per sq. cm. as the current density (c.d.) we arrive at the following equation:

$$\text{c.d. (amp./cm.}^2\text{)} = 0.0223 DCn \text{ (20}^\circ\text{ C.)}$$

with concentration ( $c$ ) given as gram-moles/litre. This "limiting current density" will increase at approximately 2.5 per cent per degree. Agitation also has a pronounced effect on the limiting current. Usually the greater the agitation rate the greater the limiting current.

The optimum "limiting current density" is only for a specific concentration of depolarizer, and therefore, to maintain maximum efficiency, the depolarizer should be replenished as it reacts, or the efficiency will diminish. Performing the reduction at a controlled potential will accomplish essentially the same purpose (39). As the depolarizer is reduced the current drops until a plateau is reached, which indicates essentially a completed reaction.

An illustration of the use of the concept of "limiting current density" in preparative studies can be found in a recent report on the reduction of N,N-dimethylaminoethyl tetrachlorophthalimide to the respective isoindoline. A comparison was also made between the optimum current efficiency obtained using constant current density and that obtained at a controlled electrode potential. With the former a 45 per cent current efficiency was obtained, whereas the use of controlled potential increased the efficiency to 77 per cent (40).

Another method which can be utilized to improve the efficiency of the process is to increase the area of the electrode either by increasing its size or by utilization of gauze electrodes.

### (11) AGITATION

A necessary factor in maintaining a high concentration of depolarizer at the electrode surface is adequate stirring of the electrolyte. The

more efficient the agitation the higher is the " limiting current density " which can be used for maximum reduction or oxidation efficiency with depolarizers which react rapidly. For more slowly reactive species the rate of agitation will not have as pronounced effect on the maximum current for optimum efficiency. However, some agitation is necessary here in order to bring unreacted depolarizer to the electrode surface.

### (12) TEMPERATURE

The temperature of the catholyte or anolyte during a cathodic reduction or anodic oxidation has an influence on a number of factors controlling the process. Firstly, an increase in temperature will decrease the overpotential of the electrode. This decrease will vary somewhat with the electrode material, but generally this variation is of the order of 0.02 to 0.03 volt for each 10° C. rise. Thus electrodes such as platinum, silver, nickel and copper, whose hydrogen overpotential values are in the vicinity of 0.15 volt at 20° C. and may be effective for certain reductions, will have essentially no action and a negligible overpotential when used at 100° C. With a high overpotential electrode, such as mercury, even at elevated temperatures the overpotential will be high enough to accomplish many difficult reductions. This temperature effect on overpotential has been utilized to stop the course of a reaction at an intermediate point. Thus if ethanol is subjected to anodic oxidation in dilute sulphuric acid at elevated temperatures a satisfactory yield of acetaldehyde is obtained. However, if the same reaction is performed at 30 degrees, the more highly oxidized product, acetic acid, is obtained (41). These results may be due partly to the increase of overpotential with the decrease in temperature, and partly to the lower volatility of the acetaldehyde at this temperature which permits its further oxidation. A second factor to consider is that at elevated temperatures it is possible to use effectively higher current densities. This will enable attainment of shorter electrolysis periods with better yields, especially in instances in which prolonged exposure of the reaction product will cause its destruction (42). Since the rate at which the unreacted specie will come in contact with the electrode surface increases as the temperature rises, the efficiency of a slow process may be considerably improved by temperature elevation. For example, the efficiency of oxidation of an alkaline formate solution at an iron anode is increased twofold when the temperature of the medium is maintained at 75° C. instead of at 16° C. (43.) We must not overlook

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the possibility of an adverse effect on the reaction being directly due to an increased electrolysis temperature. The reduction of a ketone to a pinacol proceeds quite satisfactorily at the lower temperatures when using an acidic medium. However, at elevated temperatures there is an excellent chance that the desired pinacol will rearrange to the pinacone. Another possibility which must be recognized is that the starting material may be unstable at elevated temperatures. Thus if a phthalimide were subjected to cathodic reduction in an acid medium under such conditions, the reduction would be preceded by hydrolysis, with the net result being a negligible yield of the isoindoline.

### (13) SUPERIMPOSITION OF ALTERNATING CURRENTS

There is little that can be said concerning this aspect at the present time, except that at one time it was thought that superimposing an alternating electric current on a direct current electrolysis would tend to lower the overpotential of the electrode (44). Reitlinger claimed that by utilizing an alternating current in this way ethyl alcohol could be oxidized to acetaldehyde without being oxidized further to acetic acid. He also reported that *p*-benzaldehyde sulphonic acid would be obtained from *p*-toluenesulphonic acid in this manner (45). An attempt was made to improve the yield of terephthalic acid obtained by anodic oxidation of *p*-toluic acid by superimposing an alternating current. Normally a great deal of carbon dioxide and water is obtained as the side product. This modification in the process did not have the desired effect (46).

### (14) INFLUENCE OF TIME ON THE ELECTROLYTIC PROCESS

If the electrolysis is performed under conditions in which the electrode potential is controlled at a predetermined value, then we need not fear too prolonged exposure of the product to the current. It has been pointed out previously that, in general, the current will drop until a plateau is reached, at which time the electrolysis is essentially completed.

In using constant current density conditions the electrolysis time should be kept at a minimum when the products of electrolysis are chemically unstable, or when further oxidation or reduction may occur. The latter may be due to an increase in electrode potential at the working electrode with decreasing depolarizer concentration. In addition we must not overlook the possibility that prolonged electrolysis may

result in partial destruction of the reaction product due to its migration to the opposite electrode. Generally it is best when exploring a new reaction to allow it to proceed for its theoretical time ( $T$ ), as computed from the following equation based on Faraday's Law:

$$T_{(\text{min.})} = \frac{MW}{g} \frac{96,500 n}{60 i}$$

Where  $MW$  is the molecular weight of the depolarizer,  $g$  the weight of reacting substance in grams,  $n$  the number of electrons involved in the process, and  $i$  the current in amperes. The results obtained then can be used as a guide to future efforts. Since the potential of the electrode increases with electrolysis time, it may be, on occasion, that a prolonged period of electrolysis will result in an increased efficiency. Also, cases where the electrolysis is performed using a suspension, prolonged electrolysis may be necessary to attain satisfactory yields because of low efficiency.

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# INSTRUMENTATION AND TECHNIQUES OF ELECTROLYSIS

## INSTRUMENTATION

### (I) CONSTANT CURRENT AND MANUAL-CONTROLLED POTENTIAL DEVICES

THE equipment required for electrolytic oxidations or reductions can be constructed from readily available components. The complexity of the equipment will depend to a great extent on the desired type of control. If a constant current electrolysis assembly is desired, the equipment will consist of a source of direct current, a voltmeter, ammeter and the necessary rheostats to control the output voltage.

It would of course be an ideal situation if it were possible to obtain the direct current from the mains. This, unfortunately, is not possible in most instances, and therefore it is necessary to depend a great deal on batteries, a rectifier unit, or a generator. Generally, batteries are not suitable because they are short-lived, dry cells needing replacement and wet cells recharging. Therefore it is best to obtain a rectifier unit which is reasonable in cost for the low current and voltage outputs required in small scale laboratory preparations.

In obtaining a rectifier one should give consideration to the "ripple voltage." It is absolutely essential that this voltage does not exceed the desired range of reference potential if the unit is also to be used for controlled potential electrolysis at the working electrode. Simply stated, if a power supply has a maximum output of 30 volts and 10 amperes and one wishes to control at maximum output to  $\pm 0.03$  volt, the ripple voltage cannot exceed 0.1 per cent. Of course with this same unit narrower limits can be attained when operating at a lower output. As the power needs increase, the cost of "low-ripple" rectification

becomes quite expensive and it is at this point that consideration should be given to a direct current generator.

There are occasions where it will be desired to investigate the possibilities of controlled potential electrolysis, either because the molecule under study has more than one reactive oxidative or reductive centre and selectivity is desired and/or one desires to obtain the maximum process efficiency. As mentioned in the previous chapter, selectivity may also be obtained by utilizing the electrode of desired overpotential characteristics and conducting the electrolysis at constant current density, with the possibility of adversely affecting the current efficiency of the process. In this instance a mercury or lead cathode may be used for reductions, or platinum for oxidations, and the applied voltage controlled so as to maintain the potential at the working electrode surface constant  $v$ . a standard reference electrode. This reference potential can be measured by a vacuum tube voltmeter, a pH meter with a voltage scale or a potentiometer connected between the reference electrode and the working electrode. The essential prerequisite of this measuring circuit is that it does not draw an appreciable current from the system, as this would result in an ambiguous reference potential value. Such a simple circuit as described for manual control of the reference potential is illustrated in Fig. 11: 1. It however suffers from

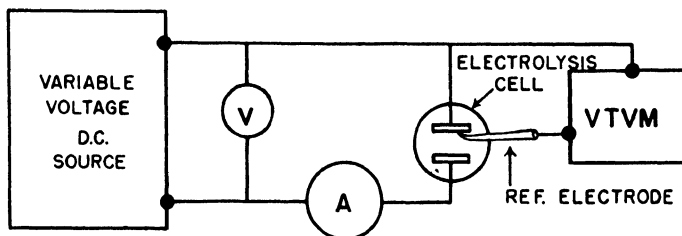


FIG. 11: 1. *Simple Electrolysis Circuit.*

the disadvantage of requiring constant supervision and thus, if considerable work is contemplated, an automatic device should be utilized for controlled potential electrolysis.

## (2) AUTOMATIC CONTROLLED POTENTIAL DEVICES

In the past, many instruments for controlled potential electrolysis have been described (1). Hickling's potentiostat, since superseded by more suitable designs, was a major contribution to the field of controlled

potential electrolysis, for it was the first such instrument which achieved automatic control at a predetermined potential. Prior to its conception, it was only possible to change or maintain the potential by altering either the applied voltage across the cell or the current density. The main disadvantage of Hickling's early instrument was the fact that a maximum of only 0.3 ampere was obtainable; this imposed a limitation on its use in preparative organic electrochemistry. The same disadvantage was present in many subsequent designs. However, with some instruments it is possible by modification of the described circuit to obtain currents larger than 5 amperes (2).

The limitations imposed by prior instruments were taken into consideration when a Redoxotrol utilizing the electronically controlled amplidyne generator as a power source and control unit was constructed (3).

Basically, the amplidyne is an externally driven d.c. generator. However, its unique use of a short circuit and compensating winding creates a precise electrical balance so that the smallest signal will control a relatively large power output (4). Essentially this instrument will give automatically controlled impressed potential to secure constant cathode or anode potentials with respect to a reference electrode. Its method of operation is illustrated by reference to the schematic diagram shown in Fig. 11:2.

The desired electrode potential is obtained by opposing the E.M.F. of the reference electrode (ESCE) with an E.M.F. from the reference supply (ERS). The error signal (EES) equals zero when the (ERS) equals (ESCE). When the (ESCE) changes, due to a change in the amount of depolarizer present in solution, there will be a flow of voltage across the error signal resistor (EES) which in turn will be transmitted to the amplifier, resulting in a change in applied voltage output by the generator. This instrument can deliver 20 amperes and 75 volts. The control sensitivity is  $\pm 0.005$  volt and response is almost instantaneous with no hunting. Generally if one uses an aqueous or predominantly aqueous system for electrolytic oxidations or reductions, a reference potential range of 2 volts is sufficient. As soon as hydrogen evolution takes place at the cathode during reductions, or oxygen evolution at the anode during oxidations, this potential becomes meaningless and it is just as satisfactory to operate at constant current density. However, as is the case with most organic compounds, their solubility in an aqueous medium is limited, and therefore it is often quite



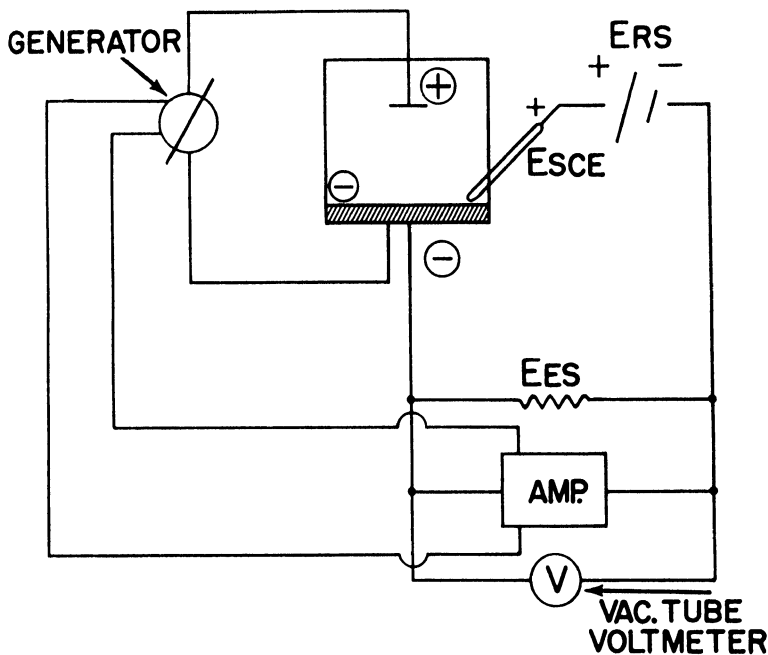
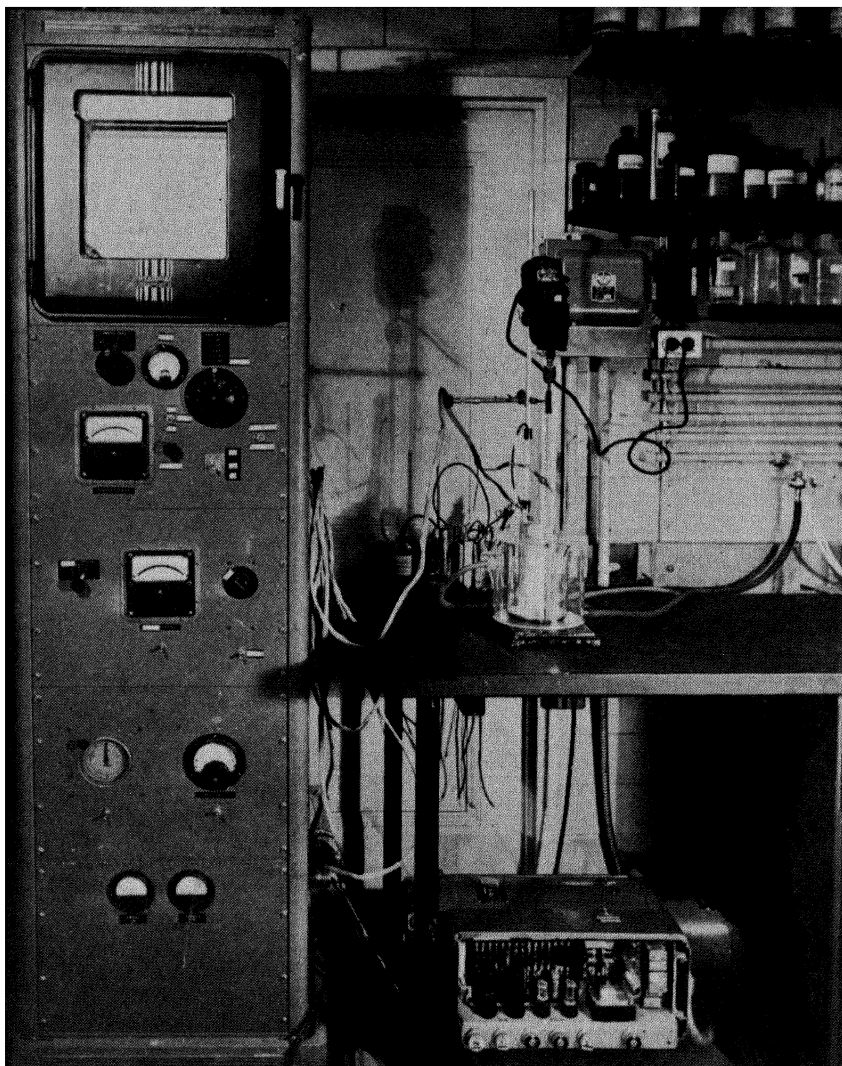


FIG. 11: 2. *Operational Schematic of Redoxotrol.*

necessary to use a mixed aqueous-nonaqueous medium such as aqueous alcohol or aqueous acetic acid with a suitable electrolyte such as a mineral acid, inorganic or organic bases, or salts such as potassium acetate or lithium chloride. Often in more difficult cases it is necessary to use alcohol, acetic acid, or even a mixture of ethylene dichloride and acetic acid with a suitable electrolyte. Therefore, as we go further away from the conductivity of an aqueous system, the reference potential attainable at the working electrode will be much greater than in an aqueous system before gas evolution occurs. Hence an available reference potential range of 6 volts was incorporated in the design of this instrument.

Since the original publication, the circuit has been modified (Fig. 11:3) so as to eliminate the small error obtained when the current-carrying line was used also to carry the signal. A more precise balancing circuit was designed, batteries eliminated from the reference voltage supply, and replaced by a stable voltage supply, and necessary switching incorporated to enable use of the instrument for electrolytic oxidations. The assembled Redoxotrol Model II is shown in Fig. 11: 4.

FIG. II: 4. *Redoxotrol Model II.*

A second instrument has been constructed which embodies many of the features of the original instrument, with the added advantage of being able to deliver higher currents and voltages. The basic system

is essentially a closed loop control system consisting of a controlled generator, a d.c. amplifier, a reference potential supply, and a sampling circuit. Since the standard d.c. generators have too long a response time the amplidyne generator was used in this instrument also. This amplidyne has a rated output of 24 amperes at 125 volts, and the two control fields have a resistance of 900 ohms each. The response time is approximately one-tenth that of a conventional generator. A power change of 0.1 watt per field will produce an output change of 600 watts; this represents a power gain of 6,000. A 440-volt, 60-cycle, 3-phase, 5 h.p. induction motor drives the generator.

A cascaded voltage regulator tube system provides a well regulated reference voltage, stable over long periods. The reference potential is variable from 0 to 6 volts through a 10-turn, 200-ohm Helipot and is indicated on the reference potential meter, whose accuracy is 0.5 per cent. In order to make it possible to obtain a voltametric curve for a preliminary evaluation of the electrochemical behaviour of a new compound, the reference voltage potentiometer is connected to a synchronous motor which drives at a constant rate of 0.3 volt per minute.

Because certain oxidations require reference potentials which are less positive than a reference electrode, such as the standard calomel electrode, a "voltage-subtractor" circuit was included in the design of the reference voltage supply. By proper switching, these opposing potentials can be set on the reference voltage meter ( $M_1$ ) (Fig. II: 5) and is variable from 0 to 0.5 volt.

The stability and gain are taken care of by use of a balanced two-stage amplifier which consists of two 6AU6 ( $VT_3$ ,  $VT_4$ ) pentodes for the input stages and two 6L6 ( $VT_1$ ,  $VT_2$ ) for the output stages. The control fields of the amplidyne form the plate loads for the 6L6 tubes. The amplifier is balanced (balanced condition indicated by zero output) by means of a potentiometer ( $P_1$ ), in the plate circuit of the output tubes. This balanced condition is extremely critical, and in order to compensate for any drift that may occur during operation, a self-balancing circuit is incorporated. This connects the input of the amplifier to the output through a 10  $M\Omega$  resistor. Thus any unbalanced condition is transmitted through the closed loop in such a phase as to cancel. In the design of any d.c. amplifier the problem of coupling together stages that have a common plate supply is always present. It was found desirable to use a common plate supply and to couple the stages together without a reduction in gain. This was accomplished

# ORGANIC ELECTRODE PROCESSES

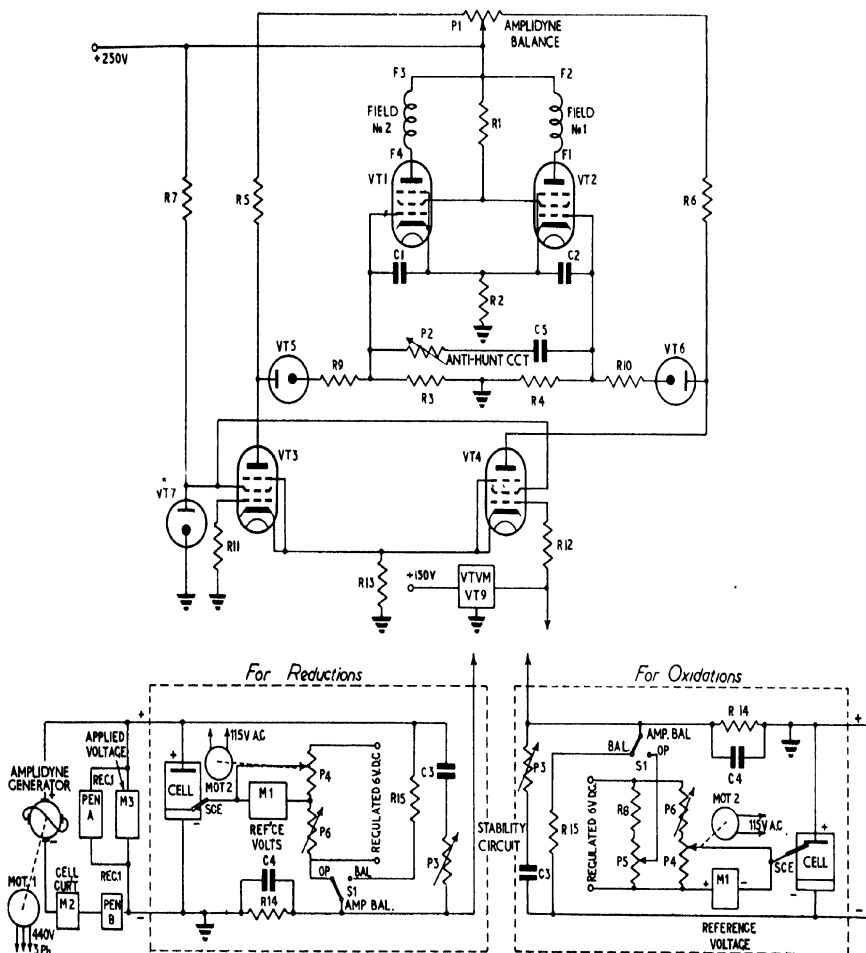


FIG. 11: 5. Schematic Circuit Diagram of Model III Redoxtrol.

# INSTRUMENTATION AND TECHNIQUES OF ELECTROLYSIS

## Components

<p>R<sub>1</sub> 1K, 25 W, W.W.                      R<sub>2</sub> 350 Ω, 25 W, W.W.                      R<sub>3</sub> .68 MΩ., ½ W, Comp.                      R<sub>4</sub> .68 MΩ., ½ W, Comp.                      R<sub>5</sub> 100 K, 1 W, Comp.                      R<sub>6</sub> 100 K, 1 W, Comp.                      R<sub>7</sub> 10 K, 5 W, W.W.                      R<sub>8</sub> 2.2 K, ½ W, Comp.                      R<sub>9</sub> 47 K, ½ W, Comp.                      R<sub>10</sub> 47 K, ½ W, Comp.                      R<sub>11</sub> .47 MΩ., ½ W, Comp.                      R<sub>12</sub> .1 MΩ., ½ W, Comp.                      R<sub>13</sub> 820 Ω, ½ W, Comp.                      R<sub>14</sub> .27 MΩ., ½ W, Comp.                      R<sub>15</sub> 10 MΩ., ½ W, Comp.                      P<sub>1</sub> 10 K, 4 W, 3 Turn                      P<sub>2</sub> 0.1 MΩ., 2 W, Comp.                      P<sub>3</sub> 1.0 MΩ., 2 W, Comp.                      P<sub>4</sub> 200 Ω, 4 W, 10 Turn                      P<sub>5</sub> 100 Ω, 4 W, 3 Turn                      P<sub>6</sub> 10 Ω, 4 W, 3 Turn                      S-1 SPDT</p>	<p>C<sub>1</sub>, C<sub>2</sub> .02 μf, 600 V d.c.                      C<sub>3</sub> 0.1 μf, 600 V d.c.                      C<sub>4</sub> 1.5 μf, 600 V d.c.                      C<sub>5</sub> 2.0 μf, 600 V d.c.                      VT<sub>1</sub>, VT<sub>2</sub> 6L6                      VT<sub>3</sub>, VT<sub>4</sub> 6AU6                      VT<sub>5</sub>, VT<sub>6</sub>, VT<sub>7</sub> OC3, VR-105                      VT<sub>9</sub> 6SC7                      M<sub>1</sub> 0-1.5, 3.0, 7.5 V d.c.                      M<sub>2</sub> 0-1, 10, 50 Amps.                      M<sub>3</sub> 0-30, 75, 150 V d.c.                      Rec. 2 Pen 100 MV Recorder.                          Same range as M<sub>2</sub> and M<sub>3</sub>                      Mot.1 5 H.P., 440 V, 60~, 3φ                      Gen.1 3 KW, 24 A, 125 V Ampli-                          dyne                      Mot. 2 115 V, 60~, 1φ Synch.                          Motor, 15 RP-HR., 3 W</p>
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### NOTES:

1. 440-Volt line was stepped down to 115 volts and stabilized with a constant voltage transformer.
2. A timer is provided to shut off all power at the end of a timed run.
3. One 250-volt, 200-mA power supply provides power for the VTVM and amplifier.
4. A separate VR tube supply provides the regulated reference voltage.
5. Separate switches are provided for selecting the applied voltage and cell current ranges.
6. A switch connects M<sub>1</sub> across P<sub>6</sub> for setting the voltage added and between P<sub>5</sub> (centre tap) and the + of the reference voltage for setting the voltage subtracted.
7. Fields of amplidyne are interchanged for oxidations
8. P<sub>6</sub> is always set to zero for oxidations

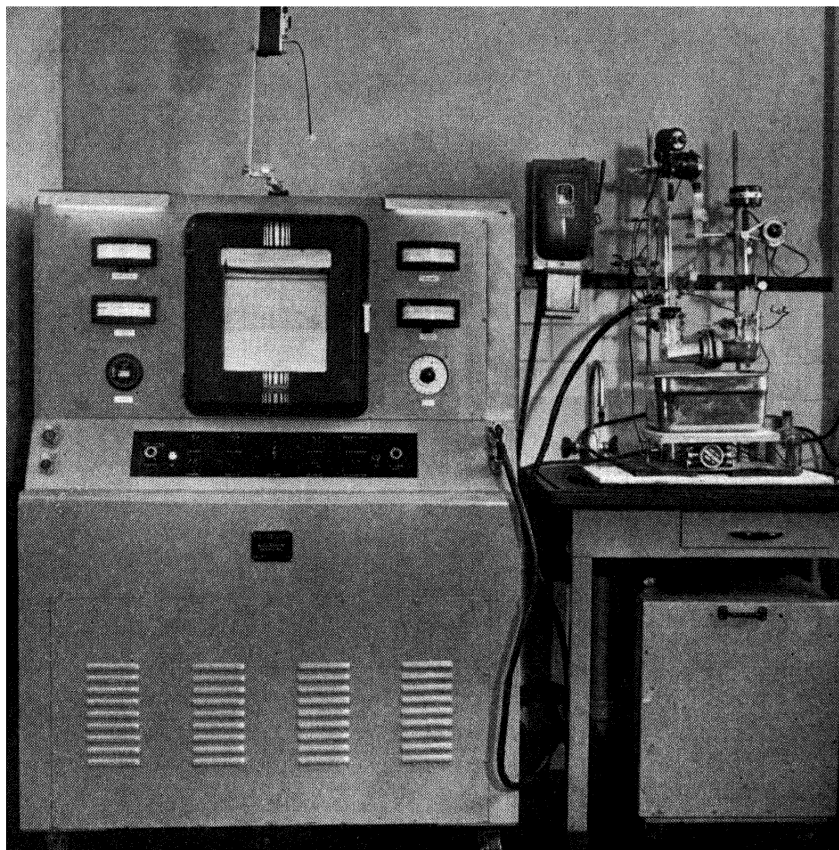
through the use of voltage regulator tube coupling VT5 (OC3) and VT6 (OC3). A single 250-volt plate supply is used. As stability is often difficult to achieve in a closed loop system, two stabilizing circuits have been incorporated into the design. The stability control (P3) is connected in series with a condenser (C3), the electrolysis cell, and the input resistor (R14) of the amplifier. The circuit eliminates very rapid changes which could cause instability in operation. To prevent hunting of the amplidyne an "anti-hunt" circuit comprising a resistor (P2) and a capacitor (C5) was connected between the two stages.

A gain of approximately  $1.5 \times 10^7$  is obtained from the amplifier. This, added to the gain of the amplidyne, gives an over-all system gain of  $9 \times 10^{10}$  which is sufficient to maintain the electrode potential within maximum limits of  $\pm 10$  millivolts over the entire voltage span.

The desired electrode potential is obtained by placing the standard reference electrode against the surface of the cathode for a reduction and the anode for an oxidation. The E.M.F. of the reference electrode is opposed by the reference potential developed across (P4). This reference potential is read on voltmeter (M1) as previously described. The off-balance between the E.M.F. of the standard reference electrode and the reference potential is developed across resistor (R14). This off-balance is referred to as the error signal, and is the input to the amplifier. When the error signal is zero the amplifier is balanced and the control fields of the amplidyne conduct equal and opposite currents, resulting in zero output from the amplidyne. An error signal will develop any time there is a difference between the electrode potential and the reference potential. The error signal is amplified and drives the control fields of the amplidyne in opposite directions. In turn, the control fields will cause the amplidyne to increase or decrease in output whichever is necessary to produce an electrode potential equal to the reference potential.

In addition, the instrument also incorporates a Leeds and Northrup two-pen Speedomax recorder which simultaneously plots cell current and applied voltage *v.* time. A one-tube (VT9-6SC7) vacuum tube voltmeter circuit monitors the error signal. The completed Redoxotrol Model III is shown in Fig. 11: 6.

An apparatus for automatic control of cathode potential published by Palmer and Vogel (5) is of interest, firstly, because all components are obtainable in Great Britain, and, secondly, it will deliver up to 10 amperes and 20 volts, making it suitable for many organic reductions.

FIG. II: 6. *Redoxotrol Model III.*

It appears that with very little modification this same instrument can also be used for electrolytic oxidations. The schematic drawing of their assembled apparatus is shown in Fig. II: 7.

The operation of the instrument depends on the detection of a d.c. "error-voltage" between the cathode and the standard reference electrode. The parts of the instrument include a d.c. output unit operating from the a.c. supply line which is used to supply the necessary current and voltage to the electrolysis cell; a motor driven "Variac" transformer to control the a.c. input to the d.c. output unit; a potenti-

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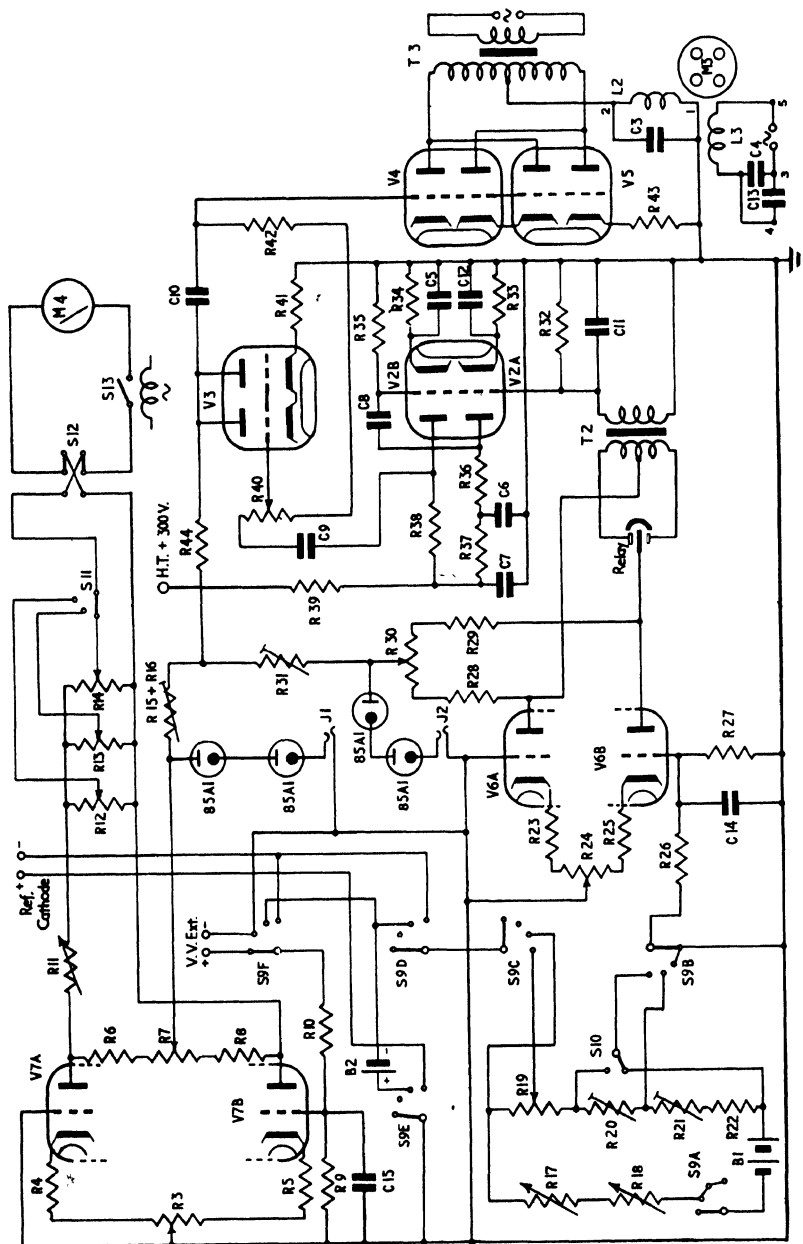


FIG. II:7. Schematic Circuit Diagram of Palmer-Vogel Apparatus.

meter that can be set to the desired potential drop between the cathode and the potential of the reference electrode; and an amplifier unit which operates at 1 millivolt d.c. and is connected to a reversible motor controlling the "Variac" transformer. The cathode reference potential is measured by a vacuum tube voltmeter. A voltage-stabilized power supply is also utilized to supply the necessary power for the amplifier unit and the vacuum tube voltmeter.

### (3) MEMBRANES

As there are a number of materials available which can be used as membranes to separate the catholyte from the anolyte, it is usually no great problem to find one suitable for the experimental conditions. The ideal membrane should have the following characteristics: firstly, it will offer little resistance to the passage of current; secondly, it will offer a maximum resistance to the passage of the depolarizer; thirdly, it will not clog during prolonged electrolysis; and, lastly, it will be able to withstand the medium and elevated temperatures, if necessary, required by the experiment. Unfortunately, the "ideal" membrane is not as yet available, but there are many suitable substitutes which the author has found satisfactory. These will be given together with a discussion of their limitations.

Cellophane sausage casing, which can be obtained in tube form, is very suitable for electrolysis when used in an aqueous acid or neutral medium. It can also be used with a 50 per cent methanol or ethanol medium. However, if the alcoholic concentration is increased beyond this, the membrane will deteriorate. This also occurs in a basic medium and at temperatures over 55° C. Regardless of these limitations, this type of membrane is extremely useful at times. In addition it has the advantage of offering little resistance to the passage of current and high resistance to the passage of the depolarizer. An added advantage is that it is probably the most inexpensive membrane material available, and therefore can be discarded after each use.

Another type of membrane material which is probably used to a greater degree than any other is some form of porous porcelain. The writer has found the most desirable to be "Alundum" (6). This can be obtained in various sizes and shapes. Of the number of mixes available, the RA 1143 mix has been found most satisfactory. Its advantages are that it can withstand almost any medium, at any temperature, and its resistance to the passage of an electric current is

quite low. Because it does not offer as great a resistance to the passage of the organic depolarizer as does cellophane, there is always danger of loss of organic material. For experimental purposes this is not a serious consequence, if electrolysis periods are not longer than eight hours. Beyond this there is a tendency for the membrane to clog, with a resultant increase in electrical resistance. These membranes are best cleaned by first washing well with water, or any other suitable solvent, then soaking overnight in a 50 per cent solution of nitric acid. This step can be accelerated by heating the medium to  $100^{\circ}\text{C}$ . and permitting the membrane to soak therein for one hour. After exposure to the nitric acid medium the membrane is washed exhaustively with water. Treatment of the membrane in this manner makes it possible to use it quite a number of times before it need be discarded.

Other materials which have been found as suitable as the porous porcelain type membrane are fine mesh sintered glass disks, and glass cloth. The former has the disadvantage of requiring a permanent mounting in the cell, and the latter, being nonrigid, requires a special type cell, as illustrated by Fig. 11: 13.

The membrane materials discussed previously are generally suitable for most purposes. Another type of membrane material is the "ion-exchange" resin membrane sold by one organization under the trade name of "Amberplex" (7). This membrane has the electrical conductivity of a 0.1 N potassium chloride solution and is extremely resistant to the diffusion of the organic depolarizer. Within the writer's experience no medium has been found which could not be used with this membrane. However, one disadvantage is that it cannot be used for electrolysis at temperatures over  $70^{\circ}\text{C}$ . This membrane shows its tremendous advantage under extremely difficult conditions. We may take as an example a situation in which the organic depolarizer requires a nonaqueous medium. In such an instance it would be necessary, if an "Alundum" membrane were used, to employ essentially the same type medium in the other compartment. This would naturally result in a relatively high resistance between the anode and cathode contributed to by the poor conductivity of the medium. Using an "ion-exchange resin" type membrane it is possible, due to the nature of the membrane material, to use an aqueous medium in the nonworking compartment. Thus a sterol can be dissolved in a mixture of ethylene dichloride and acetic acid with an acid such as sulphuric acid, and the whole placed either in the anode or

cathode compartment, depending on the type of reaction desired. In the other compartment can then be placed an aqueous solution of the electrolyte without concern to clogging of the membrane or appreciable diffusion of the aqueous solution, with resultant precipitation of the sterol.

The only prerequisite for using these membranes is that a new membrane must be properly prepared prior to its use, by soaking for at least two hours in the experimental medium. Thereafter it may be used any number of times with the same medium without removing it from its mounting in the cell. A cell designed for use with this as well as other types of non-rigid membranes will be illustrated in another section of this chapter.

There are occasions, of course, when a membrane is unnecessary. If, in an oxidation, the product formed is not readily reduced, a low overpotential cathode such as platinum may be used, and a membrane is thus of no consequence. Also, in reductions, wherein oxidation of the reduced product is not liable to oxidation, a low overpotential anode, such as iron or stainless steel, may be used. To further diminish the possibility of reaction at the non-working electrode this electrode should be of a considerably smaller area than the working electrode.

#### (4) ELECTROLYSIS CELLS

The cells used for electrolysis can be as varied as one's imagination will permit. There are a few general types which will be described merely to serve as a guide.

The simplest type can be constructed from a beaker. It will consist of an anode, cathode, membrane, a reference electrode if a controlled potential electrolysis is to be performed, and an agitator. A cooling bath is placed around the beaker to maintain the desired electrolysis temperature. Such a cell is schematically described in Fig. II: 8.

If a solid cathode is used it is not necessary to utilize a side-arm on the beaker. It is merely necessary to extend a length of the solid cathode material through the rubber stopper and make necessary wire contact in this manner. With the larger cells of this design, that is, over a 125 ml. capacity, it is preferable to use a paddle-type stirrer to obtain uniform agitation. The cell design illustrated in Fig. II: 9 has been found most suitable for quantities of 25 to 50 ml. This design can also be utilized for performing electrolysis at reflux temperature by merely inserting an additional side-arm to which is attached a reflux condenser.

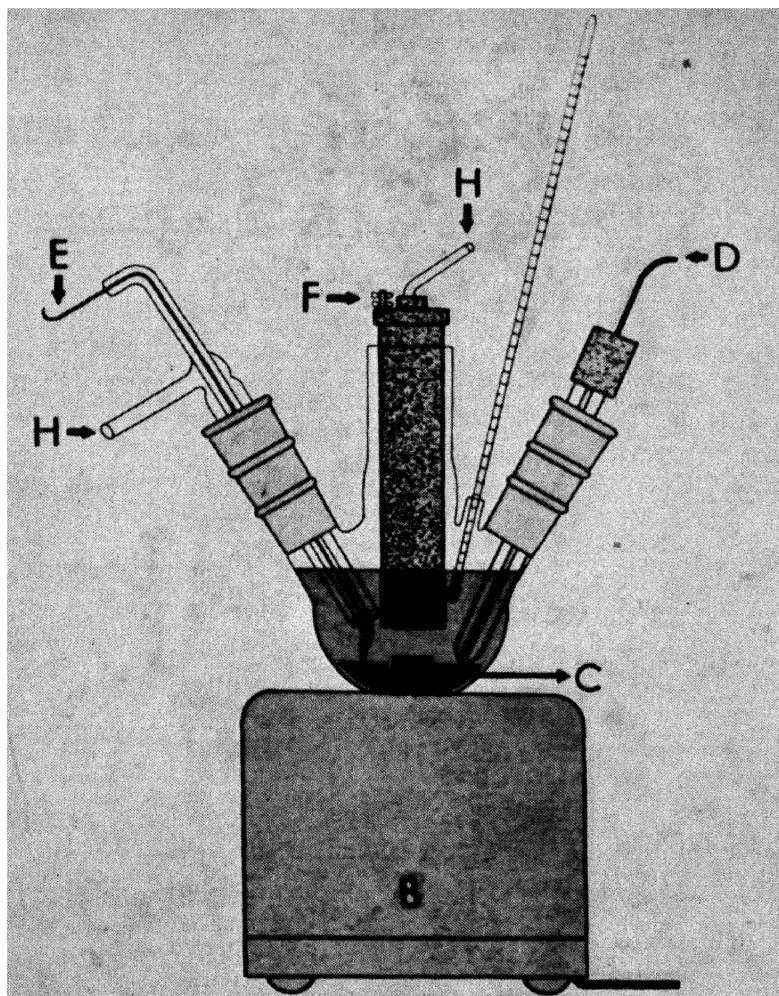


FIG. 11: 9. *Micro-Cell*. *B*. Magnetic stirrer; *C*. Cathode; *D*. Reference electrode; *E*. Cathode contact; *H*. Nitrogen gas (outlet not shown); *F*. Anode contact.

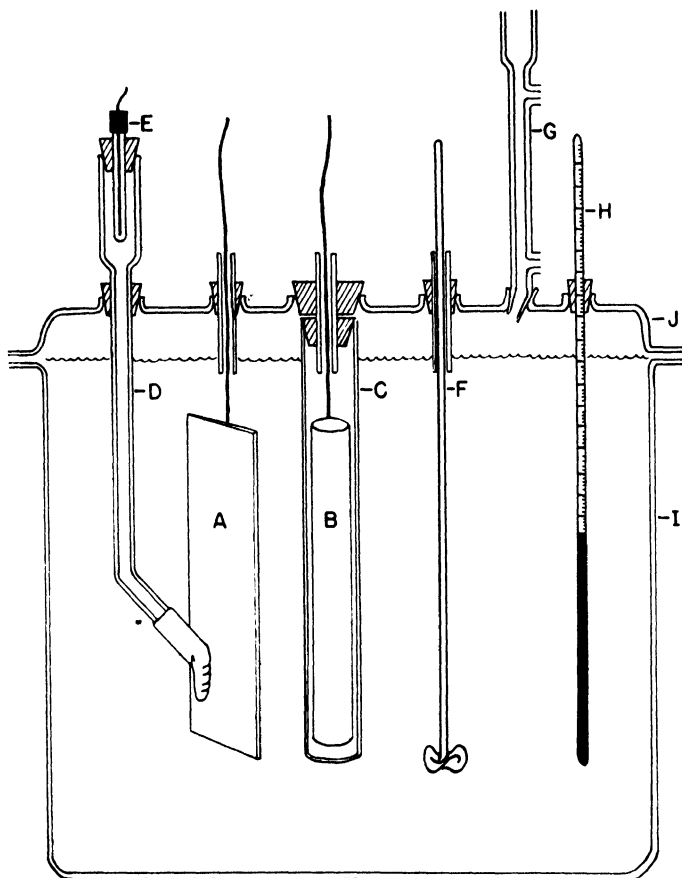


Fig. 11: 10. *Resin Flask Electrolysis Vessel*. *A*. Solid anode for oxidation, or solid cathode when cell used for reductions; *B*. Solid cathode for oxidations or solid anode for reductions; *C*. Alundum membrane; *D*. Salt bridge with fibre contact (see Fig. 11: 16); *E*. Reference electrode; *F*. Paddle stirrer; *G*. Condenser; *H*. Thermometer; *I*. Resin-flask; *J*. Cover, with multi-standard taper openings.

When this cell is used with a mercury cathode, *A* is eliminated and a tube similar to Fig. 11: 12-*J* is used to make electrical contact between cathode and power supply. The salt bridge *D* is replaced by the type described in Fig. 11: 12-*G* or Fig. 11: 16.

The cell illustrated in Fig. 11: 11 contains an internal cooling coil and is suitable for reactions in which considerable heat is generated.

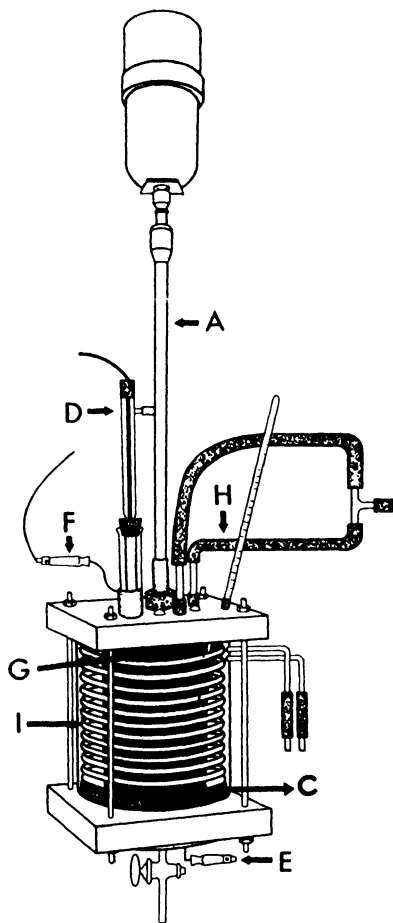


FIG. II: 11 *Internally Cooled Electrolysis Cell.* A. Paddle type stirrer; C. Cathode; D. Reference electrode; E. Cathode contact; F. Anode contact; G. anode (membrane surrounding anode is not shown); H. Nitrogen inlets; I. Cooling coil.

A cell designed to handle larger quantities of material, approximately 3.5 litres, is illustrated in Fig. II: 12. The capacity can be increased further by modification of the given dimensions. As illustrated, the cell is used for reductions with a mercury cathode, but this too can be modified so as to use other cathodes or anodes, if the larger chamber is to be used for oxidations.

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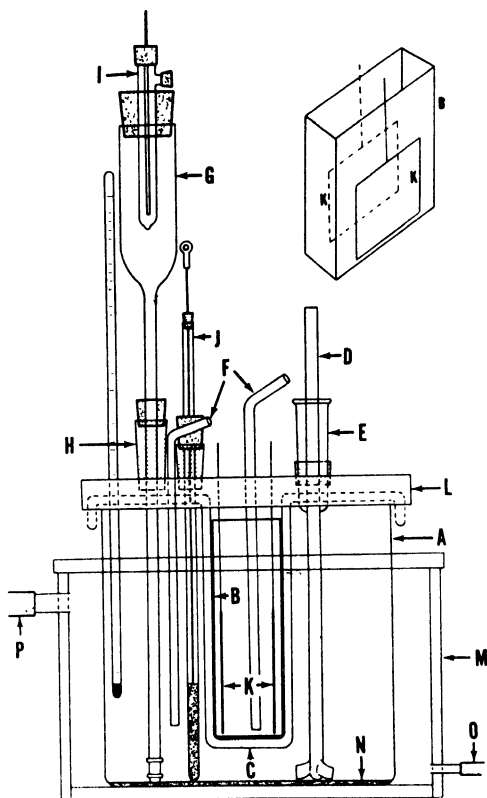


FIG. 11:12. *Large Scale Electrolysis Cell.* A. Glass container  $8\frac{1}{2}'$  i.d.  $\times$   $8\frac{3}{4}"$  high; B. Alundum membrane  $2"$  wide  $\times$   $6"$  long  $\times$   $6"$  deep,  $\frac{1}{8}"$  wall, mix RA 1143 (Norton Company); C. Membrane support  $\frac{1}{4}"$  diameter rod; D. Stirrer  $16"$  long  $\times$   $\frac{3}{8}"$  diameter; E. Mercury seal type bearing with  $\frac{1}{2}"$  joint; F. Nitrogen inlet tubes to cathode and anode chambers; G. Salt bridge, top portion  $2"$  diameter  $\times$   $4"$  high narrowing to  $\frac{1}{16}"$   $\times$   $12"$  long, at end of which is sealed a  $\frac{3}{8}"$  male joint,  $\frac{3}{8}"$  up from the bottom of this joint is a  $\frac{1}{16}"$  hole, over this is a female collar  $\frac{3}{8}"$  in length; H. Support for salt bridge,  $\frac{3}{8}"$  joint extended  $1.5"$ ; I. Reference electrode; J. Contact to mercury cathode, consisting of tube  $\frac{1}{16}"$  o.d.  $14"$  long, at bottom of which is sealed a piece of platinum wire. The tube is partly filled with mercury and connected to the negative side of power supply for reductions. This tube passes through a rubber stoppered  $\frac{3}{8}"$  joint; K. Platinum anode  $4" \times 4"$ ; L. Perspex cover; M. Cooling chamber  $11" \times 11" \times 7\frac{1}{4}"$  high o.d.  $\frac{1}{4}"$  thick Perspex; O. Water inlet to cooling chamber  $\frac{1}{4}"$  i.d.; P. Water outlets,  $\frac{1}{4}"$  i.d.; N. Cathode

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The type of cell illustrated in Fig. 11: 13 has been found satisfactory if an ion-exchange resin type membrane, or any other sheet type membrane, such as cellophane, to is be used. This type can be constructed of two elbows manufactured of Pyrex industrial pipe which is available in many diameters. The membrane is placed between two teflon or neoprene gaskets and held between the two ends of the pipe by the flanges. This cell can be immersed in a bath for cooling, or heated by wrapping with tape heaters.

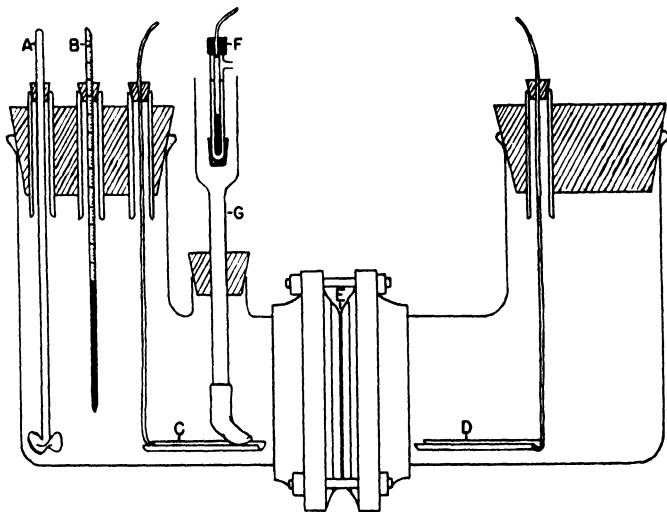


FIG. 11: 13. *Cell for Non-rigid Type Membranes.* A. Stirrer; B. Thermometer; C. Working electrode; D. Non-working electrode; E. Gasketed membrane; F. Reference electrode; G. Salt bridge of the type illustrated by Fig. 11: 16.

Although the cells previously described are constructed of glass, it is not meant that the electrolysis cells cannot be constructed of other materials. In fact, any rigid material can be used, so long as it does not react with the electrolysis medium, or serve as an electrical conductor. Thus, cells can be constructed of glass-lined or resin-coated steel, hard rubber, polyethylene, etc. As mentioned, it is not usually desirable to construct the cell of a conductor. However, on occasion this may have a distinct advantage. For example, if a cathodic process required a lead cathode, it might be advantageous to have the electrolysis cell constructed of this same material, which would result in the availability of a greater electrode area.

In general, the cooling coils should be constructed of a chemically and electrically inert material, such as glass. Here too, it may be possible to have the electrodes serve a dual purpose. Thus an oxidation performed at a platinum anode can utilize a platinum-plated coil, through which water is passed for cooling the anode chamber. In the cathode chamber one can use a stainless steel coil for the dual purpose of cathode and cooling coil. Of course, in such a system one must be extremely careful that the conductivity of the coolant is considerably lower than that of the electrolysis medium, otherwise the usual consequence of a short circuit will result. In general practice, however, it is usually possible to cool at least the external chamber with a cooling bath or coil and, therefore, it would only be necessary to use a cooling-coil-electrode in the internal chamber if it were isolated from the cooling bath itself, as in cells illustrated in Figs. II: 8-12.

#### (5) ELECTRODE MATERIALS

Many of the metals generally used for electrodes require no extensive purification prior to use, as they are readily available in pure form. However, after being used once, they require some form of cleaning.

Mercury, reagent grade, can be used directly for the electrolytic reaction. If a batch process is in progress it is generally not necessary to change the electrode for each electrolysis. However, in the laboratory, where the same cell may be used for various types of electrolysis, it is necessary to use fresh mercury for each procedure. In our laboratories the mercury is purified in the following manner: A suction flask is filled to approximately one-third its height with the contaminated mercury. The surface scum is removed by allowing water to flow through the top of the flask for half an hour. The water is decanted and to the flask is added a 20 per cent solution of nitric acid in water, equivalent in volume to the mercury. The flask is closed with a rubber stopper through which is passed a 1 mm. bore capillary tube, which extends to the bottom of the flask. The side-arm of the flask is connected to a vacuum line and air is pulled through the capillary for approximately twelve hours. At the termination of this period, the supernatant liquid is decanted from the mercury, the mercury is washed well with distilled water, and then filtered through a mercury filter of the type based on the gold adhesion principle (8). Use of this method results in a product of exceptional purity.

Lead, although essentially quite pure, has a surface layer of grease

and other contaminants which must be removed prior to use. After the lead is washed well with a suitable grease solvent, it is placed centrally in a beaker, the internal periphery of which is coated with aluminium foil. The positive lead from a d.c. power supply is connected to the lead electrode and the negative lead to the aluminium electrode. Using a medium consisting of a 20 per cent solution of sulphuric acid, the lead electrode is subjected to anodic electrolysis for ten minutes at a current density of  $0.02 \text{ amp./cm.}^2$ . The leads are then reversed and the electrolysis continued for an additional ten minutes. Finally the leads are reversed a second time, and after a ten-minute electrolysis, the lead electrode is removed, washed well with distilled water, hot ethanol and air dried (9). Prior to use as a cathode the lead electrode is subjected to a ten minute pre-electrolysis in the experimental background medium. If a number of experiments are to be performed with essentially the same medium, it is not usually necessary to repurify the electrode prior to use, providing of course that the electrode is kept dry and protected from air. In instances in which an oxidation process requires a lead oxide anode, the treated lead electrode need not be further subjected to pre-electrolysis as an anode.

Generally, other electrode materials such as copper, cadmium, platinum, tin, zinc, and nickel require only a degreasing and pre-electrolysis in the medium to be used for the electrolytic experiment. At all times, the metals obtained for electrolytic studies should be of the purest quality available. In addition to the use of sheet stock for solid electrodes, one may find it desirable to use gauze electrodes in order to increase the electrode area within a given space. This effect can also be achieved to a lesser extent by pleating the solid electrode.

In addition to the solid electrodes, it might on occasion be desirable to plate the desired metal on a sheet of the same metal, or another metal, to obtain an exceptionally pure electrode surface. Plated electrodes such as platinum black on copper (10), lead on lead, lead on copper, and copper on copper have been used for electrolytic processes (11).

There is in many instances a need for alloy electrodes, either from the point of view of obtaining a catalytic plus a high overpotential effect, or simply for obtaining a physically workable electrode. Thus a vertical electrode of the high overpotential characteristics of mercury can be obtained by the amalgamation of lead with mercury. This is accomplished by using a lead sheet as the supporting material and coating with mercury, by either allowing the lead to stand in a solution

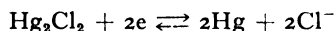
of mercuric chloride (12), or by simply rubbing mercury on the lead surface (13). Amalgamated nickel and zinc have also been prepared by allowing sheets of these metals to be exposed to a solution of mercuric chloride (14). Other alloy electrodes such as phosphor bronze and Monel metal have also been used as electrodes (15).

Platinum, lead oxide, iron, and nickel have been used as anodes for electrolytic oxidation. Platinum, because of its inertness, permits one to obtain graded potentials. However, caution must be observed in using this electrode in a halogen medium, as there is some attack on the metal. This can be overcome by using a platinum electrode containing a small amount of iridium. Iron and nickel should only be used as anodes when the electrolysis is performed in an alkaline medium.

## (6) REFERENCE ELECTRODES

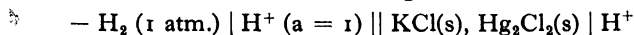
In general, any half-cell of known constant value can be used as a reference electrode. However, the prime prerequisite of such an electrode is that its potential shall not be altered to any significant degree by the passage of small currents, as would be the case even were a high-resistance voltmeter to be used to measure the potential between the working electrode and the reference electrode. Thus the only satisfactory reference electrodes are essentially the saturated calomel half-cell and the silver-silver chloride half-cell. These electrodes are easily prepared and their potentials remain constant almost indefinitely.

The saturated calomel electrode is probably the more commonly used electrode, of the two mentioned. It consists of a solution that is saturated with respect to both potassium chloride as well as mercurous chloride. This is in direct contact with a mercury pool, resulting in the reaction:



The chloride ion activity is constant at a given temperature due to the presence of an excess of potassium chloride. Since there also is present an excess of mercurous chloride, the mercurous ion (which is responsible for the potential of the cell) is also kept constant. Therefore passage of small currents in either direction does not affect the half-cell potential.

The potential of the saturated calomel electrode (S.C.E.) by definition is the E.M.F. of the following cell:



which is expressed as:

$$E = + 0.242 - 7.6 \times 10^{-4} (t - 25)$$

Thus at  $25^{\circ}$  C. the saturated calomel electrode has a potential of  $+0.242$  volt *v.* the normal hydrogen electrode (N.H.E.). It will be noted from the equation that this electrode has a large temperature coefficient. In most electrolytic processes, a precision of  $\pm 10$  millivolt is sufficient, thus this is of no consequence.

A number of instrument manufacturers can supply saturated calomel electrodes of various designs. As most of these usually have a high resistance they can only be used with a vacuum tube voltmeter type measuring circuit. When this type electrode is not available, a saturated calomel electrode of the type seen in Fig. 11: 14 can be constructed.

The bottom of the vessel is filled to approximately 3 mm. with mercury, over which is placed an equivalent amount of mercurous chloride and potassium chloride. The vessel is then filled with saturated potassium chloride. Electrical connection is made through a platinum wire sealed in a glass tube and extending through the stopper used to seal the vessel. Contact between the calomel cell and the working electrode is made by placing a rubber "policeman" on the end of the side-arm tube, through the bottom of which has been threaded a number of asbestos fibres. The resistance of this electrode is quite low and, therefore, a high resistance voltmeter can be used to measure the potential between the reference electrode and the working electrode.

The silver-silver chloride electrode can also be used as a reference electrode. The potential of this electrode is  $+0.197$  volt *v.* N.H.E. or  $-0.045$  volt *v.* S.C.E. This electrode can also be purchased from

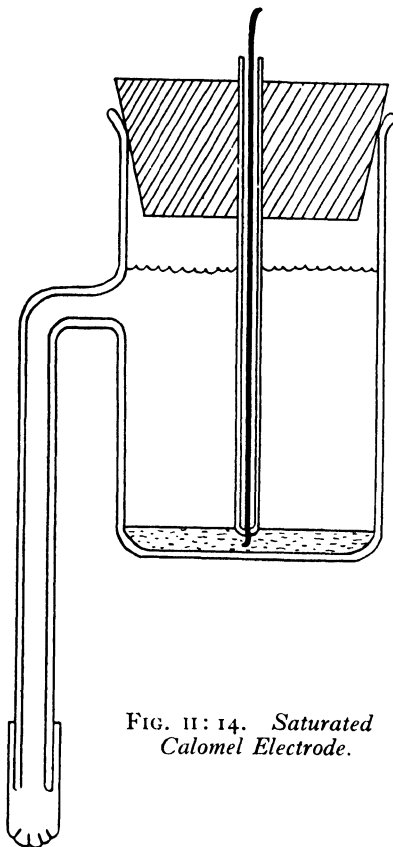


FIG. 11: 14. *Saturated Calomel Electrode.*

various manufacturers, or can be constructed as shown in Fig. II: 15, from a glass tube, one end of which is sealed by a rubber "policeman," pierced in a number of places at the tip, with asbestos fibres, as illustrated in the fabrication of the calomel electrode. The tube is then filled with a solution saturated with respect to both silver chloride and potassium chloride. Through the rubber stoppered closure is passed a silver wire.

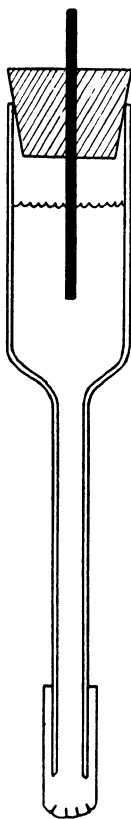


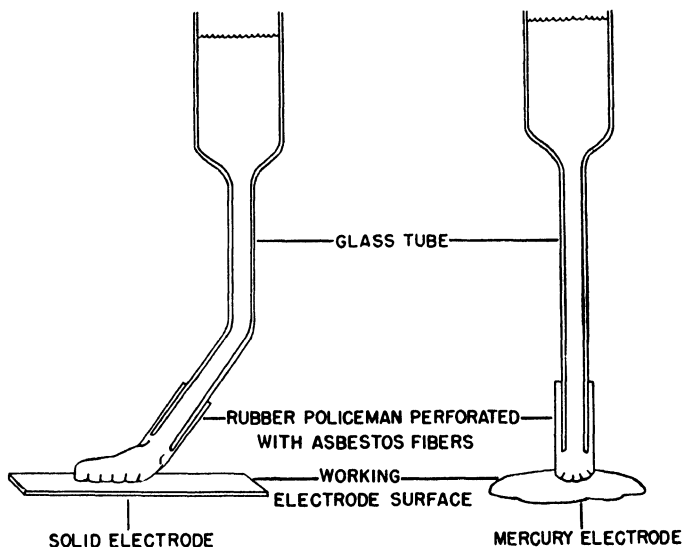
FIG. II: 15.  
Silver-Silver Chloride Electrode.

In measuring the true potential of the working electrode with respect to the reference electrode, we are confronted with the unavoidable difficulty of an  $IR$  drop between the tip of the reference electrode and the surface of the working electrode. Therefore what is observed is related to the true potential by the equation:

$$E_{\text{obs.}} = E_{\text{actual}} + IR$$

Thus in reductions we appear to work at potentials more negative and in oxidations more positive than the actual potentials at the working electrodes. This in no way interferes with obtaining the desired results, except in so far as it has a small effect on the efficiency of the reaction. Since in organic electrolytic processes an actual 100 per cent efficiency is generally not attainable, this slight effect is of no consequence.

In order to minimize this  $IR$  drop the contact point on the reference electrode should be as close to the electrode surface as possible. This is extremely important when working with nonaqueous or partially aqueous systems. With a mercury cathode there is no great problem with the reference electrodes described, except in cases wherein a salt bridge is necessary, due to the height of the electrolysis vessel. With mercury it is possible to obtain satisfactory contact with the sleeve type salt bridge (Fig. II: 12). However, with solid electrodes it is extremely difficult to obtain good contact between the solid surface of the commercially available reference electrode and the working electrode. For this reason the salt bridges illustrated in Fig. II: 16 have proved most suitable.

FIG. 11:16. *Salt Bridges.*

The multi-perforated rubber "policeman" offers the advantage of flexibility and softness, which makes it possible, by exertion of the proper amount of pressure, to achieve good contact with the working electrode. With solid electrodes it is possible to minimize the  $IR$  drop still further by placing the reference electrode in the region of minimal current flux. Thus, if the anode were opposite to the cathode, and the reference electrode contact made on the reverse side of the working electrode, it would be outside the region of high potential gradient.

### GENERAL TECHNIQUE

It is extremely difficult to set forth a general technique which will enable one to obtain the desired results immediately. Usually, from a knowledge of the substance one wishes to oxidize or reduce, it is possible to develop the proper electrolysis medium. It is always most desirable to have the depolarizer in solution. This enables attainment of maximum efficiency. The next step is to obtain an insight into the reactivity of the oxidizable or reducible groups in the molecule. This can be accomplished by obtaining a voltametric curve (Fig. 1:1), or a polarogram when possible, either at a dropping mercury cathode or a

rotating platinum anode (16). With the knowledge gained from these curves it is possible to decide on the potential and/or the electrode material to be used. If the oxidation or reduction goes in a stepwise manner it will be necessary to investigate various potentials and the products obtained at each, until the proper conditions which will yield the desired results are found.

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## CATHODIC REDUCTION

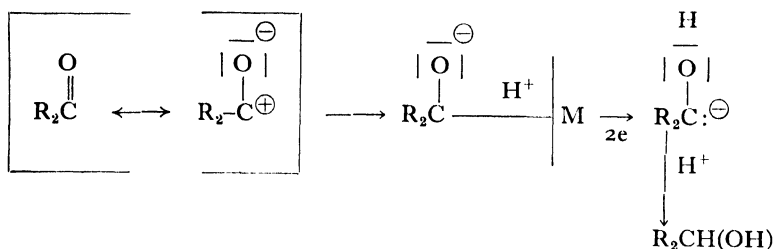
### (1) MECHANISM OF CATHODIC REDUCTION

As previously mentioned, Fritz Haber pointed out that it was the cathodic potential which was probably the most important factor in determining the outcome of an electrolysis. Quite often it is possible, by maintaining constant conditions, i.e. electrode material, medium, and temperature, to obtain different products by merely varying the electrode potential.

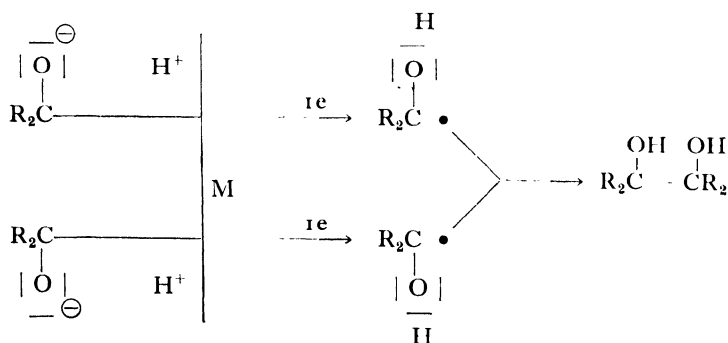
A number of theories have been proposed to describe the potential acquired by the electrode. The most widely accepted one states that the higher the cathode potential, the higher the potential energy of the hydrogen atoms liberated at the electrode surface. Therefore, for a given electrode, it is possible to obtain different energies for the discharge hydrogen atoms by merely changing the cathodic potential. Generally, then, the reduction efficiency of a cathode depends on the cathode potential. The higher the potential, the higher the efficiency. Thus it would be expected that a ketone or aldehyde would be reduced to the hydrol at a lower cathodic potential than that required to induce free-radical formation, with subsequent bimolecular reduction to the pinacol (1), or as has been amply demonstrated by Haber and others (2, 3), nitrobenzene can be reduced in a stepwise manner by merely changing the cathodic potential at which the reaction was being performed.

Another way of looking at the situation is to take advantage of the experimental results of Eyring, *et al.* (4), in which it was demonstrated that a low overpotential metal forms a strong metal-hydrogen bond, and a high overpotential metal forms a relatively weak metal-hydrogen bond. We may extend this idea to protons in general. Thus the reduction of a ketone to the hydrol, at a mercury cathode and at a relatively low potential, would proceed as follows:

## ORGANIC ELECTRODE PROCESSES



The charged mesomeric form is attracted to the cathode, where the oxygen atom, which has a pair of unshared electrons, accepts a hydrogen atom as indicated. Simultaneously, at the relatively lower cathodic potential, because of the strength of the metal-proton bond, the charged molecule is held at the cathode a sufficient length of time to undergo a two-electron change, with resultant hydrol formation. At the higher cathodic potential we have the following:

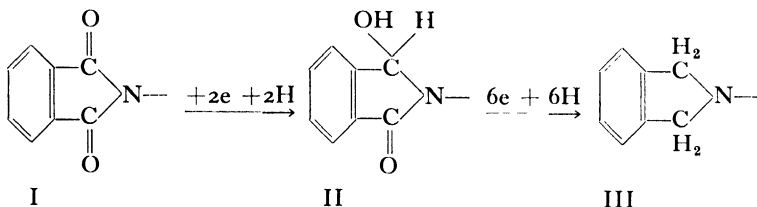


wherein the charged form, because of the weak metal-proton bond, remains only long enough for a one-electron transfer to the electron deficient carbon, with the resultant formation of a highly reactive free radical, which combines with another to form the pinacol (5). This free radical mechanism is further substantiated by the fact that mixed pinacols can be obtained by the electrolytic reduction at a mercury cathode, of a mixture of *p*-dimethylaminoacetophenone and *p*-methoxyacetophenone (5).

The first theory involving the potential energy of the hydrogen liberated, does not adequately explain the reactivities of organic compounds. The reactivity of the charged form with the electrode appears to fill in the picture to the point where it is possible to visualize so-called free-radical formation.

## CATHODIC REDUCTION

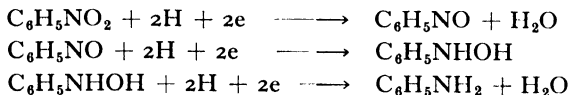
We might also rationalize elimination of a hydroxyl group as being a replacement reaction, similar in nature to an electrolytic dehalogenation. It has been found that phthalimides (I) in an acidic dehalogen undergo a two-electron change to the respective hydrol (II) at a lower cathodic potential than that required for complete reduction to the isoindoline (III), thus:



If the hydrol (II), or the phthalimide (I), is reduced at the higher potential the isoindoline (III) is obtained (7). An interesting observation that has been made is that the potential required for formation of the isoindoline is essentially the same as that required for the partially reduced phthalimidine. The latter can be isolated in good yield if the electrolysis is interrupted before completion. This would tend to indicate that the reduction of the first carbonyl group may possibly be the rate-determining step in the reduction of the phthalimide to the isoindoline.

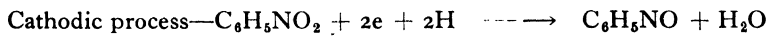
### (2) REDUCTION OF NITRO COMPOUNDS

Nitro compounds have been studied quite extensively, and therefore there is probably more information available on the electrochemical reactivity of these compounds than on other types. Haber and others (2, 3), in their experiments on the reduction of nitrobenzene, found that this compound, in an acidic or basic medium, is first reduced to nitrobenzene, then to phenylhydroxylamine, and finally to aniline, depending on the electrode potential used in the experiment:

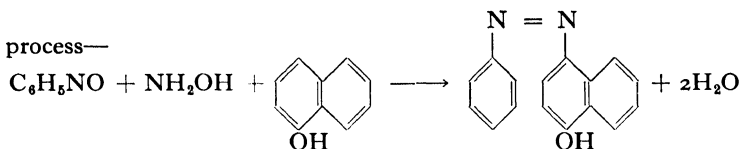


As the electrode potential for the reduction of nitrosobenzene in an alkaline medium is  $-0.48$  volt, it is a far better depolarizer than nitrobenzene, which requires an electrode potential of  $-0.78$  volt to initiate the cathodic process. Thus the consequence in the overall scheme is

that the nitrosobenzene is rapidly reduced to the phenylhydroxylamine, and thence to aniline and/or other side reaction products, depending on the experimental conditions. Haber verified the formation of nitrosobenzene as an intermediate by performing a reduction on nitrobenzene in an alcoholic-alkaline medium, at an electrode potential of  $-0.98$  volt, in the presence of  $\alpha$ -naphthol and hydroxylamine. As a result, as soon as the nitrosoamine formed it reacted to give the azo dye, 4-(phenyl-azo)-1-naphthol:

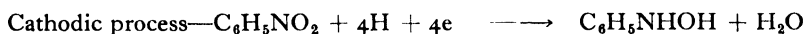


Chemical process—



The formation of nitrosobenzene in an acidic medium was verified by performing the electrolysis in the presence of  $\alpha$ -naphthylamine and hydroxylamine, which resulted in the formation of 4-(phenyl-azo)-1-naphthylamine.

Although nitrosobenzene is a good depolarizer and is easily reduced, it can be obtained with satisfactory yields by performing the electrolysis in a cell without a membrane, using a magnesium sulphate medium, with a nickel cathode and a lead anode (8). The phenylhydroxylamine, as formed at the cathode, is oxidized to nitrosobenzene at the anode, thus:

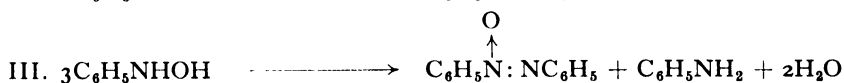
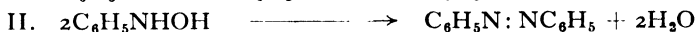
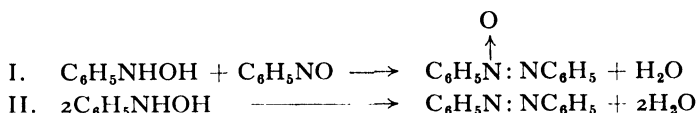


The presence of the intermediate, phenylhydroxylamine, in the reduction of nitrobenzene, was proved by reduction of the nitrobenzene at a platinum cathode, in an alcoholic ammonium hydroxide solution containing sufficient ammonium chloride to increase the conductivity. In addition to the above major product, a smaller quantity of azoxybenzene is also obtained (2). The formation of phenylhydroxylamine as an intermediate in an acid medium, was substantiated by Gatterman (9), who reduced a mixture of nitrobenzene and benzaldehyde in a concentrated sulphuric or acetic acid medium, and obtained benzylidenehydroxylamine in the following manner:

CATHODIC REDUCTION



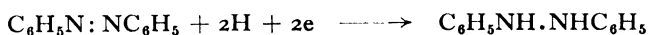
The side reactions, which may take place between the intermediates obtained as a result of the electrolytic reduction of nitrobenzene, have been investigated by Bamberger and his associates (10). They found that the following three processes, that is the formation of azoxybenzene (I), azobenzene (II) and a mixture of azoxybenzene and aniline (III), occur predominantly in an alkaline medium, and also, to a very much smaller extent, in an acid or neutral solution.



The above are given in their respective rate orders, with the first being the fastest.

To obtain the maximum amount of the azoxybenzene (I) the reaction should be carried out in a slightly basic medium, and the electrode potential controlled so that this compound cannot be further reduced (2). Another way in which this can be accomplished is to use a suspension of the nitrobenzene in a dilute aqueous alkaline solution, with a low overpotential electrode, such as nickel. The nitrobenzene is a better depolarizer than the azoxybenzene, and therefore, if the temperature is not high, the azoxy-compound will precipitate out as it is formed, and will not be further reduced.

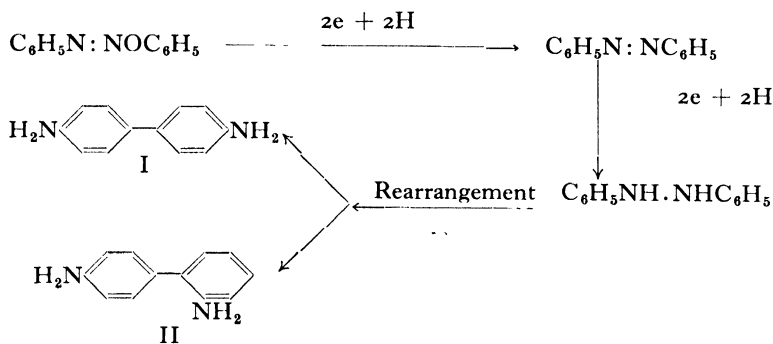
If the alkalinity of the medium is not kept low and the potential is permitted to approach a high value, one will obtain the hydrazo compound, thus:



To obtain the best yields of the hydrazobenzene, this reaction should be performed in a basic aqueous-alcohol solution at an elevated temperature with a lead, tin, or zinc cathode. To prepare the hydrazobenzene from nitrobenzene directly it is necessary to carry out the reaction in two stages. In the first stage a suspension of the nitrobenzene is

electrolysed in a dilute alkaline solution, using an iron-gauze cathode and moderate temperatures. As soon as the nitrobenzene has been reduced, a high overpotential cathode is inserted and the temperature increased; thereupon further reduction will occur (11). Utilization of more drastic conditions initially would, of course, have resulted primarily in the formation of aniline.

Benzidine (I), which is quite important to the dye industry, can be prepared by reduction of azoxy- or azo-benzene in a weakly acidic medium, to the hydrazobenzene, with subsequent rearrangement according to the following scheme:



If the rearrangement of hydrazobenzene is performed at temperatures of 20 to 30° C., only small quantities of the biphenyl (II) will be obtained (12).

The ease with which the hydroxylamine is reduced to aniline depends on the cathode potential. If a high overpotential metal, such as mercury, lead, or zinc, is used in an acidic or basic medium, then aniline is obtained as the main product. It is reduced so rapidly that it does not have much opportunity to undergo any side reactions.

Aminophenols, a side reaction product, can generally be obtained by the reduction of a nitrobenzene in a sulphuric acid medium at a low overpotential electrode, such as platinum (13). Thus, nitrobenzene is reduced to phenylhydroxylamine, and then rearranged:



Of course, if this same reduction were carried out with a high overpotential electrode, the phenylhydroxylamine would not exist as such

## CATHODIC REDUCTION

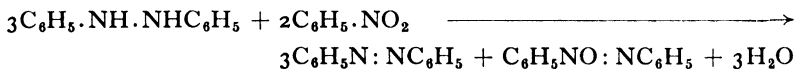
in the medium for a sufficient period to undergo rearrangement to the amino phenol. Were a hydrochloric acid medium to be used instead of the sulphuric acid, a mixture of ortho and parachloroanilines would be obtained, probably with a chloroamine as the intermediate (14).



When ethanol is used in the sulphuric acid electrolyte, the *p*-aminophenol is esterified to yield *p*-phenetidine ( $\text{NH}_2\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$ ). The aminophenol can be simultaneously sulphonated if the nitrobenzene is reduced in a fuming sulphuric acid medium, with the resultant formation of 2-hydroxy-5-amino benzenesulphonic acid (15). If the para position of the nitrobenzene is occupied by a  $-\text{Cl}$  or  $-\text{COOH}$  it is replaced by an  $-\text{OH}$  to yield *p*-aminophenol; if there is an  $-\text{OH}$  or  $-\text{NH}_2$  in the para position the nitro group undergoes the usual reductive changes without any rearrangement (16). Nitrobenzenes containing  $-\text{N}(\text{CH}_3)_2$ ,  $-\text{COCH}_3$ ,  $-\text{OCH}_3$ , or  $-\text{CH}_3$  in the ortho position, when reduced to the respective hydroxylamine, rearrange so rapidly to the *p*-aminophenol, or a derivative, in a concentrated acid medium, that even the use of a high overpotential electrode does not interfere (17).

Of course, it is possible to obtain the phenyl hydroxylamine without the risk of rearrangement by utilizing a low overpotential electrode such as platinum, and a medium close to neutral, preferably buffered with either ammonium chloride-ammonia or sodium acetate-acetic acid (2). This latter condition is obviously necessary, as the electrolyte in the vicinity of the electrode becomes more acidic due to the liberation of hydrogen ions at the cathode, and would result in the formation of *p*-aminophenol.

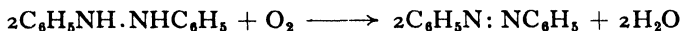
Azobenzene can be obtained in good yield by performing the electrolysis on an alkaline-alcoholic solution containing a high concentration of hydrazobenzene and nitrobenzene. This reaction requires a low overpotential electrode and reflux temperature (18):



The azobenzene and azoxybenzene formed can only be reduced to hydrazobenzene when using a high overpotential electrode, and preferably with the aid of added catalysts.

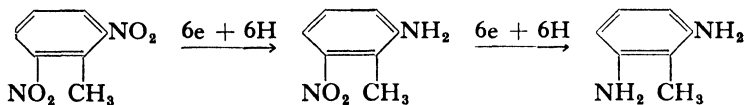
As hydrazobenzene is very susceptible to air oxidation, azobenzene

is readily obtained by passing a stream of oxygen through a solution of the above-mentioned compound (19):



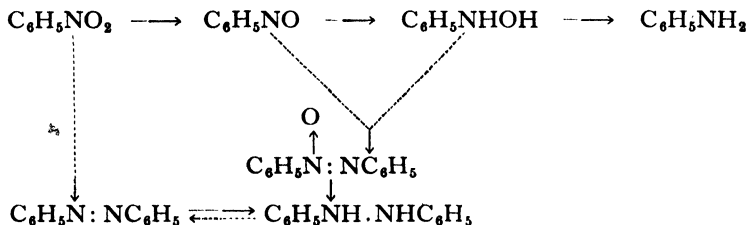
Substituted nitro compounds generally undergo the same type of reduction as the unsubstituted compounds. However, there are instances where other types of reactions will take place. For example, when a methyl group is in the meta position, the respective nitroso- and hydroxylamine derivatives react chemically in a basic medium to give the azoxy-compound. When the methyl group is ortho or para, the hydroxylamine and nitroso do not readily react, and as a result, the reduction continues on to the amine (20). One finds very similar characteristics amongst other derivatives, such as *m*-nitrophenol and *m*-nitroaniline. The nitrophenol and nitroaniline will yield, on reduction, the azoxy compounds; whereas the *ortho* and *para* substituted compound will give the amine (21).

A number of poly-nitro compounds have been reduced electrolytically to the expected products (22). Thus, 1,5-dinitronaphthalene yields the 1,5-naphthalene-diamine when the reduction is performed in a sulphuric acid medium at a lead cathode (23). In a similar manner 2,6-dinitrotoluene is first reduced to 2-amino-6-nitrotoluene, and finally to 2,6-diaminotoluene.



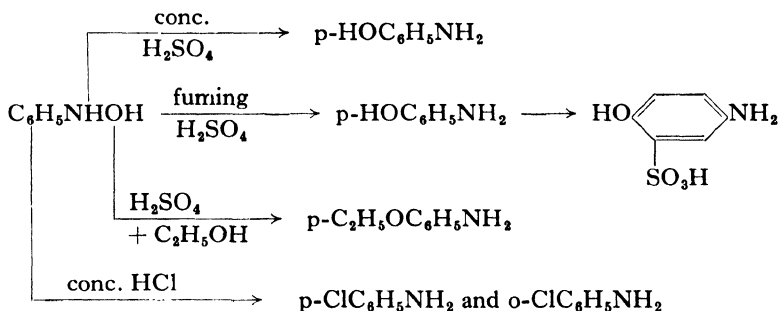
However, it must be remembered that the presence of more than one nitro group may lead to complex mixtures.

From the previous discussions we can present the following reactions obtained by direct electrolytic reduction, as represented by continuous lines, and the secondary chemical reactions, as represented by dotted lines:

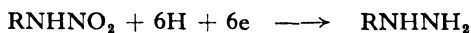
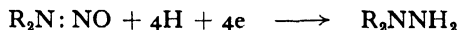


## CATHODIC REDUCTION

In addition, the following chemical transformations occur in an acidic medium:



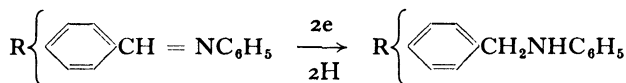
The electrolytic reduction of aliphatic nitro compounds has not been investigated as extensively as those previously discussed. Generally they are first reduced to the hydroxylamine, and then to the amine. Pierron (25) found that nitromethane was reduced to methylhydroxylamine, using a nickel cathode, a medium consisting of a 10 to 15 per cent solution of sulphuric acid in alcohol, and a temperature of 20° C. Using a higher temperature, he was able to cause the reduction to go to the amine. In a strongly acidic medium the nitromethane was reduced to the formaldehyde oxime [CH<sub>2</sub>:NOH], which hydrolysed to hydroxylamine and formaldehyde. He also found that under the conditions described above, nitroethane could be reduced to ethylhydroxylamine, and nitropropane to propylhydroxylamine. When chloropicrin [CCl<sub>3</sub>.NO<sub>2</sub>] was reduced in a weakly acidic medium at a platinum cathode the dechlorinated methylhydroxylamine was obtained. If a lead cathode was used the reaction yielded methylamine (26). When nitrosamines or nitramines are reduced in a dilute acid medium, hydrazines are obtained (27).



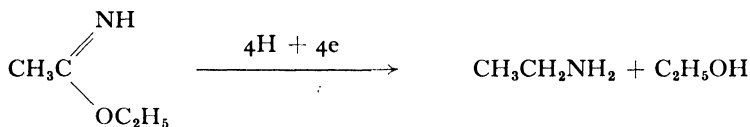
### (3) REDUCTION OF IMINES AND IMIDIC ESTERS

Imines and Imidic esters can readily be reduced to their respective amines in either an acidic or basic medium, using a relatively high cathode potential metal, such as lead or mercury. Law (28) reported on the reduction of a number of substituted benzalanilines to their respective benzylanilines, thus:

ORGANIC ELECTRODE PROCESSES



Imidic esters, such as ethyl acetimidate, have been reduced to ethylamine, using a 2N sulphuric acid medium and maintaining the temperature at 0° C. (29):



This same worker also accomplished the reduction of some substituted ethyl benzimidates to their respective amines with satisfactory yields being obtained.

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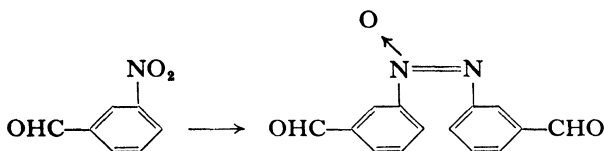
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## CATHODIC REDUCTION

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## CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS

THE electrochemical reactivity of the carbonyl group which is common to aldehydes, ketones, acids, esters, amides, and imides, has been investigated almost as extensively as the nitro group. That this group is not as easily reduced as the nitro group is demonstrated by the fact that *m*-nitrobenzaldehyde can be reduced to azoxybenzaldehyde in an alcoholic-sulphuric acid medium, at a copper cathode, without disturbing the aldehyde portion of the molecule (1).



Generally the cathodic reduction of the carbonyl group requires a relatively high overpotential, such as that obtained with a mercury or lead electrode. However, depending on the type of reduction desired, it may be necessary, at times, to depend on a catalytic electrode which will yield a more highly reduced form, even though the overpotential of the electrode is lower than that of mercury or lead.

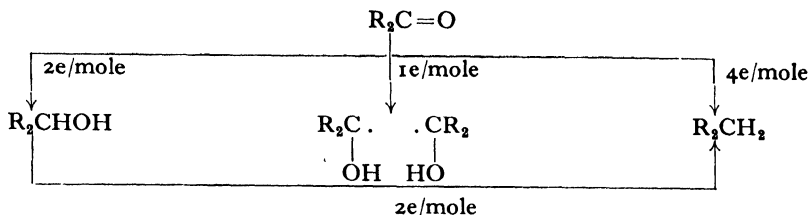
The mechanism as proposed for the reduction of aldehydes and ketones (p. 47) may very well apply to other carbonyl compounds. The formation of dimers is not too common in types other than aldehydes and ketones, possibly because the energy required for the formation of the free radical is beyond experimental capabilities at the present time.

### (1) REDUCTION OF ALDEHYDES AND KETONES

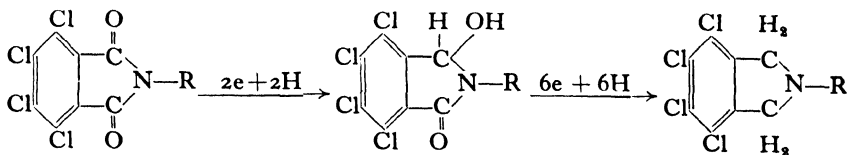
The reduction of aldehydes can be accomplished a little more readily than the reduction of ketones. Usually it requires a somewhat

CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS

lower electrode potential to reduce the carbonyl group to the alcohol than to the pinacol. In order to attain the more highly reduced form, a hydrocarbon, it is necessary in most instances to utilize a so-called catalytic electrode. For this purpose a cadmium electrode has been found quite satisfactory. Thus the reduction of an aldehyde or ketone may result in the formation of three different compounds, depending on the conditions of the electrolysis and the electrodes used (2).



The process wherein the pinacol is obtained is independent of the other processes and cannot be obtained by cathodic reduction from the alcohol. The complete reduction may involve the alcohol as an intermediate. This assumption is based on studies performed with N-substituted tetrachlorophthalimides, wherein it was possible, in an aqueous-acetic sulphuric acid medium, to obtain the hydroxyphthalimide by using a lead cathode and maintaining the potential  $v$ . a standard calomel electrode at  $-0.68$  volt. This compound could then be further reduced to the isoindoline at a reference potential of  $-1.10$  volt (3). The reaction sequence is:

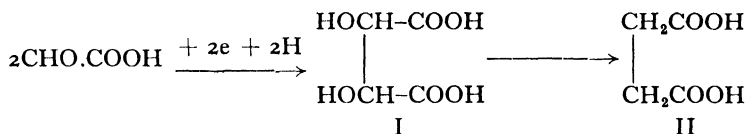


Aliphatic aldehydes are generally reduced to the corresponding alcohols, although in some cases it is possible to obtain the glycol (4). Formaldehyde and acetaldehyde in a basic medium, at copper or silver cathode, give excellent yields of the respective alcohols. In an acidic medium there is a tendency to obtain the hydrocarbon using the above electrodes. Using cadmium, it is also possible to obtain good yields of the hydrocarbon (5). If a high overpotential cathode, such



otherwise, such side products as butanediol, ethyl ether, and butyl alcohol will result.

Glyoxylic acid, when reduced at an iron, nickel, or silver electrode in a neutral or alkaline medium, yields tartaric acid (I), whereas at a lead, cadmium, or mercury cathode, the more highly reduced form, succinic acid (II) is obtained (9):



Aliphatic ketones are generally somewhat more susceptible to cathodic reduction. However, the use of a basic medium is undesirable, because of the ease with which these compounds undergo self-condensation. Although a quantity of condensation products is obtained, it is possible to obtain the pinacol and isopropyl alcohol, using a lead cathode and a 4 per cent aqueous sodium hydroxide medium for the reduction of acetone. Using a lead cathode and an acid medium results in the formation of both the pinacol and isopropyl alcohol without any condensation products. With mercury, no pinacol is obtained; but isopropyl alcohol and a small quantity of propane are isolated (10). So far as can be determined, no electrolytic method has been found to give satisfactory yields of the pinacol, although yields of isopropyl alcohol as high as 40 per cent have been reported (11).

If the reduction is allowed to proceed in the absence of air at a lead cathode, lead di-isopropyl [ $\text{Pb}(\text{C}_3\text{H}_7)_2$ ] and lead tetra-isopropyl [ $\text{Pb}(\text{C}_3\text{H}_7)_4$ ] are obtained (12). This parallels the results obtained chemically, when a sulphuric acid solution of acetone is treated with lead-sodium (13).

Methyl ethyl ketone, when reduced at a lead cathode in a sodium bicarbonate medium, yields secondary butyl alcohol (14). Using a lead cathode and a 5 to 10 per cent sulphuric acid medium, the predominant product is methyl ethyl pinacol, with a small quantity of secondary butyl alcohol (15). Other aliphatic ketones usually respond to cathodic reduction in the same manner, with the product being either the alcohol, pinacol, or hydrocarbon, or a mixture of these end-products.

Aromatic aldehydes and ketones generally are similar in their electrolytic behaviour to the aliphatic aldehydes and ketones. How-

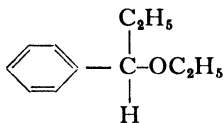
ever, they can form pinacols more readily. The products obtained, of course, depend on the conditions of electrolysis. For the preparation of pinacols, in an acidic medium, the temperature generally must be kept below 40° C.; otherwise, rearrangement to the pinacone may occur. The use of a basic medium must also be avoided when there is the possibility of condensation taking place, as for example with amino ketones, such as *p*-aminopropiophenone, and cycloparaffin ketones, such as cyclopentanone (16). It has been found in many cases, that aromatic aldehydes will form hydrobenzoin, and in some cases hydrocarbons more readily than will ketones (17).

Benzaldehyde, upon reduction in a medium of alcohol and acid or base, at cathodes of nickel, platinum, iron, or copper, yields benzyl alcohol. Under certain conditions it has been reported (18) that in an acidic medium it is possible to obtain benzyl alcohol, stilbene, and benzene.

The same investigator reports that in an alkaline medium the following hydrobenzoin, were obtained in 10 to 95 per cent yields.

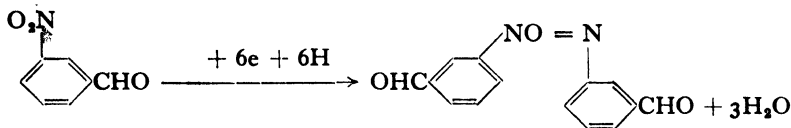
Benzaldehyde	—————>	hydro- and isohydrobenzoin
Cuminaldehyde	—————>	hydro- and isohydrocuminoïn
Anisaldehyde	—————>	hydro- and isohydroanisoin
Vanillin	—————>	hydrovanilloïn
Salicylaldehyde	—————>	hydrosalicyloïn

The reduction of a mixture of benzaldehyde, ethyl iodide, and triethylamine at a copper cathode, to yield predominantly the ethyl ether of ethyl phenyl carbinol (19), is also of interest.



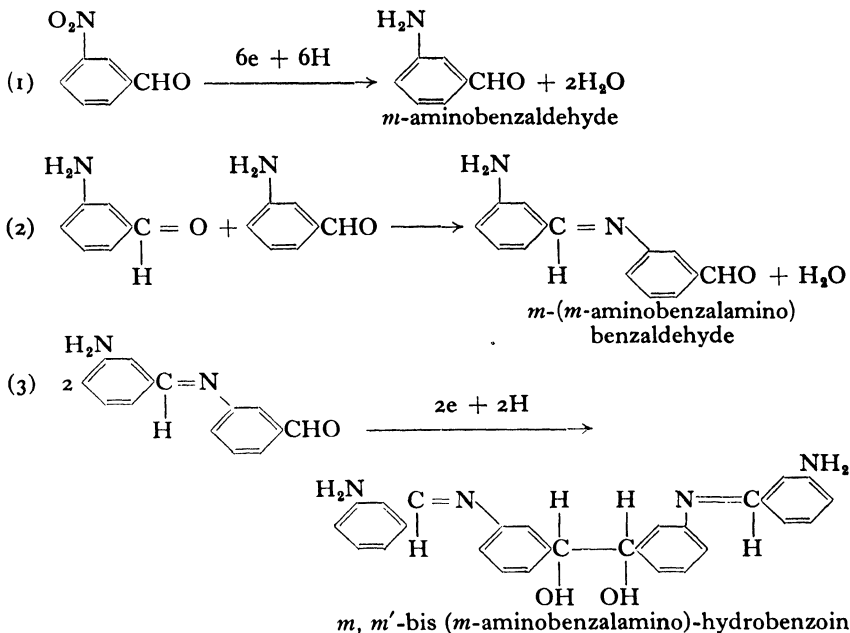
Halogenated benzaldehydes, such as ortho, meta, and para chlorobenzaldehyde, have also been reduced electrolytically to the hydrobenzoin, the stilbene, the benzyl alcohol and the toluene (20).

When *m*-nitrobenzaldehyde is reduced in an alcoholic-acid medium at a copper cathode, azoxybenzaldehyde is obtained in the following manner:

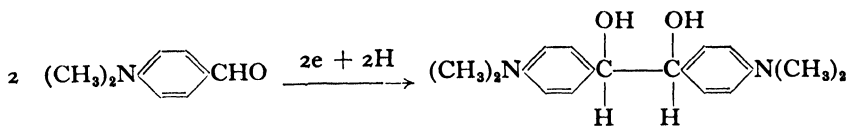


CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS

At a higher overpotential electrode, such as lead, the *m, m'*-bis (*m*-aminobenzalamino)-hydrobenzoin was obtained with excellent yield (21). This product was obtained as a result of combined electrolytic and chemical reactions in the following manner:

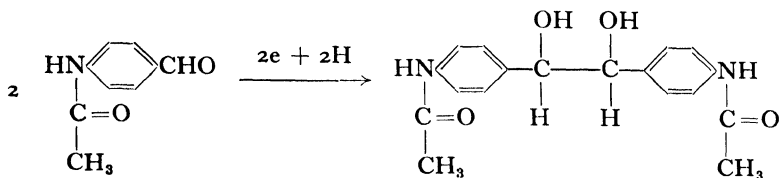


The reduction of *p*-dimethylaminobenzaldehyde in an aqueous-alcoholic potassium hydroxide medium at a reference potential *v.* S.C.E. of -1.9 volts, with a mercury cathode, results in a 97 per cent yield of the bimolecular compound (22). The high melting form of the 4,4'-*bis*-dimethylaminohydrobenzoin precipitated out during the reaction, and was obtained in a 39 per cent yield. The lower melting form was obtained from the mother liquor in a 58 per cent yield:



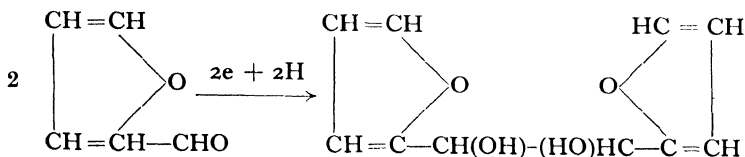
The reduction of *p*-acetamidobenzaldehyde to 4,4'-*bis*-*p*-acetamidohydrobenzoin was accomplished using a mercury cathode at a reference

potential of  $-1.55$  volts *v.* S.C.E. in an aqueous-alcoholic potassium acetate medium at reflux temperature (23).



*p*-Hydroxybenzaldehyde, when reduced in an aqueous-alkaline medium at a reference potential of  $-2.0$  volts *v.* S.C.E., using a mercury cathode, resulted in a 95 per cent yield of the desired hydrobenzoin (24). A 93 per cent yield of *p*-hydroxybenzyl alcohol was obtained, using a sodium bicarbonate medium and a mercury cathode (25). At a cadmium cathode in an acidic medium, *p*-cresol was obtained (26).

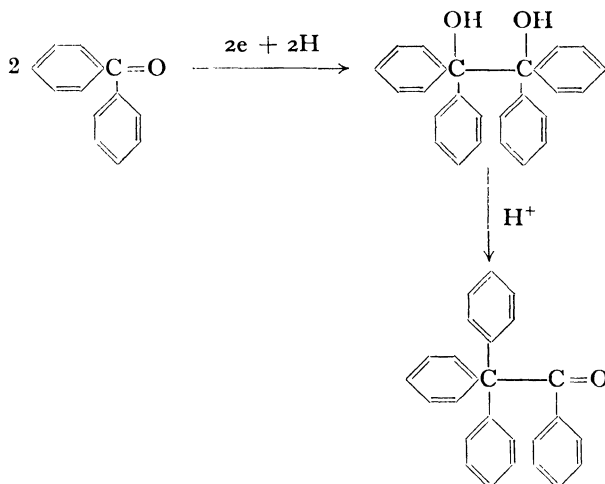
A 63 per cent yield of a mixture of hydrofuroin and isohydrofuroin has been obtained (27) from the reduction of furfural with a lead cathode in a potassium dihydrogen phosphate buffer, in the following manner:



Aromatic ketones generally can also be reduced with satisfactory yields to either the alcohol, the pinacol, or the fully reduced hydrocarbon (28). Usually the alcohol is obtained with a lower overpotential cathode, whereas the pinacol requires a higher overpotential electrode. As with the aromatic aldehydes and the aliphatic ketones, aromatic ketones are more readily reduced completely if a catalytic type electrode is used.

It has been reported (29) that benzophenone, when subjected to cathodic reduction in an aqueous-acidic medium at a high overpotential electrode, will give satisfactory yields of the rearranged benzpinacol, benzpinacone, thus:

## CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS



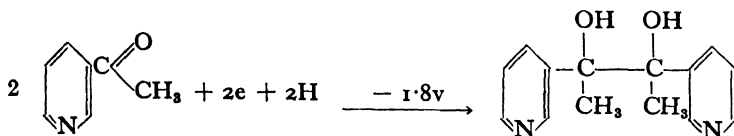
If this reduction is performed in an acetic-sulphuric acid medium the resultant pinacolone will be obtained, even at relatively low overpotential electrodes, such as iron, nickel, and copper. Thus the effect of the medium on the reaction can be seen, in an increase in the overpotentials of those electrodes (30) so that they were comparable in activity to a high overpotential electrode in an aqueous medium.

The pinacols of *p*-aminoacetophenone and *p*-aminopropiophenone can be obtained by reduction of the respective ketones in an aqueous hydrochloric acid medium, at a mercury cathode, using a cathodic reference potential of  $-1.5$  volts *v.* S.C.E. (31).

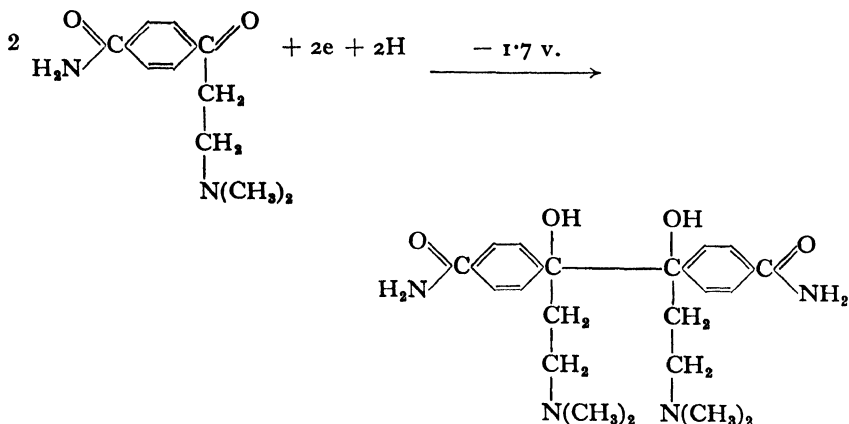
It might be of interest to point out that this is one of the instances wherein the desired compound, 2,3-*bis*-(*p*-aminophenyl)-2,3-butanediol, could only be obtained using an electrolytic procedure. The usual chemical methods gave only the carbinol.

The reduction of the *p*-aminoacetophenone at a reference potential *v.* S.C.E. of  $-1.1$  volts in the same medium yields the carbinol. The pinacol of *p*-aminoacetophenone can also be obtained using a tin cathode (32). At a cathodic reference potential of  $-2.2$  volts *v.* S.C.E. using a mercury cathode, *p*-hydroxyacetophenone, upon electrolysis in an aqueous sodium hydroxide medium, gave a 77 per cent yield of the respective pinacol. The pinacol, 2,3-*bis*-( $\beta$ -pyridyl)-2,3-butanediol, can also be obtained, by reduction of  $\beta$ -acetyl pyridine in aqueous hydrochloric acid using a mercury cathode under controlled potential conditions (22):

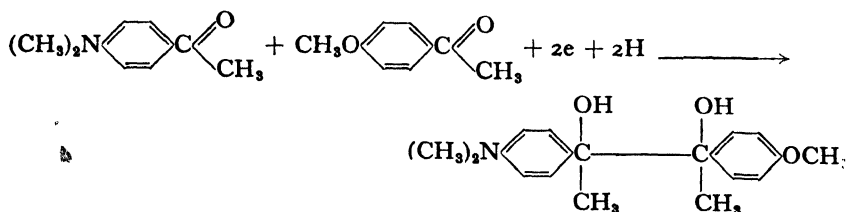
ORGANIC ELECTRODE PROCESSES



Utilization of controlled potential conditions at a mercury cathode has also resulted in the selective reduction of *p*-carboxyacetophenone and *p*-dimethylaminoacetophenone to their respective pinacols (33). A number of Mannich bases have also successfully yielded the desired pinacols under similar conditions (34). The Mannich base, *p*-acetamido- $\omega$ -dimethyl-aminopropiophenone in an aqueous hydrochloric acid medium, yielded 3,4-*bis-p*-acetamidophenyl-1,6-*bis*-dimethylaminohexane-3,4-diol:



Of interest is the preparation of the unsymmetrical pinacol, 2-*p*-dimethylaminophenyl-3-*p*-methoxyphenylbutane-2,3-diol from a mixture of the ketones, using a mercury cathode (35).

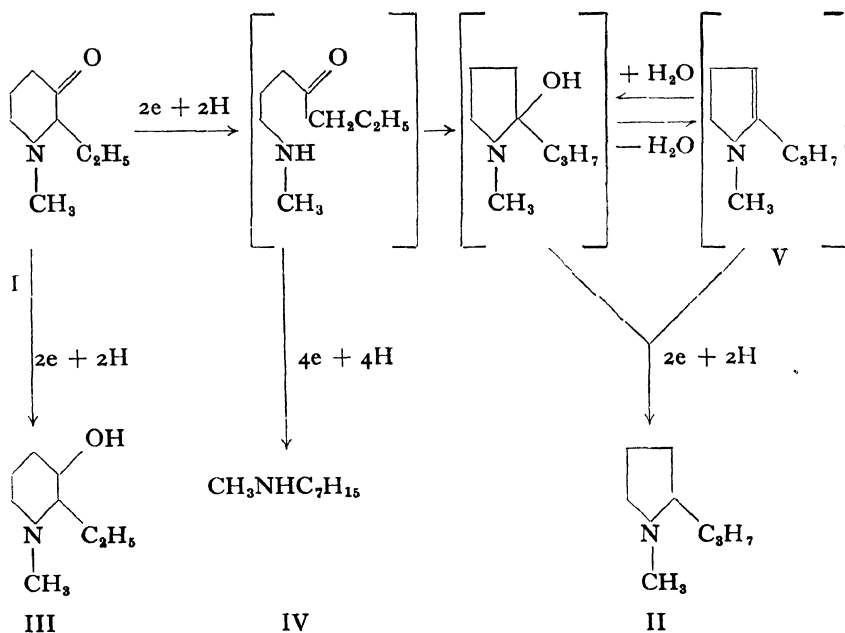


This compound was obtained using either an aqueous-ethanol

CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS

hydrochloric acid medium at a reference potential of  $-1.06$  volts *v.* S.C.E., an aqueous-ethanolic-potassium acetate medium at a reference potential of  $-1.97$  volts *v.* S.C.E., or an aqueous-ethanolic-potassium hydroxide medium at a reference potential of  $-1.86$  volts *v.* S.C.E. The latter two media were kept at reflux temperature during the reaction. The yield of unsymmetrical pinacol was 30 to 37 per cent, depending upon the medium used.

The reduction of a number of  $\alpha$ -aminoketones, in an aqueous sulphuric acid medium, at various electrodes and different temperatures, has been reported (36). The reduction of 1-methyl-2-ethyl-3-piperidone (I) at  $60^\circ\text{C}$ . with a cadmium electrode, yielded 1-methyl-2-propylpyrrolidine (II) and 1-methyl-2-ethyl-3-hydroxypiperidine (III). At a temperature of  $20^\circ\text{C}$ . only N-methyl-heptylamine (IV) could be isolated:

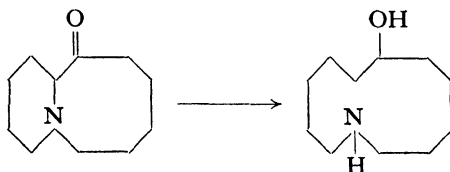


With a lead cathode at  $60^\circ\text{C}$ . N-methylheptylamine (IV) and 1-methyl-2-propylpyrrolidine (II) were obtained. The same cathode at  $20^\circ\text{C}$ . yielded only the N-methylheptylamine (IV). A copper cathode at

60° C. yielded 1-methyl-2-propyl-2-pyrroline (V) and 1-methyl-2-propylpyrrolidine (II). This same electrolysis, when performed at 20° C., gave a quantitative recovery of the starting material. Similar results were obtained when a tin electrode was used, with electrolysis temperatures of 20° C. and 60° C.

The results indicate that it is possible to obtain a reductive-rearrangement of the Clemmensen type, by electrolysis. The fact that no apparent reaction took place with a tin electrode might indicate that this type reaction is not dependent only on the potential of the electrode, but possibly on the catalytic effects of the electrode material. Tin is a higher overpotential electrode than copper or cadmium but lower than lead. It is interesting to observe that reduction at 20° C. gave only N-methylheptylamine. At this temperature the overpotential of the electrode would be higher, and thus one might expect the more highly reduced form. At the lead cathode at 60° C., the N-methylheptylamine and 1-methyl-2-propylpyrrolidine are obtained, with the former compound predominating. Increasing the potential of this already high potential electrode by performing the reaction at 20° C. yielded only the N-methylheptylamine.

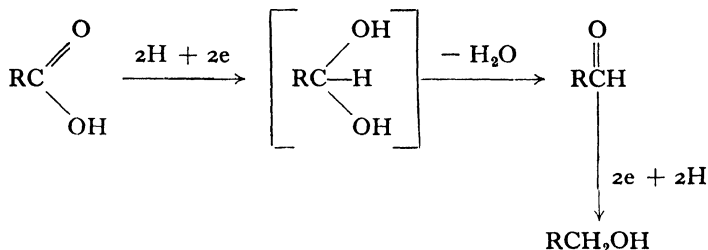
The electrolytic method has also been applied to the synthesis of medium-size ring compounds containing a nitrogen atom (37). This is achieved by reduction of bicyclic or tricyclic  $\alpha$ -aminoketones at 60° C. in an aqueous sulphuric acid medium, using a lead cathode. As an example, 7-keto-1-azabicyclo 6.4.0 dodecane, upon reduction under these conditions, yields 7-hydroxyazacyclododecane, thus:



## (2) REDUCTION OF CARBOXYLIC ACIDS

The two available possibilities for the reduction of the carbonyl group of a carboxylic acid result in the formation of an aldehyde which can be further reduced to the alcohol, depending on the conditions of electrolysis:

CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS



Generally, when the reduction is performed in an acidic medium at a low overpotential electrode such as platinum, nickel, or iron, no reaction takes place. However, at a higher overpotential electrode, such as lead, the primary alcohol will be obtained.

The monobasic acids do not usually behave in this manner, although the lowest members of the aliphatic series, that is, formic, phenylacetic, oxalic, and glyoxylic acid, do respond to electrolytic reduction. Formic acid, when dissolved in a 10 per cent sulphuric acid medium and subjected to cathodic electrolysis in a divided cell at a lead electrode, especially in the presence of a "hydrogen carrier" such as ceric sulphate, has been reported by Ellis and McElroy to yield either formaldehyde at a low current density (low electrode potential) or methanol at a high current density (high electrode potential) (38):

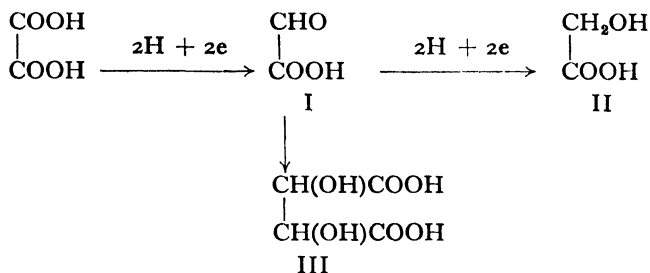


However, it should be mentioned that a subsequent investigator (39) was unable to duplicate the results of Ellis and McElroy.

Phenylacetic acid can also be reduced to the corresponding alcohol (40). However, the ease of reduction of this acid when substituents are present on the benzene ring will, to a great extent, possibly be determined by the inductive effect of these substituents. In an acid medium at a mercury cathode, *p*-hydroxyphenyl acetic acid is not reduced to the corresponding alcohol, whereas *p*-dimethylaminophenyl acetic acid will give the desired carbinol (41).

Oxalic acid, upon reduction in an aqueous sulphuric acid medium at a mercury or lead cathode, will yield glyoxylic acid (I) when the reaction is performed at temperatures below 10° C., and glycolic acid (II) at temperatures over 40° C. (42).

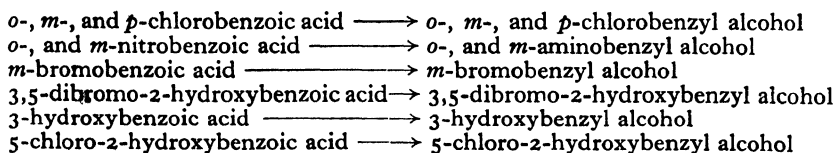
ORGANIC ELECTRODE PROCESSES



As glyoxylic acid will, upon reduction in an acid medium, yield tartaric acid (III) (43) in a manner similar to that in which aldehydes and ketones will yield bimolecular products, it is possible that glyoxylic acid as such may not be intermediate to glycollic acid. It is, however, entirely possible that if the glyoxylic acid were present in low concentration, the opportunity for collision of the activated intermediate (the free radical form) with another of its kind would be minimized, and thus further reduction to the alcohol would be anticipated. This is further indicated by experiments in which the carbinol was obtained from *p*-aminoacetophenone, when the latter was present in small quantities in the medium and subjected to electrolysis conditions which would have normally yielded the pinacol at a higher ketone concentration (44). Thus it is entirely possible, due primarily to the concentration of the depolarizer, to obtain either of two products.

Of interest is the reduction of carbonic acid, as the carbonate, at mercury, amalgamated lead, amalgamated zinc, or zinc electrodes, to give almost quantitative yields of formic acid (45). The reduction of carbon monoxide to formaldehyde has also been claimed (46).

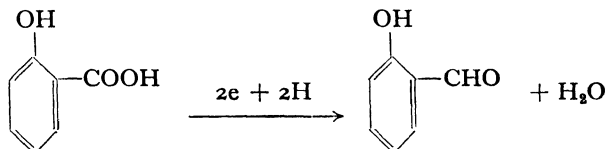
Aromatic acids are readily reduced to the alcohol in an acidic medium at a high overpotential electrode, such as lead or mercury (47). This method has been successfully applied to the preparation of substituted benzyl alcohols (48), which in many instances are difficult to obtain by purely chemical means, whereas the respective benzoic acids are readily obtainable. Some of the reductions achieved are as follows:



Reductions of this type are usually performed in an aqueous-ethanol

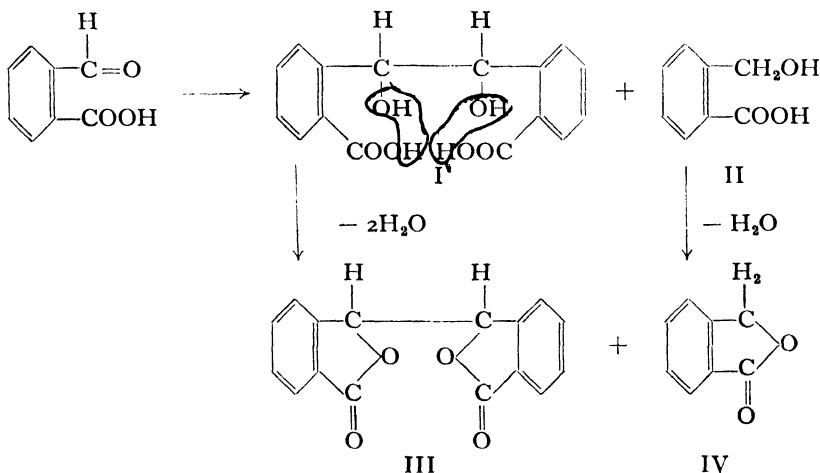
CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS

sulphuric acid medium, and in order to preclude ester formation, the temperature is maintained below 30° C. If it is possible to eliminate the ethanol from the medium, higher temperatures may be used. However, caution must be used with the substituted benzoic acids, as there is always present the possibility of decarboxylation at elevated temperature (49). The aldehyde is only obtained in the presence of a sodium salt and boric acid at a mercury cathode (50), thus salicylic acid under these conditions yields salicylaldehyde:

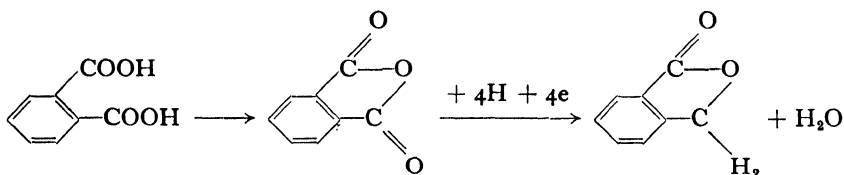


The reduction of the carboxyl group does not usually take place in a basic medium, as indicated by the fact that *p*-carboxyacetophenone, when subjected to cathodic reduction at a mercury cathode, at a reference potential of -2.0 volts *v.* S.C.E. in an aqueous sodium hydroxide medium, yields the respective pinacol (51).

Another interesting example is the reduction of the potassium salt of 2-carboxybenzaldehyde at a mercury cathode to yield hydrodiphthalyl (III), and a small quantity of phthalide (IV) (52). It is probable that the initial reaction is electrolytic in nature, with the reduction of the aldehyde group to the pinacol (I) and 2-carboxybenzyl alcohol (II). These then lactonize to yield the isolated products, thus:

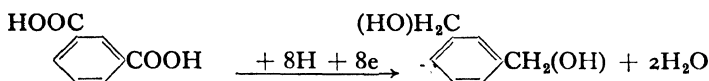


Aromatic dicarboxylic acids are reduced to the corresponding phthalide, or dihydric alcohol, depending on the position on the ring of the carboxyl groups. Phthalic acid, when reduced at a lead cathode in a neutral or weakly acidic medium, will give phthalide (53), with phthalic anhydride being intermediate in the reaction, thus:



The phthalide can also be prepared by reduction of phthalic anhydride.

Isophthalic acid upon reduction at a lead cathode gives  $\omega, \omega'$ -dihydroxy-*m*-xylene (54), thus:

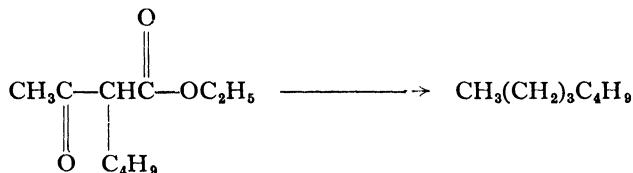


The carboxyl group of  $\beta$ -keto acids is not attacked but the ketone group is reduced to either carbinol or methylene compound.

### (3) REDUCTION OF ESTERS

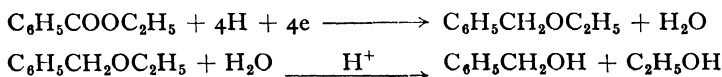
In some cases the esters of aliphatic acids respond to cathodic reduction. There is, however, an indication that the nature of the acid portion of the molecule influences the ease of reduction. The ethyl esters of acetic, phenylacetic, and cyanoacetic acids are not reduced, whereas those of fumaric, tartaric, and succinic acids are reduced slowly. The esters of oxalic, malonic, acetoacetic, oxalacetic, benzoic, halo-benzoic, and phthalic acids are reduced quite readily at a high overpotential electrode in an acidic medium.

The products obtained from the reduction of acetoacetic acid, and its derivatives, result in a number of compounds in which either or both carbonyl groups are acted upon electrolytically. Generally, the final product is the hydrocarbon. Using a lead cathode, an aqueous-alcohol sulphuric acid medium and elevated temperatures results in the formation of butane from the ethyl ester of acetoacetic acid (56). The reduction of butylacetoacetic acid at a lead cathode in an aqueous-alcohol sulphuric acid medium yields *n*-octane, thus:



This indicates that an isomerization has occurred during the course of the reduction; otherwise, 3-methyl heptane, would have been obtained. Isobutylacetoacetic ester yields octane, and not the expected product, 2,4-dimethylhexane (57).

In the aromatic series the corresponding alcohol or ether is generally obtained. The initial reaction is the cathodic reduction of the carbonyl group to the fully reduced form, to yield the ether, which may then cleave, due to the acidity of the medium, to give the alcohol (58):



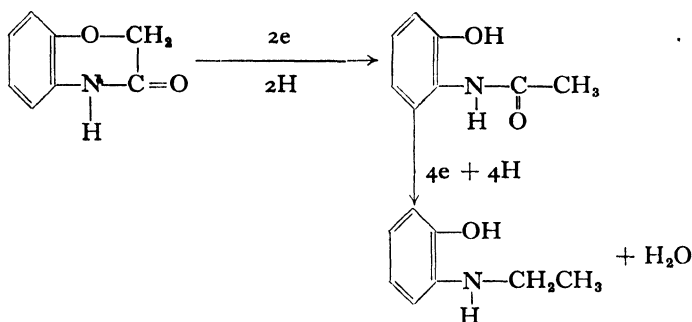
#### (4) REDUCTION OF AMIDES AND IMIDES

The carbonyl groups of both amides and imides can generally be fully reduced at a high overpotential electrode in an acidic medium. The ease with which this group is reduced in amides and thio-amides, is to a great extent dependent upon the nature of the substituent on the nitrogen atom (59). It has been found that the greater the number of methyl groups attached to the nitrogen of  $\alpha$ -phenylacetamide the more rapidly does the electrochemical reduction occur. Thus the reduction of  $\alpha$ -phenylacetamide will yield less than 1 per cent of  $\beta$ -phenylethylamine, whereas N-methyl- $\alpha$ -phenylacetamide yields 80 per cent of N-methyl- $\beta$ -phenylethylamine, and N,N-dimethyl- $\alpha$ -phenylacetamide yields 92 per cent of the corresponding amine. It was also found that a lead cathode gives a better yield of amine in the reduction of N,N-dimethyl- $\alpha$ -phenylacetamide, than a zinc-amalgam electrode. Addition of a small quantity of arsenious or antimonious oxides increased the yield at a lead cathode still further (60).

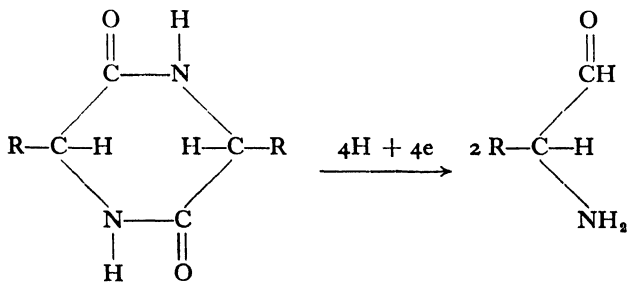
In addition to the effect of replacement of the N-hydrogens by methyl groups on the ease of reduction of amides, other workers (61) found that replacement by phenyl groups also had a desirable effect. Their findings further indicated that substitution of one or more phenyl

groups on the  $\alpha$ -carbon of acetamide improved ease of reduction. However, the best results are obtained when the aryl group is linked directly to the carbonyl. The reactivity is decreased as the carbonyl and aryl group are separated by  $\text{CH}_2$  groups. It appears that the greater the electron donating effect of the substituents on the nitrogen and the  $\alpha$ -carbon, the easier it is for reduction to occur.

Compounds of the morpholinone series which are essentially cyclic amides, can be reduced electrolytically (62). The first step is a cleavage, via a two-electron change, to form the N-substituted acetamide; then a four electron change to yield the secondary amine, thus:



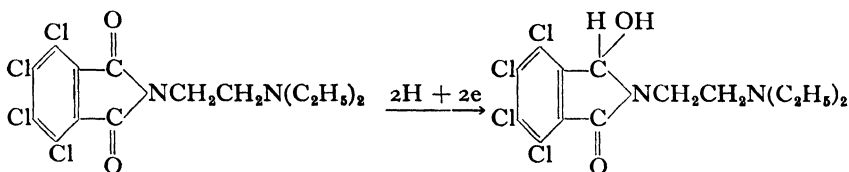
The electrolytic reduction of diketopiperazines is of interest, as it is by this method that it is possible to obtain  $\alpha$ -aminoaldehydes. Chemical methods for the preparation of such compounds are not generally successful. Upon reduction, the carbon-nitrogen bond is usually ruptured, resulting in two  $\alpha$ -aminoaldehyde molecules (63).



In many respects the cathodic reduction of imides is similar to that of the amides. Whereas an intermediate has never been isolated from the

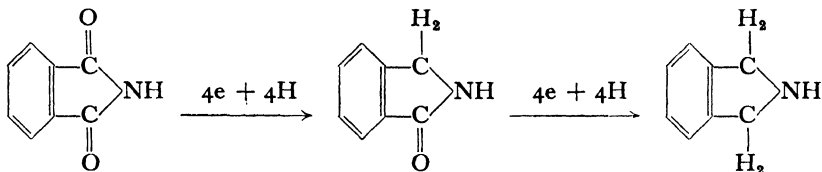
CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS

reduction medium of an amide, a partially reduced hydroxy-phthalimidine has been obtained by reduction of N,N-diethylaminoethyl tetrachlorophthalimide in an acetic-hydrochloric acid medium at a mercury cathode, utilizing a reference potential of  $-1.2$  volts *v. a* S.C.E. (64).



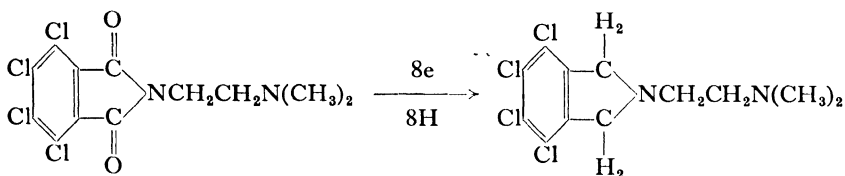
The same results were obtained with a similar phthalimide at a lead cathode in an aqueous-acetic sulphuric acid medium, at a reference potential of  $-0.68$  volt *v. a* S.C.E. (3). The preparation of hydroxy-phthalimidine has also been accomplished by performing the reduction in an acid medium at a copper electrode (65).

In the literature can be found many examples wherein phthalimides have been successfully reduced to the phthalimidine, and thence on to the isoindoline (66), thus:



In many cases, although satisfactory yields of the desired isoindolines are obtained at a high overpotential electrode in an aqueous acid medium, the current efficiency is generally quite poor. As an example, we might consider the results obtained in the reduction of a suspension N-methyl phthalimide at a lead electrode in an aqueous-sulphuric acid medium (67). At a current density of  $0.0445$  amp./cm.<sup>2</sup> a 57.7 per cent yield of the respective isoindoline was obtained with a 14.4 per cent current efficiency. At this current density, even in the initial period of electrolysis, there is considerable hydrogen evolution, which explains the reason for low current efficiency. The simple expedient of increasing the solubility of the compound and the overpotential of the electrode, by addition of glacial acetic acid to the medium, increased the current efficiency of the reaction to 42 per cent

with an 82 per cent material yield of N-methylisoindoline (68). Thus it appears that, as would be expected, by increasing the concentration, the "limiting current" for the reaction was increased, with the net result being that less of the current was used for gas production and more for the actual reduction of the carbonyl groups. It is possible that the current efficiency might have been improved still further by decreasing the current density as the reduction proceeded, to the true "limiting current" for the particular concentration of depolarizer; of course, the increase in electrode overpotential in this medium, as compared with that in an aqueous medium, must not be overlooked as a contributing factor in the improved results. N,N-Dimethylaminoethyl tetrachlorophthalimide, upon reduction in an aqueous-acetic-sulphuric acid medium at a lead cathode and at a current density of 0.049 amp./cm.<sup>2</sup>, results in a 91 per cent material yield of the N,N-dimethylaminoethyl tetrachloroisoindoline (3).



The efficiency of the reduction, based on the material yield of isoindoline, is 46 per cent. The same reduction, performed at a controlled potential of  $-1.10$  volts *v.* S.C.E., results in a 77.7 per cent efficiency, based on the material yield of the isoindoline. The current density, when the electrolysis is performed under these conditions, diminishes as the electrolysis progresses. This increased efficiency is to be expected, for from the concept of "limiting current," which is directly related to the concentration of the depolarizer, only that current is being supplied which is necessary for the reduction of the phthalimide. As a consequence there is a negligible amount of hydrogen evolved.

In the same report (3), are the results obtained with three high overpotential electrodes; namely cadmium, lead and mercury. These are shown in Fig. IV:1. Despite the high overpotential characteristics of the mercury electrode, the best yield obtainable was approximately 80 per cent, whereas with lead, a slightly lower overpotential electrode, under these experimental conditions, gave yields of over 90 per cent.

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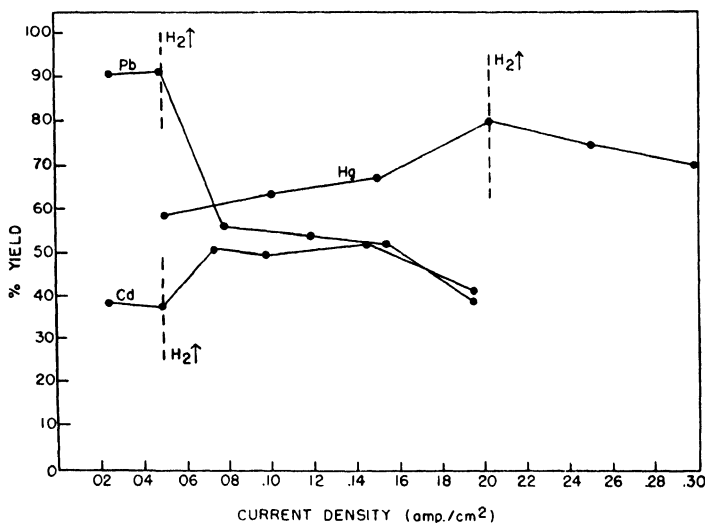


FIG. IV: I *Dependence of isoindoline yield on current density*

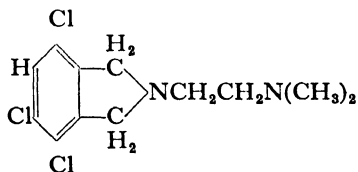
This would tend to indicate a possible catalytic effect of this electrode material on the reduction. A cadmium electrode, which is the lowest overpotential electrode of the three studied, gave relatively poor yields of the desired isoindoline. In all cases in which high yields of the isoindoline were not obtained, the partially reduced phthalimidine was also isolated from the reaction mixture.

The two carbonyl groups in the tetrachlorophthalimide molecule are not reduced simultaneously. It is possible to obtain excellent yields of the phthalimidine by merely permitting the electrolysis to proceed for only 50 per cent of the time required for complete reduction to the isoindoline.

If a completely aqueous system is used the desired isoindoline may not be obtained. This holds with phthalimides, which have halogen substituents in the benzene ring. As an example, we might consider the electrolytic reduction of *N,N*-dimethylaminoethyl tetrachlorophthalimide in a 5.7 per cent aqueous sulphuric acid medium, using a lead electrode (69). The medium, current density, temperature, and ampere hours per mole were the same as used to successfully reduce *N*-methylphthalimide to *N*-methylisoindoline, with, however, the accompanying low current efficiency (67). Throughout the course of the reaction gas evolution was excessive, with the suspended imide finally

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going into solution. From the catholyte was isolated a compound which, upon analysis, and from degradation studies, was found to be N,N-dimethylaminoethyl-3,4,6-trichloroisindoline.

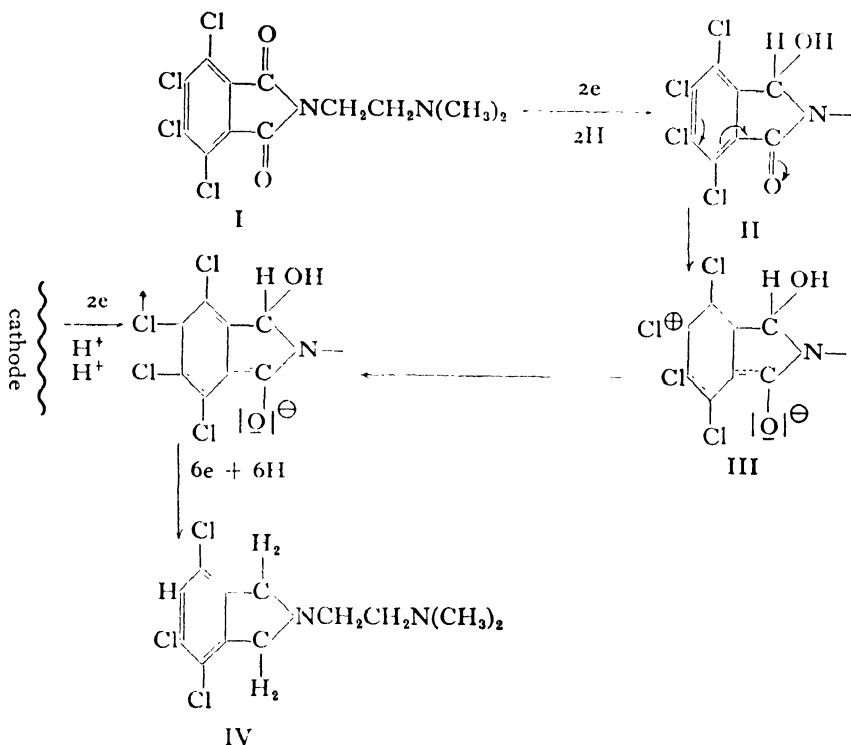


If the electrolysis is allowed to proceed for approximately one-third the time used to obtain the trichloroisindoline, three products are isolated: N,N-dimethylaminoethyl tetrachlorophthalimide (I), N,N-dimethylaminoethyl-3,4,5,6-tetrachloro-2-hydroxyphthalimidine (II), and the N,N-dimethylaminoethyl-3,4,6-trichloroisindoline (III). Prolonged electrolysis did not remove more than the one ring halogen. It might be of interest to deviate slightly and discuss briefly the mechanism of this reaction, so as to better understand how, under certain conditions, competitive electrochemical reactions are possible, because of a lack of energy sufficient to drive the reaction in the desired direction in an efficient manner.

Based on the results, the mechanism shown on page 79 was proposed.

As the hydroxyphthalimidine (II) was obtained from the short period electrolysis it may be assumed to be an intermediate prior to dehalogenation. As a result of the low efficiency of the system the subsequent reduction of the hydroxyphthalimidine (II) to the isindoline (IV) is relatively slower than under more efficient conditions, i.e. an aqueous-acetic-sulphuric acid medium (p. 75). Therefore, the intermediate suggested by (III), which is possibly stabilized in this *p*-quinoid form by adsorption on the cathode surface, undergoes nucleophilic substitution on carbon —5, with a two-electron change, and the addition of hydrogen. As the energy required for the molecule to assume an *o*-quinoid structure may be too great, the probability of any amount of the 4,5,6-trichloro-2-(2-dimethylaminoethyl)-isindoline being formed is quite unlikely. The proposed mechanism also accounts for the fact that only one chlorine is removed from the ring, for as soon as the carbonyl group is reduced resonance with the benzene ring is impossible. Were this not so, the expected product would be the 4,7-dichloroisindoline. This was confirmed by the fact that N,N-dimethyl-

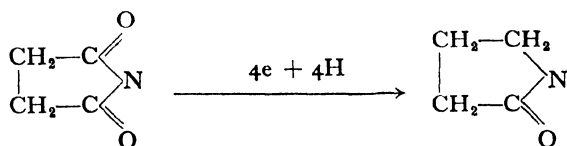
CATHODIC REDUCTION OF CARBONYL TYPE COMPOUNDS



aminoethyl tetrachlorophthalimide, when reduced under identical conditions, yielded the trichloroisindoline.

This demonstrates an instance in which an electrolysis on a low efficiency level permitted the energy within the molecule to dominate the path of reaction. Using more efficient conditions, the carbonyl reduction was fast enough to minimize the effect of resonance with resultant substitution.

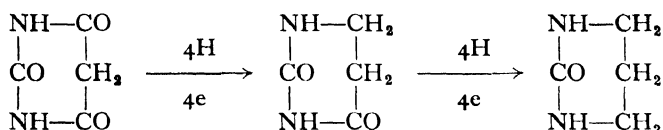
The cyclic imides also respond satisfactorily to reduction at a high overpotential electrode in an acidic medium. Succinimide is readily reduced to pyrrolidone at a lead electrode (70).



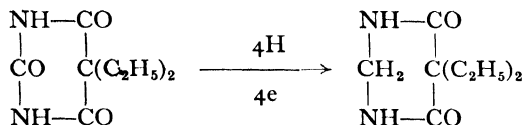
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At a zinc-amalgam electrode the completely reduced product, pyrrolidine (71) is obtained. Substituted succinimides, such as the N-methyl, N-ethyl, N-isopropyl, and N-phenyl, have been reduced to their respective pyrrolidines (72). The glutarimides also respond to cathodic reduction in the same manner (73).

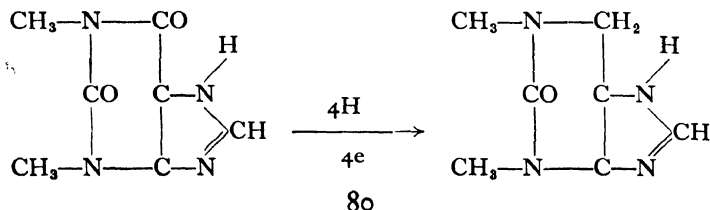
We might consider purine compounds as belonging in the general category of imides. Generally, the carbonyl group of the acid is reduced preferentially to the urea carbonyl group, and thus reduction of barbituric acid at a lead cathode in a 50 per cent sulphuric acid medium gives dihydrouracil and finally trimethylene urea (74).



However, if we activate the urea carbonyl by replacement of the methylene group by a  $>\text{C}(\text{C}_2\text{H}_5)_2$  the urea carbonyl group is reduced, in preference to the carboxyl carbonyls (75). Thus 5,5-diethylbarbituric acid will give 5,5-diethyl-4,6-dioxy-1,2-dihydropyrimidine.



Xanthine and its derivatives, such as theophyllin, behave in a manner very similar to that of barbituric acid, in that the urea carbonyl remains unaffected by cathodic reduction (76). Theophyllin will, on reduction at a lead cathode in an aqueous sulphuric acid medium, yield desoxy-theophyllin.



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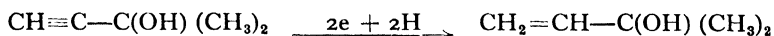
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- (75) Tafel and Thompson, *Ber.*, 1907, 40, 4490.
- (76) Tafel, *et al.*, *Ber.*, 1900, 33, 3370; 1901, 34, 1170; 1907, 40, 3752.

## MISCELLANEOUS CATHODIC REACTIONS

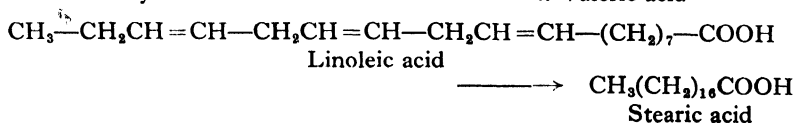
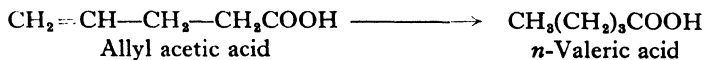
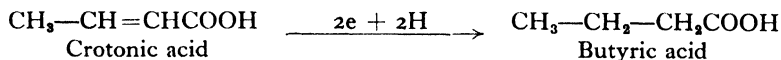
### (1) ADDITION OF HYDROGEN TO UNSATURATED COMPOUNDS

THE addition of hydrogen to unsaturated compounds has been accomplished electrolytically. However, the ease with which this occurs, especially with double bond carbon compounds, is not as great as one might anticipate. Generally, to obtain saturation of a double bond a catalytic type electrode such as platinum, covered with spongy platinum, or nickel with a spongy nickel coating is required. At times it is possible to achieve the desired results by use of an uncoated nickel electrode and a mercury or lead electrode. Reactions of this type have been performed in both acidic and basic media.

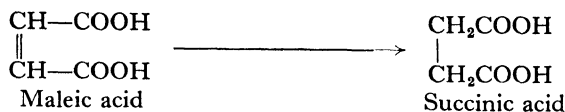
Acetylene has been reported to yield ethylene when subjected to electrolysis at a platinized-platinum electrode in a basic medium. Increasing the potential of the reaction results in the formation of ethane (1). Under similar conditions, 2-methyl-3-butyn-2-ol gives a 95 per cent yield of dimethyl-vinyl-carbinol (2):



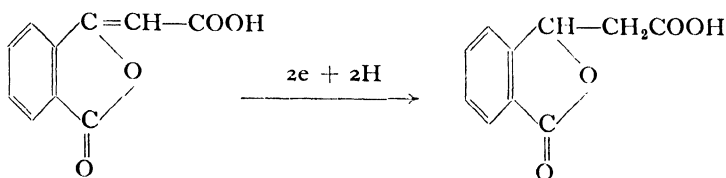
In the manner already discussed, it has been possible to hydrogenate many simple unsaturated acids (3), thus:



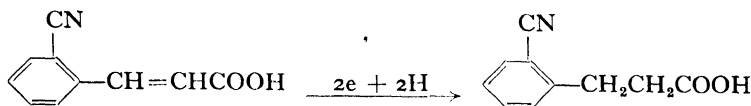
MISCELLANEOUS CATHODIC REACTIONS



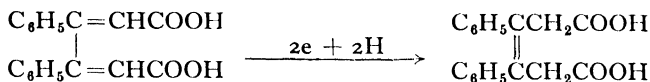
Some of the more complex acids also respond to electrolytic methods. For example, 3, $\alpha$ -dehydro-3-phthalideacetic acid, when reduced in an aqueous sodium carbonate medium, will yield 3-phthalideacetic acid (4):



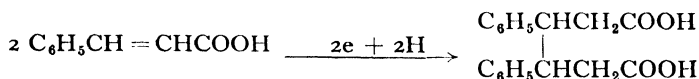
Using similar conditions enabled these investigators to prepare 2-cyanohydrocinnamic acid, thus:



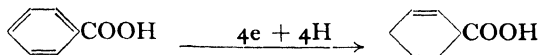
The diene acid,  $\beta$ ,  $\gamma$ -diphenylmuconic acid, has been reduced with excellent yield to the monene,  $\beta$ ,  $\gamma$ -diphenyl-dihydromuconic acid, via a 1,4-hydrogen addition (5):



The reduction of cinnamic acid in an acid medium has been reported to yield the dimeric acid,  $\beta$ ,  $\gamma$ -diphenyl-adipic acid, thus (6):

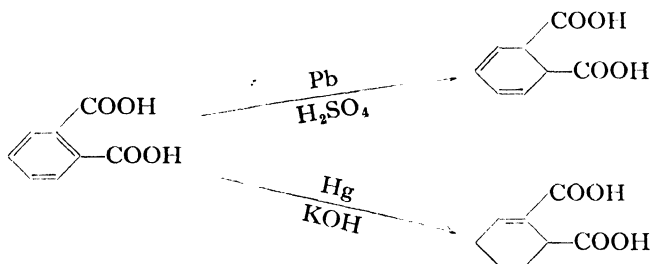


Reduction, at least partly, of the aromatic character of the benzene ring has been found possible. If benzoic acid is reduced in a basic medium at a high overpotential electrode, the  $\Delta^2$ -tetrahydrobenzoic acid is obtained (7):



This same reaction performed in an acid medium results in the reduction

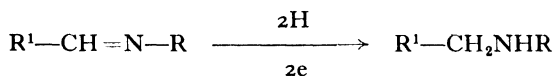
of the carboxyl group to a hydroxy methyl, without any attack on the aromatic character of the benzene ring. Phthalic acid, however, has its ring structure attacked in both acidic and basic media. In the former medium, at a lead electrode, the less highly reduced structure 1,2-dihydrophthalic acid is obtained (7), whereas in the basic medium at a mercury cathode  $\Delta^2$ -tetrahydrophthalic acid is the main product (8):



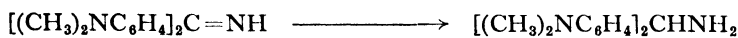
If the monoethylester of phthalic acid is similarly treated at a mercury cathode, and in an aqueous potassium chloride medium, the monoethylester of 3,4-dihydrophthalic acid is obtained (9).

It has also been reported that phenol can be reduced at a platinum electrode coated with platinum black in an aqueous sulphuric acid medium, to yield cyclohexanol (10). Using a lead electrode and an aqueous sulphuric acid medium, pyridine is readily reduced to piperidine, and quinoline to either the dihydro- or tetrahydro-quinoline. Dihydropyrrole and indoline are readily obtained by electrolytic reduction of pyrrole or indole respectively (11).

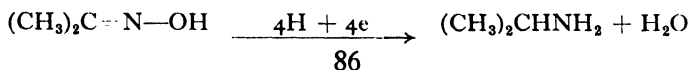
Unsaturated compounds of the imino type ( $>C=N-$ ) are readily reduced in an acidic medium at a high overpotential electrode such as lead or mercury. Schiff bases, for example, upon electrolytic hydrogenation, yield the respective secondary amine (12).



Thus auramine gives a 90 per cent yield of the reduction product, leucauramine (13):

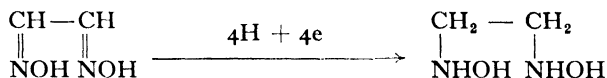


Oximes, such as acetoxime, add four hydrogens to form isopropylamine (14):

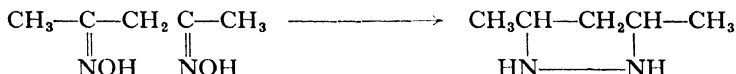


MISCELLANEOUS CATHODIC REACTIONS

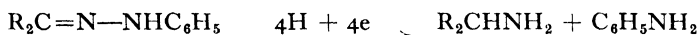
However, glyoxime, upon reduction, only adds two hydrogens to each oxime group, with resultant formation of the  $\beta$ -ethylene dihydroxylamine (15), thus:



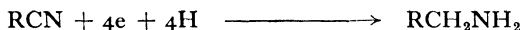
Acetylacetone dioxime will yield the 3,5-dimethyl pyrazolidine (16):



Cathodic reduction of phenylhydrazone results in cleavage of the  $>\text{N}-\text{N}<$  bond with formation of the respective amine and aniline (17):

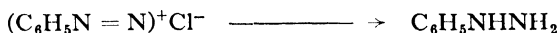


The reduction of nitriles is generally accomplished at a high overpotential electrode, such as lead or mercury in an aqueous-acid medium, to yield the respective primary amine and some ammonia (18):



In this manner nitriles such as propionitrile, benzonitrile, *p*-toluonitrile, and succinonitrile, have yielded *n*-propylamine, benzylamine, 4-methyl-benzylamine, and putrescine, respectively.

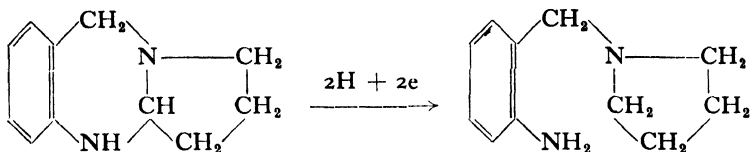
The reduction of benzene diazonium salts at a mercury cathode in an acid medium yields the corresponding phenylhydrazines. Thus benzene diazonium chloride yields phenylhydrazine (19):



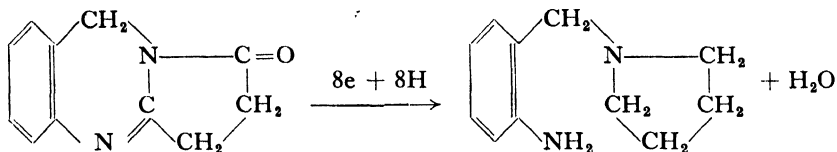
## (2) REDUCTION OF ALKALOIDS

In this complex group of compounds there are many focal points of attack by electrolytic reduction. If oxygen is present as a carbonyl group, its reduction is possible. Double bonds in the molecule can also be reduced, as well as the reductive cleavage of rings containing nitrogen. An illustration of the latter is the reduction of pegan at a lead electrode in an aqueous sulphuric acid medium to yield N-[*o*-aminobenzyl]-pyrrolidine (20):

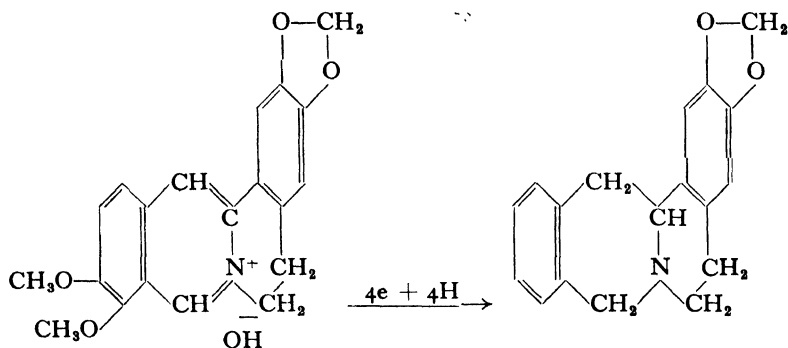
## ORGANIC ELECTRODE PROCESSES



Pegene-9-one-(1) which contains both a ring nitrogen and a carbonyl group can be cathodically reduced to N-[o-aminobenzyl]pyrrolidine under the same conditions as the pegan (21):



An example for the hydrogenation of the double bond can be seen from the cathodic reduction in an acidic medium at a lead cathode of berberine, which yields tetrahydroberberin (22):



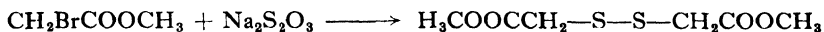
Using similar conditions of electrolysis, strychnine ( $C_{21}H_{22}O_2N_2$ ) has been reduced to tetrahydrostrychnine ( $C_{21}H_{26}O_2N_2$ ), brucine ( $C_{23}H_{26}O_4N_2$ ) to tetrahydrobrucine ( $C_{23}H_{30}O_4N_2$ ), and methoxy-methyl-dihydrobrucidine ( $C_{25}H_{34}O_4N_2$ ) to methoxy-methyl-tetrahydrobrucidine ( $C_{25}H_{38}O_4N_2$ ) (23).

### (3) REDUCTION OF SULPHUR, SULPHONYL CHLORIDE, AND ARSENIC-CONTAINING COMPOUNDS

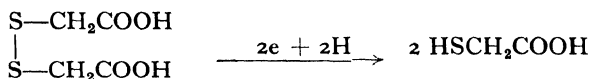
The literature does not indicate an extensive amount of research in this category of compounds. The application of the electrochemical technique does give relatively pure products in many of the reactions

MISCELLANEOUS CATHODIC REACTIONS

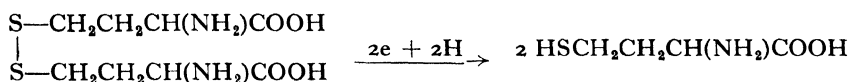
investigated. The reduction of the esters of  $\alpha$ -bromo aliphatic acids in the presence of sodium thiosulphate and an aqueous alcoholic medium of potassium carbonate at a low overpotential electrode, such as platinum, leads to a dithio acid (24). The reduction of the methyl ester of  $\alpha$ -bromoacetic acid under such conditions yields the dimethyl ester of dithiodiglycolic acid:



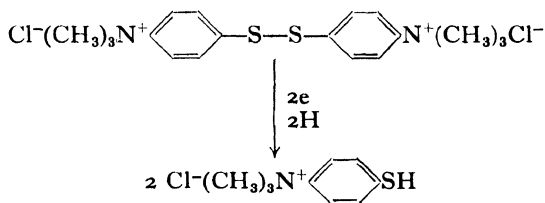
Reduction of the free acid  $\alpha, \alpha'$ -dithiodiglycolic acid at a higher overpotential electrode, namely lead, in a 2N sulphuric acid medium gives a good yield of thioglycolic acid, thus (25):



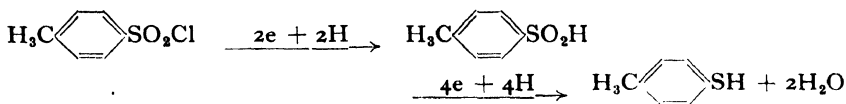
Using a mercury cathode and a basic medium, it has been possible to quantitatively convert homocystine to homocysteine (26):



The reduction of the dimethochloride of bis-[4-dimethylamino-phenyl]-disulphide also responds satisfactorily to the electrolytic method, to yield the corresponding thiol (27):

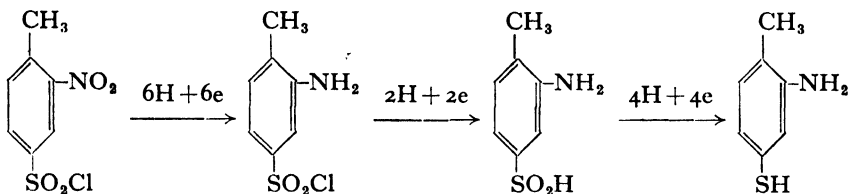


Sulphonyl chlorides are reduced in a stepwise manner, first to the respective sulphinic acid, and thence to the mercaptan. For example, *p*-toluenesulphonyl chloride at a lead electrode in an alcoholic-acid medium is first reduced to *p*-toluene sulphinic acid and then to the mercaptan, thus (28):

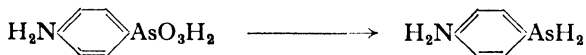


ORGANIC ELECTRODE PROCESSES

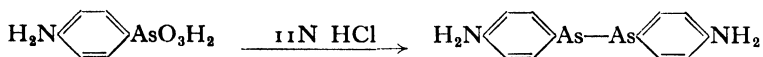
Caution must be used in the isolation of these mercaptans, for they are generally very easily "air oxidized" to the disulphide. It is possible, if there is a nitro group present in the compound, to preferentially reduce it to the amino group at a low potential electrode. Using a higher potential electrode such as lead, will cause both the nitro group and the sulphonyl chloride group to be reduced, according to the following scheme (29):



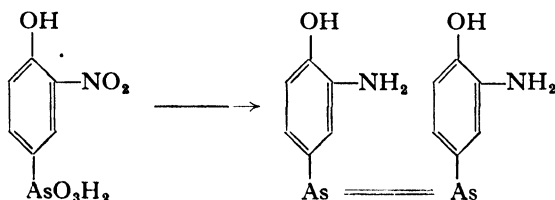
In an acidic medium at a high overpotential electrode such as lead, zinc amalgam, or mercury, arsenic acids will be reduced to the respective arsine, which, in the presence of air, is readily converted to the respective arseno compound. An example is the reduction of 4-aminophenyl-arsonic acid in a 2N aqueous hydrochloric acid medium at a zinc amalgam cathode, to yield 4-aminophenylarsine (30):



With a higher acid concentration (11N) the same compound will yield *p*-arseno-anilin (31):



In a dilute acid medium this product can be reduced back to the 4-aminophenylarsine. An interesting application of the electrolytic process has been in the preparation of Salvarsan (32). The reduction of 3-nitro-4-hydroxyphenylarsonic acid at a mercury cathode yields the 3,3'-diamino 4,4'-dihydroxyarsenobenzene dihydrochloride (Salvarsan):



## (4) DEHALOGENATION

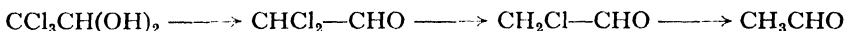
The electrolytic removal of aliphatic halogen poses no great problem and is readily accomplished in an acidic medium with a low overpotential electrode such as copper, which is used to achieve partial dehalogenation, and a high overpotential electrode such as lead or mercury, to obtain complete or further dehalogenation (33). Carbon tetrachloride, when reduced at a copper electrode, will yield chloroform, which can be further reduced to dichloromethane with a lead electrode.



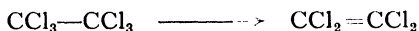
In a similar manner, trichloroacetic acid can be reduced stepwise to chloroacetic acid:



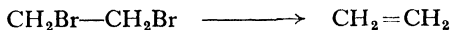
Chloral hydrate responds similarly, to yield acetaldehyde:



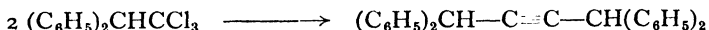
In many instances, especially where the halogen is on adjacent carbons, the unsaturated compound is obtained. Thus hexachloroethane will yield tetrachloroethylene:



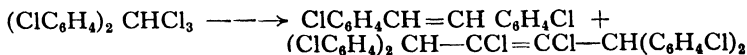
Dibromoethylene will yield ethylene at a lead electrode:



Apparently, if there is halogen present on a terminal position of an aliphatic chain attached to a ring, the compound can, on reduction, dimerize to form either the acetylene or ethylene type compound, thus 1,1,1-trichloro-2,2-diphenylethane can be reduced at a lead electrode, in hot alcoholic-hydrochloric acid, to the tetraphenylbutyne:



Using similar conditions it is possible to obtain a mixture of *p,p'*-dichlorostilbene and 1,1,4,4-(tetrachlorophenyl)-2,3-dichlorobutene-2 from 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl) ethane:

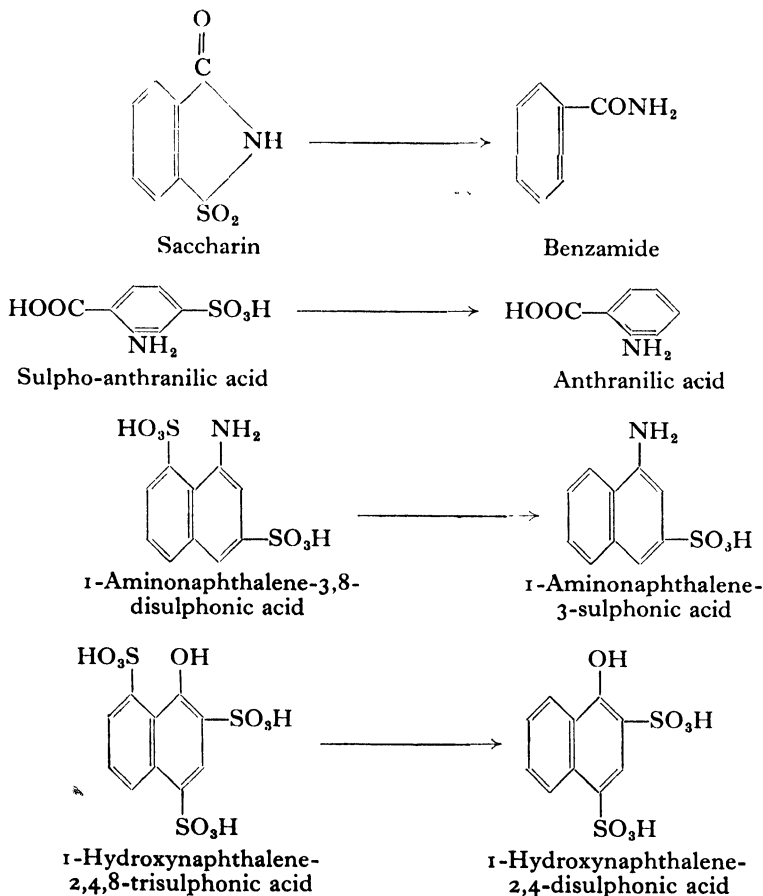


The removal of an aromatic halogen cannot generally be anticipated when utilizing the electrochemical method, although the reduction of bromobenzene to benzene has been reported (34) as well as the reduction of N,N-dimethylaminoethyl tetrachlorophthalimide to the respective trichloroisindoline (35). In such a compound, containing a ring

halogen as well as other reducible groups, one would generally not expect a reduced compound lacking one or more of the originally present halogen atoms.

### (5) DESULPHONATION

There have been a number of patents issued for the desulphonation of aromatic compounds using a high overpotential electrode in a neutral or basic medium, which indicates the practicality of such an electrochemical process in the dyestuff field. The reactions are generally performed in a basic medium at a mercury cathode (36). The following are a few examples illustrating the reaction:





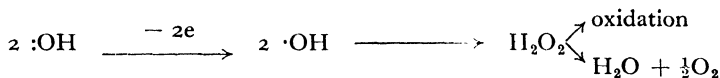
## ORGANIC ELECTRODE PROCESSES

- (12) Brand, *Ber.*, 1909, 42, 3460; Knudsen, *ibid.*, 1909, 42, 3994; Brand and Höing, *Z. Elektrochem.*, 1912, 18, 745; Law, *J. chem. Soc.*, 1912, 101, 154.
- (13) Hoffman, Diss. Giessen, 1914.
- (14) Tafel and Pffermann, *Ber.*, 1902, 35, 1510; Ishibashi, *Mem. Coll. Sci. Kyoto*, 1923, 7A, 39; *Trans. Amer. electrochem. Soc.*, 1924, 45, 335; Anziegin and Gulewivich, *Z. physiol. Chem.*, 1926, 158, 32; Kaplansky, *Ber.*, 1927, 60, 1842; Ruzicka, Goldberg, Hürbin and Boekenooogen, *Helv. Chim. Acta*, 1933, 16, 1329; Sugawara, Satoda, and Yanagisawa, *J. pharm. Soc. Japan*, 1938, 58, 29.
- (15) Tafel and Pffermann, *loc. cit.*, ref. 14.
- (16) Tafel and Pffermann, *Ber.*, 1903, 36, 219.
- (17) Tafel and Pffermann, *Ber.*, 1902, 35, 1512.
- (18) Ahrens, *Z. Elektrochem.*, 1896, 3, 99; Ogura, *Mem. Coll. Sci. Kyoto*, 1929, 12A, 339; Ohta, *Bull. chem. Soc. Japan*, 1942, 17, 485; *J. chem. Soc. Japan*, 1942, 63, 1762.
- (19) McClure and Lowry, *Trans. Amer. electrochem. Soc.*, 56, 445; See also Fichter and Willi, *Helv. Chim. Acta*, 1934, 17, 1416; Takayanagi, *J. chem. Soc. Japan*, 1936, 57, 64.
- (20) Späth, Kuffner and Lintner, *Ber.*, 1936, 69, 2055.
- (21) Späth and Platzer, *Ber.*, 1936, 69, 392.
- (22) Freund and Fleischer, *Liebigs. Ann.*, 1915, 409, 188.
- (23) Tafel, *Liebigs. Ann.*, 1898, 301, 291; Tafel and Naumann, *Ber.*, 1901, 34, 3291; Clemo, Perkin, Jr., and Robinson, *J. chem. Soc.*, 1927, 1589; Gulland, Perkin, Jr., and Robinson, *ibid.*, 1927, 1635; Leuchs and Wegener, *Ber.*, 1930, 63, 2219; Leuchs and Beyer, *ibid.*, 1931, 64, 2157, 2162.
- (24) Price and Twiss, *J. chem. Soc.*, 1908, 93, 1650; 1909, 95, 1052.
- (25) Larsson, *Ber.*, 1928, 61, 1439; *Sv. kem. Tidskr.*, 1928, 40, 149.
- (26) Allen and Steinman, *J. Amer. chem. Soc.*, 1952, 74, 3932.
- (27) Schwarzenbach and Kuden, *Helv. Chim. Acta*, 1939, 22, 371.
- (28) Fichter and Bernoulli, *Z. Elektrochem.*, 1907, 13, 210; Fichter, *Verh. Naturf. Ges. Basel*, 1908, 19, 37; Fichter and Tamm, *Ber.*, 1910, 43, 3032.
- (29) Fichter and Beck, *Ber.*, 1911, 44, 3636.
- (30) Fichter and Elkind, *Ber.*, 1916, 49, 239.
- (31) Matsumiya and Nakata, *Mem. Coll. Sci. Kyoto*, 1927, 10, 199; D.R.P., 270568, 1911; U.S.P., 1713475, 1927.
- (32) Matsumiya and Nakata, *loc. cit.*, ref. 31.
- (33) Fokin, *Z. Elektrochem.*, 1906, 12, 761; Askenasy and Vogelsohn, *ibid.*, 1909, 15, 7773; Brand, *et al.*, *ibid.*, 1910, 16, 669; *Ber.*, 1913, 46, 2938, 2945; 1921, 54, 2017; *J. Prakt. Chem.*, 1930, (2), 127, 240; *Ber.*, 1939, 72, 1029, 1668; Midgley, Jr., Hochwalt and Calingaert, *J. Amer. chem. Soc.*, 1923, 45, 1821; Maynard and Howard, Jr., *J. chem. Soc.*, 1923, 123, 960; Yoshitomi, *J. Pharm. Soc. Japan*, 1924, 3; Streight and Hallonquist, *Trans. Amer. electrochem. Soc.*, 1929, 56, 485; Hood and Imes, *J. phys. Chem.*, 1932, 36, 927; Sandonnini and Borghello, *Atti Accad. naz. Lincei*, 1934, 20, 334; 1935, 21, 30; Riccoboni, *Atti. Ist. Veneto. Sci. Lett.*, 1935, 96II, 183; Melnikow and Rokitzkaja, *J. Chim. gin.*, 1937, 7, 2596; Hein, Klein and Nebe, *Ber.*, 1938, 71, 2381; Plump and Hammet, *Trans. Amer. electrochem. Soc.*, 1938, 73, 523.
- (34) Busch and Weber, *Ber.*, 1937, 70, 744.
- (35) Allen and Ocampo, *Trans. Amer. electrochem. Soc.*, 1956, 103, 682.
- (36) D.R.P., 147228, 1902; 248527, 255724, 1911; B.P., 273043, 1926; Matsui and Sakurada, *Mem. Coll. Sci. Kyoto*, 1932, 15 (A), 151, 181.

## ANODIC OXIDATION

## (1) MECHANISM OF ANODIC OXIDATION

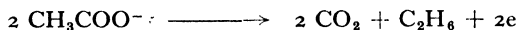
THE oxidation of an organic compound by electrolytic means is in many respects quite similar to the action of a strong oxidizing agent. The exact mechanism involved in the oxidative process is still, however, not a certainty. One proposal was put forth by Glasstone and Hickling (1) in which it was suggested that, in aqueous solution, hydroxyl ions are discharged at low potentials to form hydroxyl radicals, which combine to form hydrogen peroxide. This then may react with the organic depolarizer with resultant oxidation, or it may decompose to give oxygen and water in the following manner:



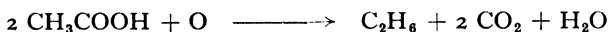
It is also possible that the intermediate hydroxyl radical may be responsible for the oxidation process (2), or that oxygen or the metallic oxides formed at the electrode surface are the responsible agents (3). Where hydroxylation occurs, as will be seen in the oxidation scheme for benzene (Chap. VII), it may very well be that the reaction is due to the presence of hydrogen peroxide or of the hydroxyl radical. However, in instances such as the oxidation of iodate to periodate, which is more readily accomplished at a lead dioxide electrode than at a platinum electrode, it is quite likely that this process is not due to the presence of hydrogen peroxide, but to active oxygen. This assumption is based on the fact that lead dioxide is an excellent agent for the decomposition of hydrogen peroxide. Unfortunately, no one idea explains every reaction, therefore each requires individual study to evaluate the oxidation mechanism. There is no doubt that far more work must be done before the knowledge of anodic processes is on a par with that of the cathode.

**(2) ANODIC OXIDATION OF FATTY ACIDS AND THEIR SALTS**

This is one of the aspects of electrolytic oxidation that has been investigated quite extensively. As early as 1834, Faraday observed that upon electrolysis of an acetate solution he obtained some hydrocarbon (4). However, with the initiation of investigation by Kolbe, detailed results became available. He showed that upon electrolysis of an alkali-metal acetate, a hydrocarbon subsequently known as ethane, and two volumes of carbon dioxide were obtained (5):



This process, known as the Kolbe reaction, was considered by its discoverer to involve the oxidation of the carbonyl group by oxygen obtained from the electrolysis of water:



A further investigation of this reaction by others showed it to be generally applicable to salts of aliphatic monobasic acids (6). The dicarboxylic and aromatic acids were found not to undergo this type reaction.

One of the interesting facts about the reaction is that in an aqueous medium the formation of the hydrocarbon occurs to an appreciable extent only at a smooth platinum or iridium electrode. If a platinized platinum, palladium, gold, nickel, or iron anode is used, the efficiency for hydrocarbon formation is considerably reduced. If a platinized electrode is poisoned with mercury, the efficiency improves tremendously. The presence of catalysts for hydrogen peroxide decomposition, either those which give deposits on the anode, for example lead or manganese salts, or those which do not, for example iron and copper salts, brings about a decrease in the formation of ethane when an aqueous solution of an acetate is submitted to electrolysis. The product in these cases consists essentially of methanol. When using a platinum electrode, the most favourable results are obtained by using temperatures below 50° C. and anode current densities over 0.25 amp./cm.<sup>2</sup>. A high concentration of salt also favours this reaction (7). If low current densities are utilized, paraffins and olefins which possess only half the carbon atoms ordinarily associated with products of the Kolbe reaction are obtained (8).

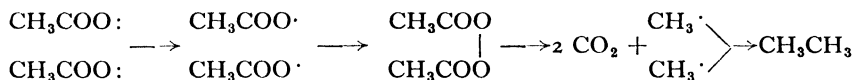
When the conditions are such that the acetate is oxidized to ethane, the anode potential is about + 2.2 volts *v.* S.C.E. However, when the

process is suppressed in favour of methyl alcohol formation, the potential is about + 1.8 volts *v.* S.C.E. The reaction in which alcohols are formed preferentially is referred to as the Hofer-Moest reaction, and is generally favoured by the use of an alkaline solution and by addition to the medium of various inorganic salts, such as perchlorates, sulphates, and bicarbonates (9).

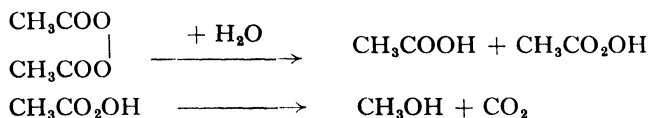
The electrolysis of solutions of the fatty-acid salt in the corresponding anhydrous fatty-acid gives results which are almost identical with those obtained in an aqueous solution (10). Methanol has also been found to be a most suitable solvent for the Kolbe reaction (11). With this medium, apparently, conditions such as electrode material, current density, temperature, and concentration of depolarizer, are not as critical as in an aqueous system. In addition, in this particular medium the yield of Kolbe product is somewhat better. The conductivity of the methanol medium can be improved by the addition of a small amount of water without detracting from its effectiveness in the Kolbe reaction.

#### (a) Mechanism of the Kolbe Reaction

There have been several theories proposed to account for the products obtained as a result of the Kolbe electrosynthesis. The first theory, the peroxide theory, was proposed by Schall and developed by Fichter (12). These investigators were of the opinion that the acetate ions were discharged directly at the anode, and the resulting radicals reacted to form the diacetyl peroxide, which then decomposed to form the alkyl radicals and thence the hydrocarbon:



As alcohols are obtained as side products of the Kolbe reaction, the explanation for their formation was suggested by decomposition of the peroxide to give a per-acid. This per-acid hydrolyzes, especially in an alkaline solution, to yield the alcohol:

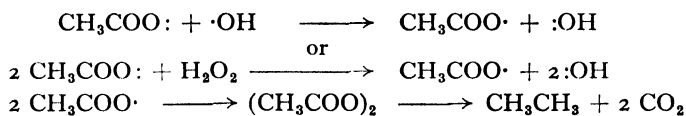


When the Kolbe reaction is carried out in an acidic medium, the

formation of olefins and esters is explained by dehydration of the alcohol, and reaction of the alcohol with the free acid respectively. This is a rather unlikely explanation, as the conditions used in the Kolbe electro-synthesis are generally not conducive chemically to such reactions.

The advocates of the peroxide theory have claimed that, by using low temperatures during their reaction, they have been able to detect small quantities of diacetyl peroxides and per-acids during the electrolytic process (13). This does not necessarily mean that these are bona-fide intermediates in the process, since we may also look upon diacetyl peroxide and the per-acid as by-products obtained under abnormal experimental conditions. The fact, too, that many diacetyl peroxides decompose on heating to give products similar to that obtained in the Kolbe electro-synthesis is also not sufficient evidence for the claim of its being intermediate in the process. The only factor in common between the electrolysis and the decomposition of the diacetyl peroxide by heating is that both presumably yield an alkyl free radical. The effects of anode material, of catalysts for hydrogen peroxide decomposition, and of added salts cannot, however, be readily explained by this theory.

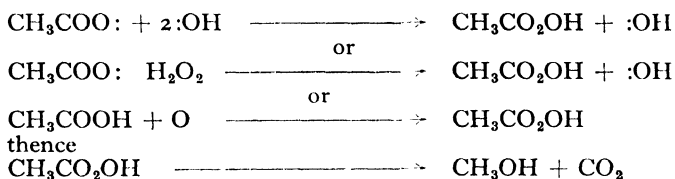
A viewpoint which consolidates some of the essential features of the previously mentioned theory, and at the same time accounts for many of the facts which these theories fail to explain, has been outlined by Glasstone and Hickling, and is referred to as the "Hydrogen Peroxide Theory" (14). As a result of detailed studies of electrolysis of acetates in aqueous solution, these investigators suggested that hydrogen peroxide, which is first formed at the anode from hydroxyl radicals, or these hydroxyl radicals themselves prior to combination in pairs, react with the acetate ions to form acetate radicals. These then combine, possibly with the intermediate formation of diacetyl peroxide, to yield ethane and carbon dioxide, thus:



It is possible that some acetate radicals are formed by the direct discharge of the ions, as is the case in nonaqueous solutions; but an additional mechanism must be introduced, such as the one just proposed, to account for the influence of electrode material and of catalysts for hydrogen peroxide decomposition. It is significant that the anodes,

## ANODIC OXIDATION

at which there is no Kolbe reaction, consist of substances which are either themselves catalysts or which become oxidized to substances which are catalysts for hydrogen peroxide decomposition. Under these conditions, as well as when access of acetate ions to the anode is prevented by the presence of foreign anions, the reactions mentioned presumably do not occur, but instead peracetic acid is probably formed, with subsequent decomposition to methanol and carbon dioxide:



One of the difficulties associated with any theory pertaining to the Kolbe reaction is that of accounting for the fact that, although the potential at which it occurs is so high, oxygen evolution does not take place preferentially. In view of the possibility that normal discharge of a hydroxyl ion leading to the anodic evolution of oxygen results from the transfer of a proton from a molecule of water adsorbed on the electrode surface, it is possible that the water molecules have been largely replaced by acetate ions. The discharge of hydroxyl ions to form oxygen is rendered difficult, and thus it does not occur until the potential is high enough for the discharge of acetate ions, and their detachment from the anode takes place. If the acetate ions are prevented from reaching the electrode by introducing neutral salts, their adsorption is relatively small, and the discharge of hydroxyl ions at the normal potential occurs. The presence of catalysts for hydrogen peroxide decomposition presumably favours the discharge of hydroxyl ions, since they facilitate the formation of oxygen. The low potentials observed under these latter conditions can thus be explained.

In nonaqueous solutions the Kolbe synthesis takes place with high efficiency at platinized platinum and gold, as well as at smooth platinum anodes. Increased temperature and the presence of catalysts for hydrogen peroxide decomposition, both of which have harmful effects in aqueous solution, have relatively little influence. The mechanism of the reaction is apparently quite different in aqueous and nonaqueous solution; in the latter no hydroxyl ions are present, and so neither hydroxyl radicals nor hydrogen peroxide can be formed. It is generally agreed that in the nonaqueous medium the initial anodic process is the discharge of the

acetate ions. If the primary anodic reaction is different in an aqueous and in a nonaqueous medium, it is difficult to explain the fact that the Kolbe reaction with acetates in an anhydrous ethylene glycol medium requires an anodic potential very similar to that for an aqueous solution (15). The resulting radicals probably combine in pairs, as in an aqueous solution, to form acetyl peroxide, which decomposes in a manner already described.

Attempts to duplicate the Kolbe reaction by addition of hydrogen peroxide to solutions of acetates have led to negligible yields of hydrocarbon being obtained (16). This, of course, offers most serious objection to the hydrogen peroxide theory. However, it must be borne in mind that conditions of a chemical experiment are entirely different from those obtained electrochemically. This type of oxidation of acetates has been effected by use of either sodium persulphate or fluorine, with the result that products very similar to those obtained electrochemically were achieved (17). Addition of carbonates to the fluorine reaction medium yields Hofer-Moest type products (18). As in the anodic process, when a catalyst for hydrogen peroxide decomposition is added to the acetate-persulphate mixture, the formation of hydrocarbon is inhibited (19).

Clusius and his associates have contributed a great deal to a better understanding of the mechanism of some of the side reactions associated with the Kolbe reaction. They performed electrolysis of fatty acids in light and heavy water and found, for example, that acetates in an aqueous medium gave methane at low current density, and ethane at high current density. From their experimental results they concluded that the products obtained depended only on the acetate, which was isotopically labelled, and not on the solvent medium (20). Thus the results obtained verify the concept that methyl radicals are formed initially. When these radicals are present in high concentrations, they dimerize to ethane, or, when present in low concentrations, they abstract hydrogen from the acetate ion or acetic acid, to give methane, thus:

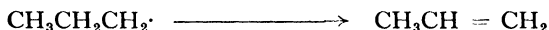


The acetic acid radical is subsequently oxidized to carbon dioxide and water.

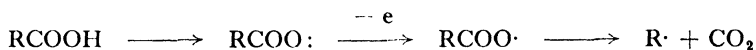
The electrolysis of propionates and butyrates yields an olefin as the main product, and a small quantity of a paraffin composed of the same number of carbon atoms as the olefin (21). Thus the olefin, propene,

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is obtained from the free radical intermediate by elimination of a hydrogen from the  $\beta$ -carbon atom of the acid:

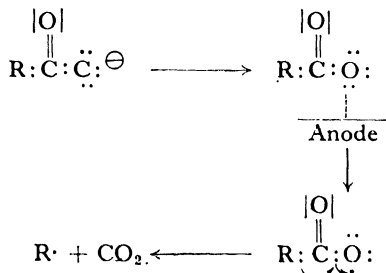


The paraffin obtained in the same reaction was probably produced as a result of some disproportionation of the alkyl free radical. The formation of alkyl free radicals does not preclude the validity of either the peroxide or the hydrogen peroxide theories. However, Clusius is more favourably inclined to the view originally put forth by Brown and Walker (22), that the carboxylate ion is oxidized to the carboxylate radical, which then decarboxylates to yield the alkyl radical:



This free radical mechanism also offers reason for the formation of 4-phenylbenzoic acid and 4-phenylpyridine from the anodic electrolysis of benzoic acid in a pyridine medium (23).

It has been shown (24) that aryl radicals, if produced, tend to attack the solvent molecules with resultant polymerization. This may explain the essential absence of the usual Kolbe dimer when aryl carboxylic acids are subjected to electrolysis. It is quite possible that the mechanism illustrated above holds in both aqueous and nonaqueous media. Therefore it may be that, in either case, we are dealing with a situation analogous to the reductions which give radicals at a high overpotential electrode (Chap. III). At this high overpotential electrode we have a relatively weak anode carboxylate bond, with the result that the molecule remains for a period sufficient only for a one-electron change, with resultant formation of the free radical:



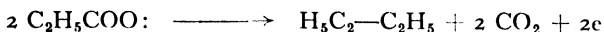
The oxygen atom in this radical tends to fill its octet, thus the R : C bond is weakened, resulting in cleavage to give the alkyl radical and

carbon dioxide. The alkyl radical then either dimerizes or forms the olefin, depending on its concentration in solution.

(b) **Monocarboxylic Acids**

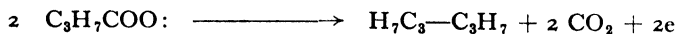
Of the straight chain fatty acids, acetic acid is the only low carbon acid which gives a high yield, of approximately 90 per cent of Kolbe product (25). Comparably good yields are obtained with acids containing six or more carbon atoms (26). The intermediate aliphatic acids give larger quantities of esters, olefins, and other by-products, which can be suppressed in favour of the Kolbe product by use of high concentrations of alkaline salts of the carboxylic acid. Unfortunately, due to the occurrence of side reactions, and the evolution of oxygen, the current efficiency is occasionally quite poor (27).

When propionates are subjected to anodic oxidation, the products obtained consist of ethylene, ethyl propionate, carbon dioxide, oxygen, and butane (28). The latter is anticipated from the Kolbe reaction.



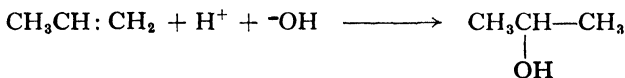
At low current densities the amount of butane formed is quite small. As the current is increased the amount of oxygen evolved at the lower current density diminishes, with formation of an increasing amount of ethylene. Further increase in current density results in the formation of the Kolbe product, butane. Electrolysis of potassium propionate at a gold or smooth platinum anode, in a medium of propionic acid and methanol, will give approximately a 70 per cent yield of butane. However, the former electrode does not give as satisfactory results when used in an aqueous medium (29). When propionates are electrolysed in the presence of inorganic ions, ethyl alcohol is obtained with low efficiency (30), as contrasted with the high yield of methyl alcohol from the electrolysis of acetates.

The products obtained from the electrolysis of salts of normal butyric acid consist of propylene, propyl butyrate, isopropyl butyrate, isopropyl alcohol, hexane, and carbon dioxide (31). The last two compounds are formed by the normal Kolbe process.



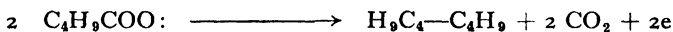
The isopropyl alcohol and its ester obtained from the reaction might very well be attributed to the addition of hydrogen and hydroxyl during the electrolysis.

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Under ordinary circumstances the mere bubbling of propylene through water does not accomplish this result. The isobutyrate gives only a trace of the Kolbe dimer, with the major organic products consisting of isopropyl alcohol, propylene, and hexane (32).

Normal valerates upon electrolysis yield the Kolbe products, octane and carbon dioxide,



in addition to quantities of alcohols, butyl valerates, and various other oxidation products (33). Isovalerates also give the anticipated diisobutyl in addition to other compounds, such as trimethyl carbinol butylenes, etc. (34).

As mentioned previously, the higher fatty acids give quite satisfactory yields of the Kolbe dimer, with paraffin hydrocarbons up to  $\text{C}_{34}\text{H}_{70}$  having been prepared by this method (35). Some of the results compiled by Moser (36) are given in Table I.

TABLE I

*Kolbe Electrolysis of Aliphatic Monobasic Carboxylates*

Acid	Structure	Percentage Yield		
		Paraffin	Olefin	Ester
Acetic .	$\text{CH}_3\text{COOH}$ . .	85	2	2
Propionic .	$\text{C}_2\text{H}_5\text{COOH}$ . .	8	66	5
<i>n</i> -Butyric .	$\text{C}_3\text{H}_7\text{COOH}$ . .	14.5	53	10
<i>iso</i> -Butyric .	$(\text{CH}_3)_2\text{CHCOOH}$ . .	trace	62	10
<i>n</i> -Valeric .	$\text{C}_4\text{H}_9\text{COOH}$ . .	50	18	4
<i>iso</i> -Valeric .	$(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$ . .	43	42	5
Methyl ethyl acetic	$(\text{CH}_3) \left. \begin{array}{l} \text{CHCOOH} \\ \text{C}_2\text{H}_5 \end{array} \right\}$ . .	10	42	10
Trimethyl acetic .	$(\text{CH}_3)_3\text{C COOH}$ . .	13	52	0
Caproic .	$\text{C}_6\text{H}_{11}\text{COOH}$ . .	75	7	1.5
Lauric .	$\text{C}_{11}\text{H}_{23}\text{COOH}$ . .	45	—	—
Myristic .	$\text{C}_{13}\text{H}_{27}\text{COOH}$ . .	33.7	—	—
Palmitic .	$\text{C}_{15}\text{H}_{31}\text{COOH}$ . .	30	—	—
Stearic .	$\text{C}_{17}\text{H}_{35}\text{COOH}$ . .	27.6	—	—

There is no really valid reason as yet as to why there should be any difference in yield of the Kolbe dimer. One opinion offered has been that the differences observed might be due to the ease with which the acid peroxide is hydrolysed. The more readily the hydrolysis occurs, the easier will be the formation of the per-acid, with resultant production of alcohols, esters, and olefins (37).

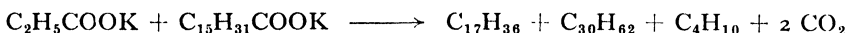
(c) **Mixtures of Carboxylic Acids**

When two carboxylic acids are subjected to anodic electrolysis, three different Kolbe dimers may be anticipated, thus:



The amounts of each dimer formed can more or less be controlled by the relative amounts of each acid present initially in the electrolysis medium. If the concentration of one acid is increased, the conversion of the other acid to the unsymmetrical dimer is improved considerably (38). A considerable difference in the size of the acid molecules can be tolerated; however, if each acid itself is not capable of forming a symmetrical dimer, it will not generally form its unsymmetrical counterpart, although there are a few exceptions to this reported in the literature (39).

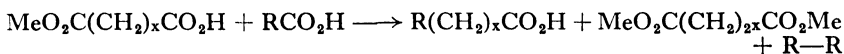
A considerable amount of experimental work has been performed by Matsui and Arakawa (40) in studying the formation of mixed hydrocarbons. These workers performed their experiments in an aqueous alcoholic medium at high current densities and at temperatures of approximately 70° C. It was found, for example, that when a mixture of the potassium salts of propionic acid and palmitic acid, the former being present in a 50 per cent molar excess, was electrolysed, the major component isolated was *n*-heptadecane, in an amount of 40 per cent more than the dimer, triacontane, from palmitic acid. The butane formed went off with the gaseous products.



Mixtures of keto-acids (41), as well as the half-esters (42), also yield the crossed dimer of the keto-acid and half-ester respectively. The coupling of two different types of compounds has been achieved by anodic oxidation, using mixtures of keto acids (43), cyano acids (44), half-esters (45), and phenyl substituted acids (46) with a fatty acid.

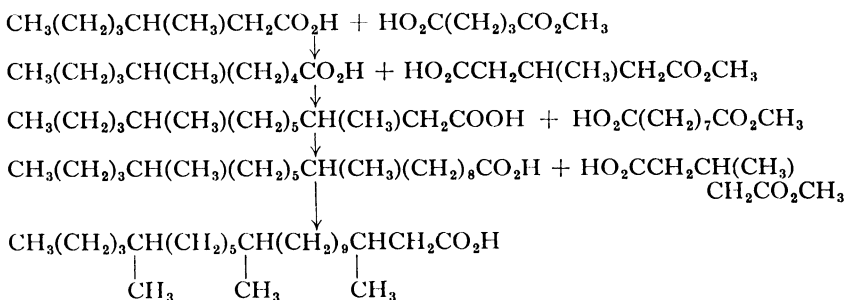
A general method has been developed for the synthesis of unsymmetrical fatty acids which involves coupling a half-ester with a monocarboxylic acid (47).

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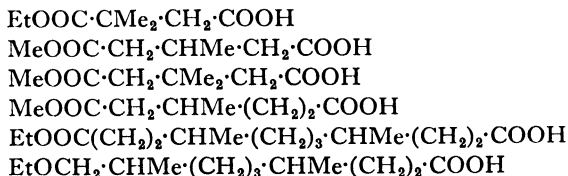
From the mixture consisting of the hydrocarbon and the mono and di-ester, the unsymmetrical acid  $\text{R}(\text{CH}_2)_x\text{CO}_2\text{H}$  can generally be separated by distillation. These same workers have prepared stearic acid by coupling such acids as decanoic with sebacic half-ester and myristic with adipic half-ester. This method has also been applied to the synthesis of trideuteropropionic acid by anodic coupling of the mono ethyl ester of malonic acid and trideuteroacetic acid (48).

The electrochemical method has been found extremely satisfactory for the synthesis of branched-chain fatty acids (49) as found in nature, which have demonstrated marked biological activity (50). One such acid,  $(\pm)$ -3,13,19-trimethyltricosanoic acid, has been reported to cause granulomatous lesions in the guinea-pig (51). This acid has been synthesized from 3-methylheptanoic acid (52), thus:

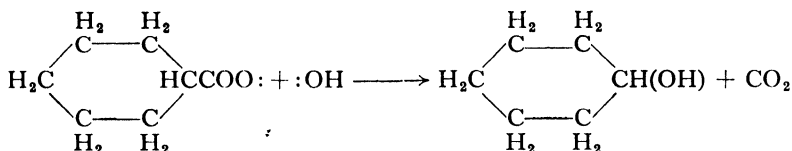


### (d) Branched-Chain Acids and Half-Esters

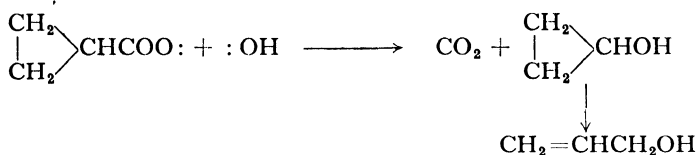
One of the most important restrictions on the type of acid which can be used is that this acid should not be substituted in the  $\alpha$ -position. Although small yields of Kolbe product have reportedly been obtained with such  $\alpha$ -alkyl and cycloalkyl acids (53), far better yields are obtained with acids whose alkyl substituent is well removed from the carboxyl group (54). The following are a few of the substituted acids which give a 50 per cent or better yield of the desired Kolbe product:



The salts of  $\alpha$ -substituted acids, when electrolysed in the presence of potassium carbonate, undergo a reaction similar to the Hofer-Moest reaction, in that the carboxyl group is replaced by a hydroxyl group to give the alcohol. Potassium cyclohexanecarboxylate upon electrolysis yields cyclohexanol (55):



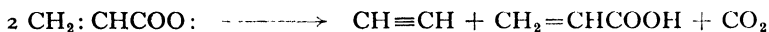
The salt of cyclopropanecarboxylate under similar conditions yields allyl alcohol, with cyclopropanol, its probable intermediate, undergoing an immediate isomeric change to give the isolated alcohol (56).



The other main product isolated from the reaction mixture was the cyclopropane carboxylic acid ester.

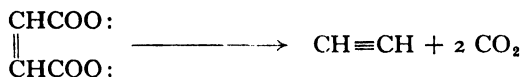
#### (e) Unsaturated Acids

An additional limitation of the Kolbe reaction is that anodic coupling cannot be consummated when either an  $\alpha$ ,  $\beta$  or a  $\beta$ ,  $\gamma$ -unsaturated acid is used. If sodium acrylate were to undergo the normal Kolbe synthesis, the expected product would be butadiene. Instead, however, acetylene is obtained, possibly via the following reaction,



together with quantities of carbon dioxide, carbon monoxide, oxygen, and ethylene (57). The salts of the higher unsaturates undergo a true Kolbe synthesis, to yield the dimer. Thus potassium oleate gives the olefin  $\text{C}_{34}\text{H}_{66}$ , and potassium undecenoate gives  $\text{C}_{20}\text{H}_{38}$  in addition to small quantities of acetylene hydrocarbons (58).

Maleate and fumarate salts, as well as the higher acids, undergo a reaction similar to the Kolbe, to yield acetylene as one of the major products of the reaction (59):



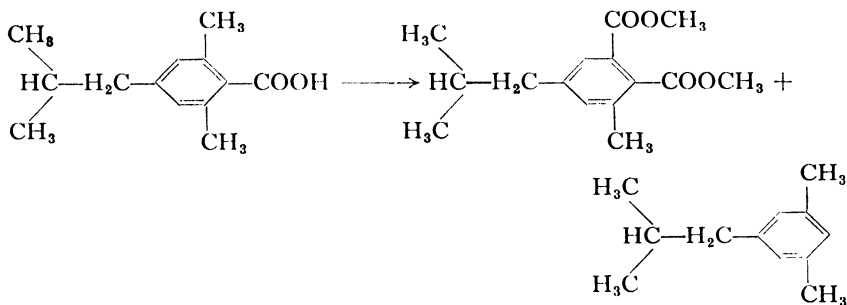
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Thus generally the Kolbe synthesis is not applicable and is of no preparative value with the acids which are unsaturated in the  $\alpha$ ,  $\beta$  or  $\beta$ ,  $\gamma$  positions. Unsaturation in other portions of the molecule results in no interference, and the anticipated products are generally obtained.

### (f) Aromatic Acids

Salts of aromatic acids also do not undergo the Kolbe reaction. When benzoates are subjected to electrolysis traces of acetylene and carbon dioxide are obtained, together with appreciable quantities of oxygen and benzoic acid (60). In a methanolic solution benzoic acid yields benzene (61), and its diethylamine salt in a pyridine medium gives 4-phenyl-pyridine, 4-phenyl-benzoic acid, and traces of diphenyl (62).

When 4-*tert*.-butyl-2,6-dimethylbenzoic acid is subjected to anodic oxidation in a methanolic medium an aromatic hydrocarbon and a substituted phthalic ester are obtained (63):



Upon electrolysis in methanol, or a mixture of pyridine and methanol, both  $\beta$ -phenylpropionic acid and phenylacetic acid will give the usual Kolbe dimer (64).

### (g) Substituted Acids

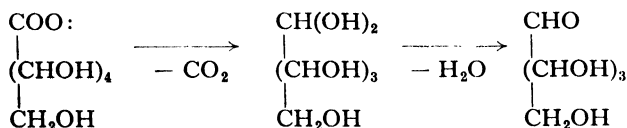
Substituents in the  $\alpha$ -position result in a suppression of the Kolbe reaction, as would be anticipated from the previous discussion of  $\alpha$ -alkyl substituted acids. Negligible dimer formation has been obtained in an aqueous medium on anodic oxidation of hydroxy, amino, halogeno, acetylamino, alkoxy, phenyl, and cyano acids containing the named substituents in the  $\alpha$ -position (65). From the reaction mixtures is generally obtained an unstable  $\alpha$ -substituted acid which decomposes to give an aldehyde or ketone and an ester.

The salts of monochloroacetic acid, for example, yield chlorine, hydrochloric acid, carbon dioxide, carbon monoxide, oxygen, and relatively smaller amounts of chloromethylchloroacetate which can be construed as being obtained via a modified Hofer-Moest reaction. In addition, small quantities of methylene chloride and traces of formaldehyde are also obtained (66).

The  $\alpha$ -amino acids, upon electrolysis, yield an aldehyde or a ketone and ammonia. This is also the case when the amino group is acetylated or sulphonated. It has been shown (67) that aminoacetic acid yields methylamine, ammonia, formaldehyde, formic acid, carbon monoxide, and carbon dioxide. The initial reaction is:



The ammonia and the formaldehyde react to form a mixture of methylamines. In a similar manner  $\alpha$ -hydroxy and  $\alpha$ -alkoxy-acids yield, in addition to other products, aldehydes containing one carbon atom less than the parent compound. For example, glycolic acid yields oxalic acid and formaldehyde (68). If the reaction is performed in an alkaline medium at an iron, copper, or nickel anode, oxalic, glyoxylic, and formic acids are obtained. At a platinum anode, however, the major product is formaldehyde (69). Lactic acid or its salt upon electrolysis yields acetic acid, acetaldehyde, and formic acid (70). If pyruvic acid is the desired product, the copper salt of lactic acid is used, thus giving copper pyruvate which precipitates as it forms, preventing further oxidation (71). A sugar with one carbon less is obtained when a salt of a sugar acid is subjected to electrolysis. For example, D-glucuronic acid yields D-arabinose (72).



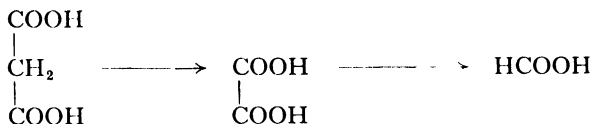
The electrolysis of the substituted fatty acids mentioned above, under the experimental conditions used in this earlier work, cannot be considered ideal in light of more recent investigations, in which anhydrous methanol or methanol-pyridine media were used. With this media,  $\alpha$ -aryloxy and  $\alpha$ -phenyl acids will undergo anodic coupling to yield the Kolbe product (73). On occasion, it is even possible to obtain anodic coupling with  $\alpha$ -acetyl-amino-acids using the same media (74).

## ANODIC OXIDATION

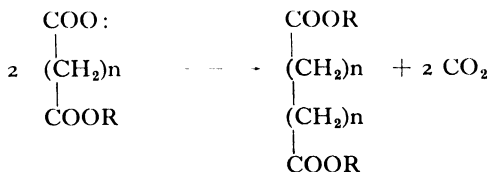
Substituents, which generally do not result in Kolbe products when in the  $\alpha$ -position, exert only a minor effect when removed to another position in the acid molecule. As an example, anodic couplings have been obtained with alkoxy (75), hydroxy (76), keto (77), acylamino (78), amino, cyano (79) acids, and also with aldehyde acid acetals (80).

### (h) Dicarboxylic Acids

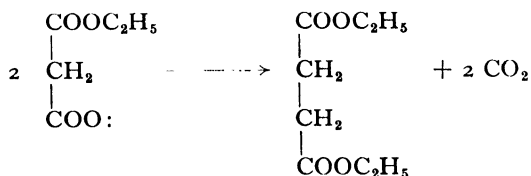
Dicarboxylic acids do not undergo reactions of the Kolbe type, but considerable oxidation occurs, with the result that numerous degradation products are formed. These products include both saturated and unsaturated acids through loss of one carbon atom, and alcohols and olefins containing two carbons less than the original starting material (81). Anodic oxidation of malonic acid at a platinum electrode in an alkaline medium yields oxalic and formic acids:



The alkali salts of the monoester dicarboxylic acid do give a Kolbe type reaction, with the products being higher dicarboxylic acid esters, thus:



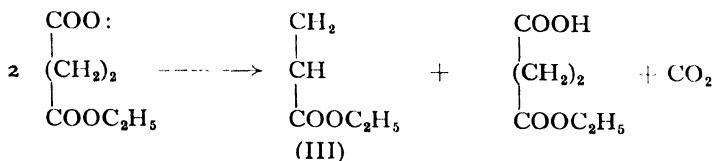
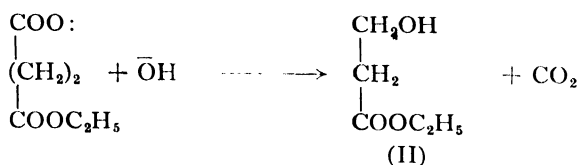
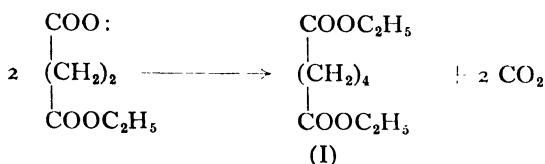
This reaction is generally referred to as the Brown-Walker synthesis (82). For example, the potassium salt of ethyl malonate in aqueous solution yields, upon anodic electrolysis, diethyl succinate:



The higher dicarboxylic acid mono esters also behave in a like manner, thus making this synthesis an excellent tool for the preparation

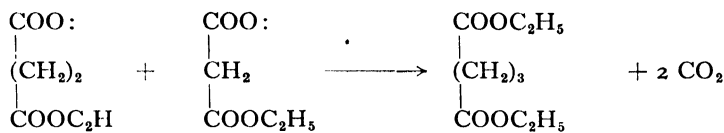
of long chain carboxylic acid diesters (83). The ideal conditions for this reaction are a high current density, high concentrations of the depolarizer, and a low temperature, which are in essence the same as those which favour the formation of ethane in the electrolysis of acetates. As the process is performed in an aqueous medium, the diester formed usually precipitates out, thus making it invulnerable to further oxidation. Since the anolyte must be prevented from becoming alkaline, it is desirable to use a membrane between the anode and cathode compartments. An alternative is to use an excess of carboxylic acid. This reaction has much in common with the Kolbe reaction, in that it does not occur either at a gold or a platinized platinum anode (84). The mechanism of this reaction is probably similar to that of the Kolbe reaction.

As a result of electrolysis of the ester salts, by-products such as olefins and alcohols are formed. For example, ethyl succinate gives, in addition to its major product, diethyl adipate (I), some hydroxyacrylate (II), and ethyl acrylate (III) (85).

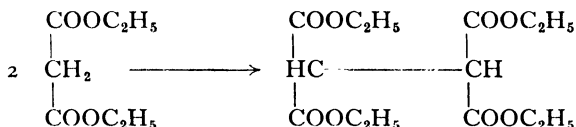


A mixture of two different esters gives an unsymmetrical diester, in addition to the products obtained from each ester separately. Thus, the salts of ethyl succinate and ethyl malonate yields diethylglutarate as the unsymmetrical product in addition to quantities of diethyl adipate and diethyl succinate (86):

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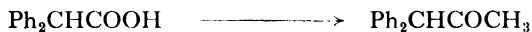
Sodium malonic ester and similar compounds couple in a manner similar to the Kolbe reaction, with the exception that no carbon dioxide is eliminated (87):



(i) **Acetoxylation, Alkoxylation, and Alkylation**

Of interest in connection with the reactivity of acids at the anode is the acetoxylation which has been reported to occur when the mono-, di-, or triphenyl acetic acids are subjected to electrolysis in a sodium acetate-acetic acid medium. Under these conditions the respective phenyl substituted methyl acetate is obtained in satisfactory yield (88). Comparable acetoxylation also takes place when  $\alpha$ -acylamino acids are subjected to electrolysis under similar conditions (89). Anisole gives a mixture of *o*- and *p*-acetoxyanisoles in a 2 : 1 ratio when subjected to electrolysis in a potassium acetate-acetic acid medium at a graphite or platinum anode (90).

Acids can also be alkoxyated in a manner similar to acetoxylation. Thus in a methanolic medium, di- (91) and tri- (92) phenyl acetic acid yield upon electrolysis the respective methyl ethers:



Monophenylacetic acid does not behave in a like manner, but instead gives dibenzyl (93). Anodic electrolysis of *N*-acylglycines and *N*-acyl- $\alpha$ -alanines in an alcoholic medium resulted in excellent yields of the respective amides (94).

It might be of interest to mention that a small quantity of trinitro-*m*-xylene has been isolated from an anodic electrolysis medium consisting of trinitrotoluene in sodium acetate-acetic acid (95):

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The above reaction is possibly the result of a direct attack on the benzene ring by the methyl free radicals formed during the Kolbe reaction.

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# ANODIC OXIDATION OF ALIPHATIC HETEROCYCLIC AND AROMATIC COMPOUNDS

## (1) OXIDATION OF ALIPHATIC COMPOUNDS

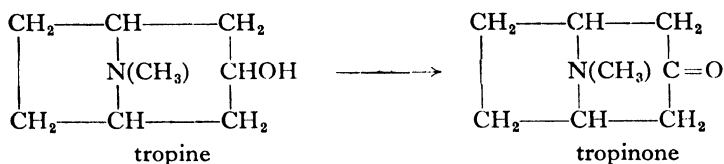
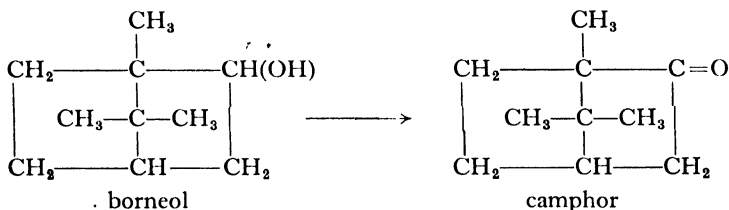
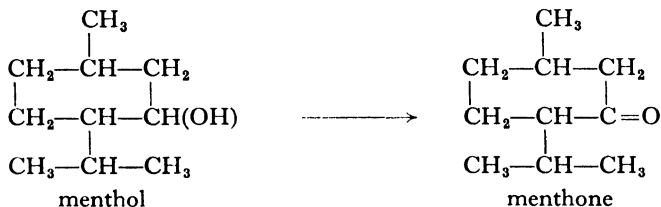
THE straightforward oxidation of aliphatic compounds does not generally lead to as interesting results as one would like, simply because the powerful effects of anodic oxidation have not as yet been completely mastered. Considerable care must be exercised in applying this technique, for it is much too easy to obtain carbon dioxide and water as end products. Considerable investigation has been done on the effects of anodic oxidation on the alcohols, aldehydes, ketones, sugars, and acids. A survey of this work may serve as a clue to future efforts.

### (a) Alcohols

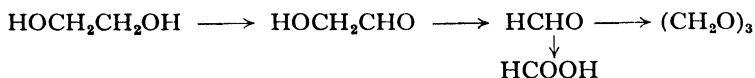
The anodic oxidation of an alcohol in an acidic medium generally leads to the formation of an aldehyde, with subsequent oxidation to the acid (1). To obtain the aldehyde it is necessary to utilize low current densities, or, if high current densities are used, it is necessary to perform the reaction at elevated temperatures, in order that the aldehyde may distill off as it is formed, and thus be protected from further oxidation (2). Should it be desired to oxidize the alcohol to the acid, precautions must be taken to keep the intermediate aldehyde which is formed in solution, in order to enable its further oxidation. Thus a dilute sulphuric acid solution of ethanol can be oxidized to acetic acid using a platinum electrode, a current density of 0.2 amp./cm.<sup>2</sup>, and maintaining the temperature at approximately 30° C. The current efficiency in this instance is about 78 per cent (3). Anodic oxidation of isopropyl alcohol under comparable conditions yields acetone. These results duplicate those obtained by chemical means (4).



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In an acid electrolyte at a lead dioxide electrode, glycol yields glycol aldehyde, glycolic acid, formaldehyde, trioxymethylene, a polymer of formaldehyde, formic acid, and a small quantity of a hexose, depending on the electrolysis conditions (12).



(b) Aldehydes

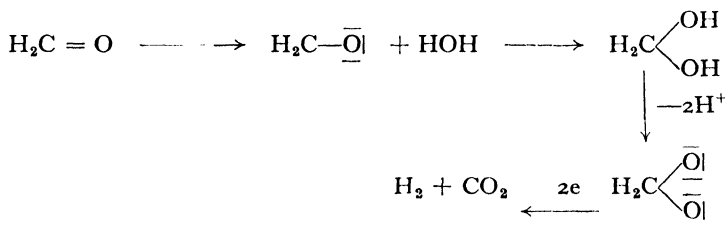
In an acid medium the aldehydes are generally oxidized to their corresponding acids, with some evolution of carbon monoxide and dioxide. Thus from acetaldehyde and propionaldehyde, acetic acid and propionic acid are the respective predominating products (13). In a basic medium acetaldehyde will give a satisfactory yield of formic acid (14), with the higher aldehydes giving some amount of saturated hydrocarbon (15). Of interest are the results obtained when formaldehyde is subjected to anodic electrolysis in a basic medium at a platinum anode. In this case there is no gas evolution observed at the anode. However, if a copper anode is substituted for the platinum anode,

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hydrogen is formed at the anode in an amount equal to that at the cathode, thus (16):



The mechanism proposed for this reaction assumes an initial hydration of the formaldehyde, followed by the formation of an ion which decomposes to hydrogen and carbon dioxide:



This result can also be obtained by utilizing anodes coated with finely divided copper or silver. However, in these instances, the evolution of hydrogen from the anode is spasmodic. The proposed mechanism is open to question since it is known that some metal oxides will catalytically decompose formaldehyde in a basic medium, with resultant hydrogen formation (17).

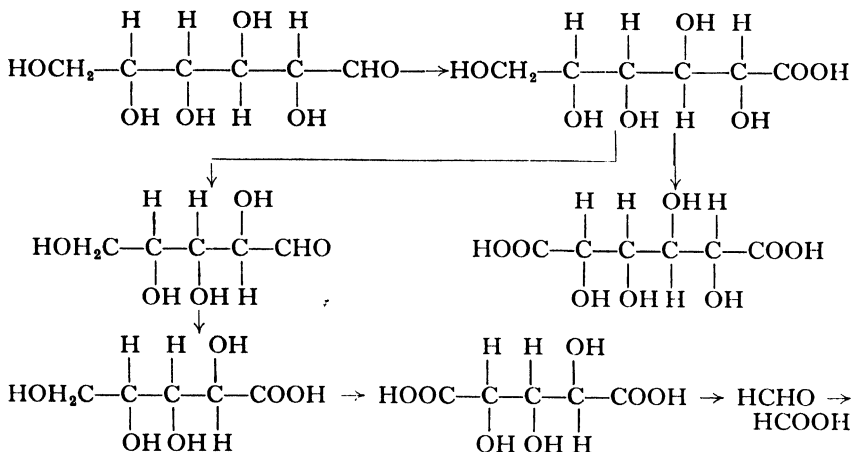
### (c) Ketones

To date very little effort has been devoted to the effects of anodic oxidation on aliphatic ketones. Utilizing a platinum anode at low current densities in an acid medium, acetone will yield acetic and formic acids (18). At higher current densities, in addition to the aforementioned acids, methane, ethane, unsaturated hydrocarbons, mesityl oxide, carbon dioxide and monoxide are obtained (19). Similar results were also obtained using an alternating current (20).

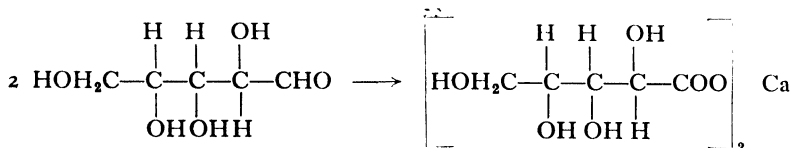
### (d) Sugars

Considerable effort has been put forth on the effects of anodic oxidation of sugars. One of the earlier investigations involved the oxidation of glucose at a lead dioxide anode in an aqueous-sulphuric acid medium (21). The results led the investigator to suggest that the initial oxidation resulted in a degradation of the molecule to gluconic acid which then oxidized to both arabinose and saccharic acid. The arabinose was further oxidized to its acid, thence to trihydroxyglutaric acid, formaldehyde, and finally formic acid, thus:

ORGANIC ELECTRODE PROCESSES



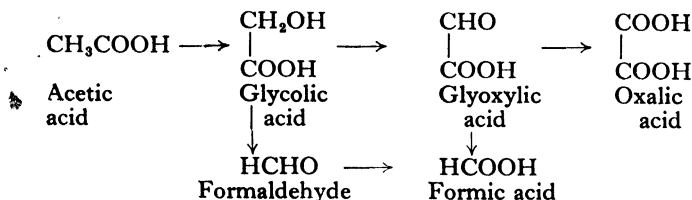
It was found that in a medium containing calcium carbonate and a small quantity of calcium bromide, arabinose could be oxidized at a platinum anode to the calcium salt of its acid (22):



The oxidation of xylose, 3-methyl-glucose, mannose, galactose, and maltose to their respective acids has been reported with varying results (23).

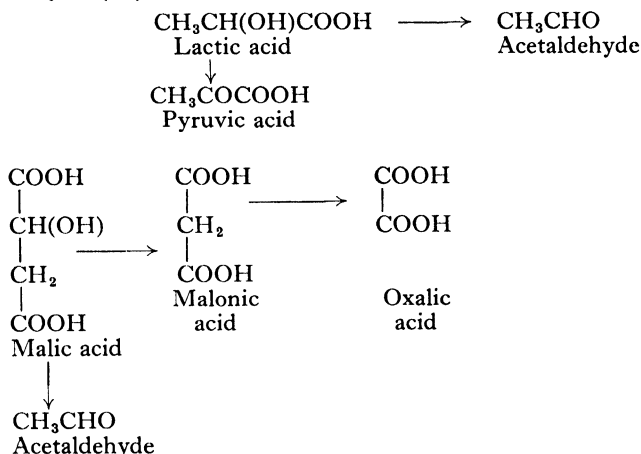
(e) Carboxylic Acids

In the previous chapter the Kolbe synthesis was discussed. However, in passing it might be of interest to briefly mention the straightforward oxidations that occur when a carboxylic acid is subjected to anodic oxidation at a platinum anode in a sulphuric acid medium. Acetic acid can be oxidized to glycolic acid, glyoxylic acid, and thence to oxalic acid, with formaldehyde and formic acid as side products (24):



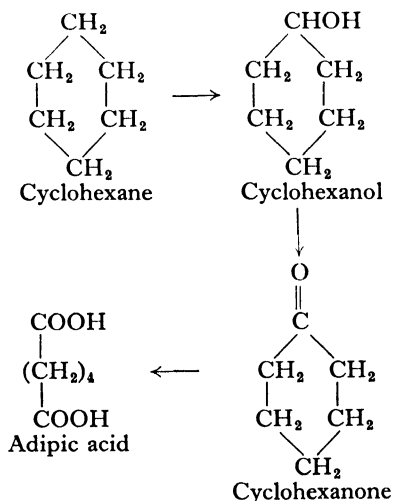
## ANODIC OXIDATION

In a similar manner lactic acid has been oxidized to acetaldehyde, and pyruvic acid (25), and malic acid to malonic acid and oxalic acid or acetaldehyde (26).



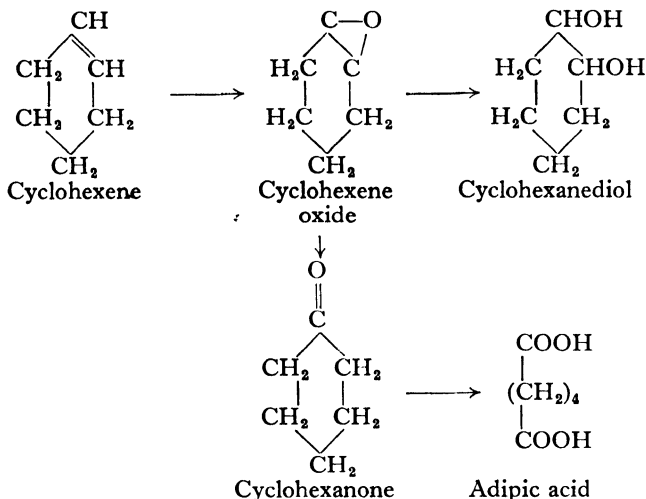
### (f) Alicyclic Compounds

Compounds of this type are quite amenable to anodic oxidation, and in many instances, under controlled conditions, will yield the desired product. Thus cyclohexane in a sulphuric acid medium at a lead dioxide anode will yield cyclohexanol, cyclohexanone, and ultimately under more drastic conditions, adipic acid, thus (27):

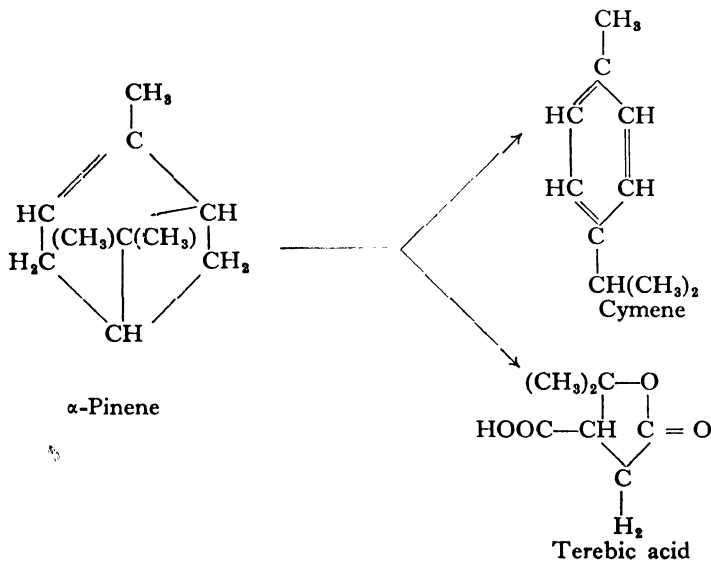


ORGANIC ELECTRODE PROCESSES

Under similar conditions the same investigators oxidized cyclohexene and obtained the following products:



Cymene has been prepared by anodic oxidation of  $\alpha$ -pinene, using a lead dioxide anode and performing the reaction in a dilute aqueous sulphuric acid medium (28). The side reaction in this anodic process leads to terebic acid.

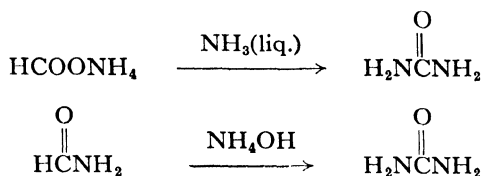


## ANODIC OXIDATION

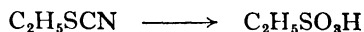
The anodic oxidation of the hydroxy group of borneol, menthol, and tropine, with the resultant isolation of the ketonic compounds camphor, menthone, and tropinone respectively, has already been mentioned (p. 117). In spite of the relative complexity of the molecule, the yield of ketone is quite good, indicating that the electrolytic process can be a nondestructive one.

### (g) Miscellaneous Aliphatic Anodic Oxidations

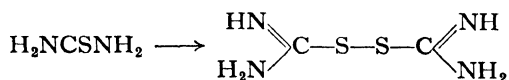
Ammonium formate and formamide will, on oxidation in liquid ammonia or in an ammonium hydroxide medium at a platinum anode, yield urea in satisfactory quantities (29):



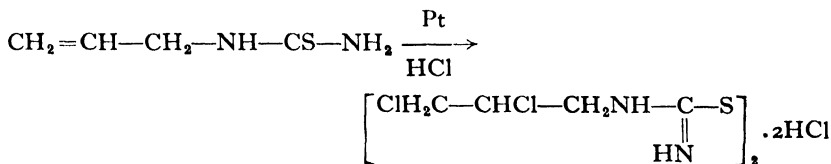
Under comparable conditions, ammonium acetate will also give urea (30). Ethyl thiocyanate, when oxidized in an acetic-hydrochloric acid medium at a platinum anode, will yield ethyl sulphonic acid (31):



Formamidine disulphide has been obtained as a salt from the anodic oxidation of thiourea in an acid medium at a platinum electrode (32). The salt obtained depends on the acid used in the electrolysis medium.



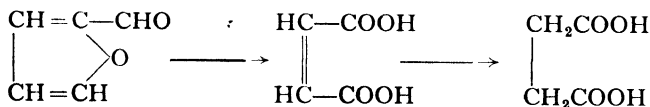
A 50 per cent yield of *bis*-( $\beta$ - $\gamma$ -dichlorophenyl)-formamidine disulphide dihydrochloride has been claimed from the anodic oxidation of allyl thiourea (33):



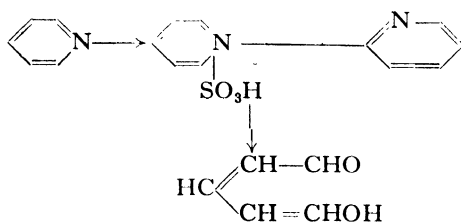
In addition, the above reaction also involves anodic halogenation, which will be discussed in greater detail later.

**(2) OXIDATION OF HETEROCYCLIC COMPOUNDS**

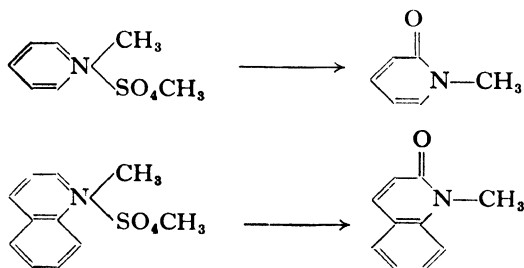
Compounds of this type can give interesting and useful products, if the techniques of anodic oxidation are applied with caution. Under rigorous conditions the oxidation will yield only small fragments of the starting product. Anodic oxidation of furfuraldehyde in a dilute sulphuric acid medium at a lead dioxide anode yields maleic acid. If the electrolysis is performed without a diaphragm succinic acid is obtained as a result of reduction of the double bond (34).



Pyridine at a platinum anode in an aqueous sulphuric acid medium yields 2-pyridyl-pyridinium sulphate, which then gives glutaconaldehyde (35), thus:



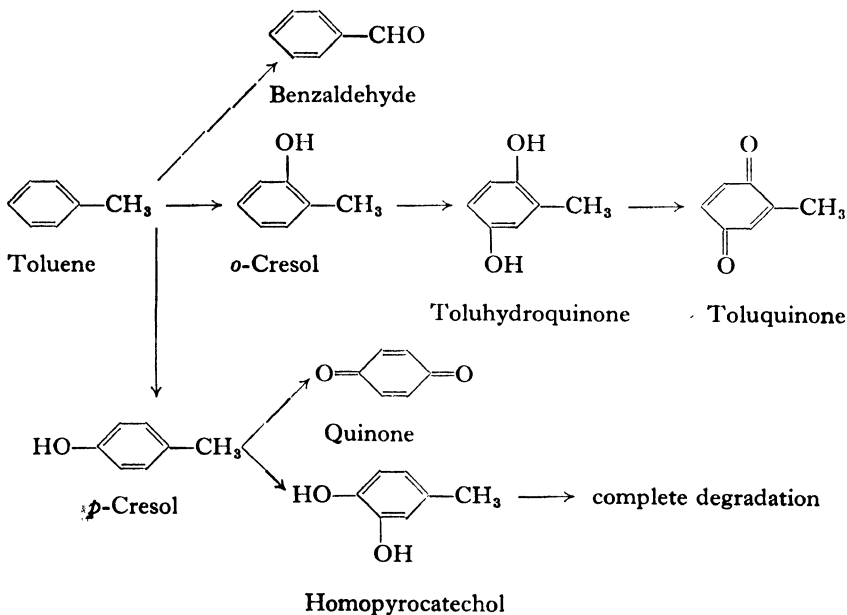
If a lead dioxide anode is used, complete decomposition occurs, with the products consisting of a mixture of formaldehyde, formic acid, methyl amine, ammonia, nitric acid, carbon monoxide and dioxide (36). Anodic oxidation of methyl N-methyl-pyridinium sulphate and methyl N-methyl-quinolinium sulphate in a basic medium at an iron electrode in the presence of a small amount of potassium ferricyanide will result in good yields of N-methyl- $\alpha$ -pyridone and N-methyl quinolone respectively (37):





quinone and catechol which can be obtained using a platinum, lead dioxide, or graphite anode in a sulphuric acid medium or a phosphoric acid medium (42). Phenol, however, can be obtained in small yields by electrolysis of benzene in an acetic acid-sodium acetate medium using a platinum anode (43). Catechol, too, can only be detected in small amounts, as it is easily decomposed at the anode. It is not too difficult to obtain high yields of quinone by performing the electrolysis on an aqueous sodium sulphate or sodium acetate suspension of benzene, using a lead dioxide anode (44). The quinone is readily converted to hydroquinone by performing the electrolysis without a diaphragm. A method which has been proposed for the preparation of hydroquinone involves an anodic oxidation of a suspension of benzene in an acetic-sulphuric acid medium, which is then passed into the cathode compartment containing a lead or zinc electrode together with a finely divided lead sulphate catalyst (45). Further oxidation of quinone yields maleic acid as well as other decomposition products (46).

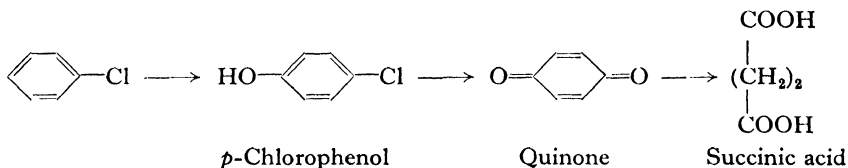
Another aromatic which has been investigated quite extensively is toluene. According to the information available as to the oxidation products obtained (47), the following scheme can be used to represent the oxidative process:



## ANODIC OXIDATION

The initial investigations of toluene indicated that the aromatic ring was quite resistant to oxidative change. However, it was found that the methyl group underwent oxidation more readily, to yield benzaldehyde (48). There are indications that benzyl alcohol is intermediate to the formation of the aldehyde, but, as the alcohol is quite unstable, it is immediately oxidized to the more stable benzaldehyde (49). Benzaldehyde may be obtained in approximately 20 per cent yield by anodic oxidation at a platinum anode and at low temperature, from an emulsion of toluene in a mixture of dilute nitric and acetic acids (50). This yield can be improved considerably by the use of an oxygen carrier (51). Similar results were obtained when toluene was dissolved or "salted-in" in an aqueous solution containing sodium xylenesulphonate (52). Other oxidative products, such as benzoic acid, are also to be found in the reaction products, together with hydroxylated derivatives of toluene, such as *o*-cresol and *p*-cresol, which are intermediate to the formation of toluquinone and quinone (53). Toluquinone can be further oxidized at a lead dioxide anode to a mixture of acids consisting of formic, mesaconic, and maleic acid (54).

Oxidation of chlorobenzene proceeds according to the following scheme:

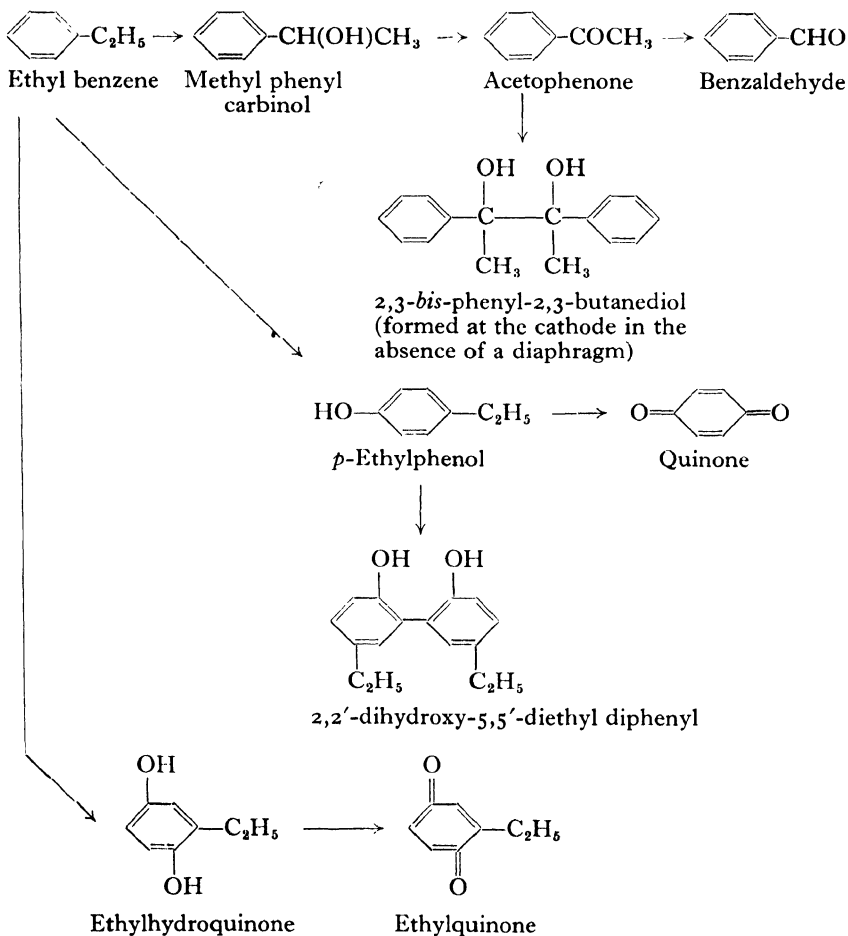


The succinic acid is only obtained in the absence of a diaphragm (55). Treatment of *p*-fluortoluol in a similar manner yields *p*-fluorbenzoic acid in approximately 10 per cent yield, with the remainder being essentially decomposition products (56). The oxidation of *p*-chlortoluene to *p*-chlorbenzoic acid in an acetic-nitric acid medium at a platinum anode has been reported (57). In this instance the value of electrolysis is questionable, as the nitric acid itself can oxidize *p*-chlorotoluene to the respective benzoic acid derivative. The anodic oxidation of *p*-nitrotoluene in an acetic-sulphuric acid medium using a platinum anode will give a 40 per cent yield of *p*-nitrobenzyl alcohol, in addition to smaller quantities of *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid (58).

Ethylbenzene yields numerous products, either as a direct result of

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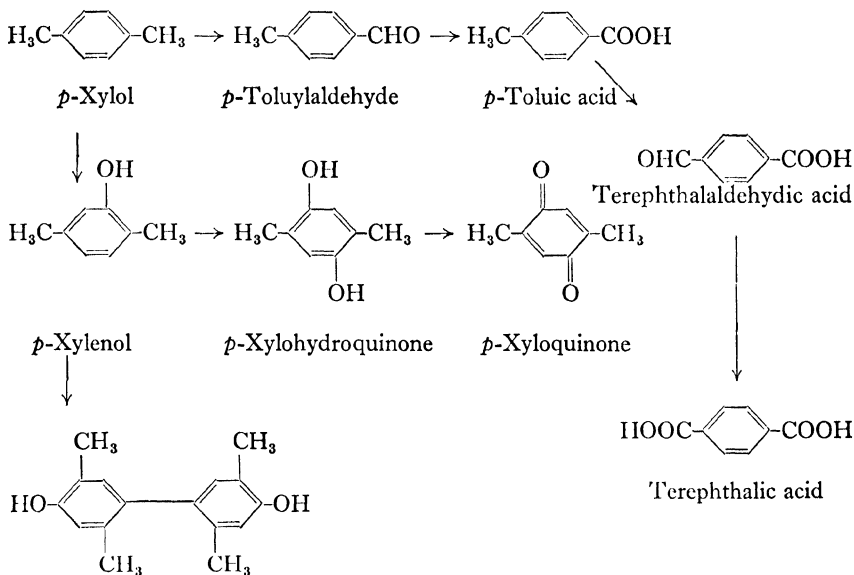
oxidation as a suspension in a dilute sulphuric acid medium at a lead dioxide anode, or as a consequence of secondary reactions (59). The following scheme illustrates the reaction paths:



The oxidation of 2,4-dinitrotoluene at a lead dioxide anode in a dilute aqueous sulphuric acid medium at temperatures of 90 to 95° C. will give approximately 26 per cent, 2,4-dinitrobenzoic acid (60). This yield can be considerably improved (74 per cent yield) by using a platinum anode, a 50 per cent aqueous sulphuric acid medium, a temperature of 75° C., and 2 per cent chromic acid as a catalyst (61).

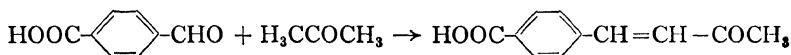
## ANODIC OXIDATION

The anodic oxidation of the xylols has also been extensively investigated (62). The products obtained can be illustrated by the scheme for *p*-xylol.



4,4'-dihydroxy-2,5,2',5'-tetramethyl-diphenyl

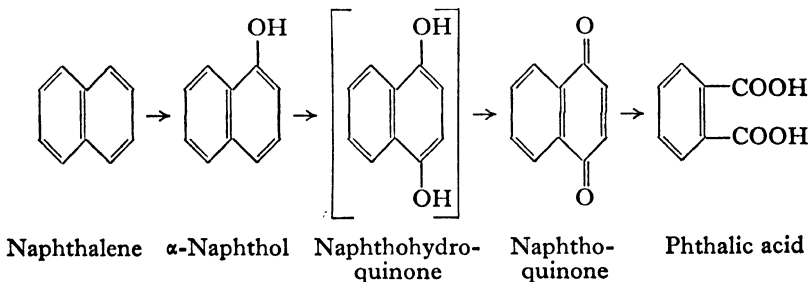
It is not unreasonable to express the opinion, at this point, that the diphenyl compounds formed in these instances, and in the illustrated example on the oxidation of ethyl benzene, came about as a result of free-radical formation. It is also of interest to mention that if the oxidation of *p*-xylene is performed in the presence of acetone the terephthalaldehydic acid condenses with the acetone, to form *p*-carboxy-benzal acetone, thus:



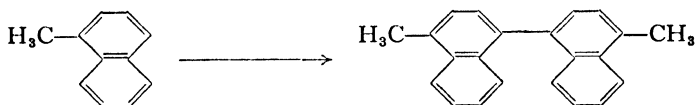
The oxidation of naphthalene will yield  $\alpha$ -naphthol, naphthoquinone, and finally phthalic acid, when the reaction is performed on a suspension of the material in a dilute sulphuric acid medium (63). The efficiency of this reaction is, as with all emulsion type reactions, extremely poor. However, the addition of an oxygen carrier such as  $\text{Ce}(\text{SO}_4)_2$  improves

ORGANIC ELECTRODE PROCESSES

the efficiency considerably (64). The process is illustrated in the following reaction scheme:



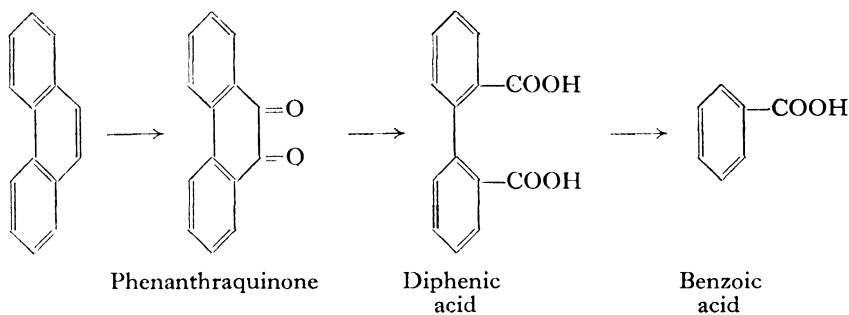
When  $\alpha$ -methyl naphthalene is oxidized anodically in an acidic acetone medium at a lead dioxide electrode, the methyl group is apparently unattacked, with the major reaction product being 1,1'-dimethyl-4,4'-dinaphthyl (65):



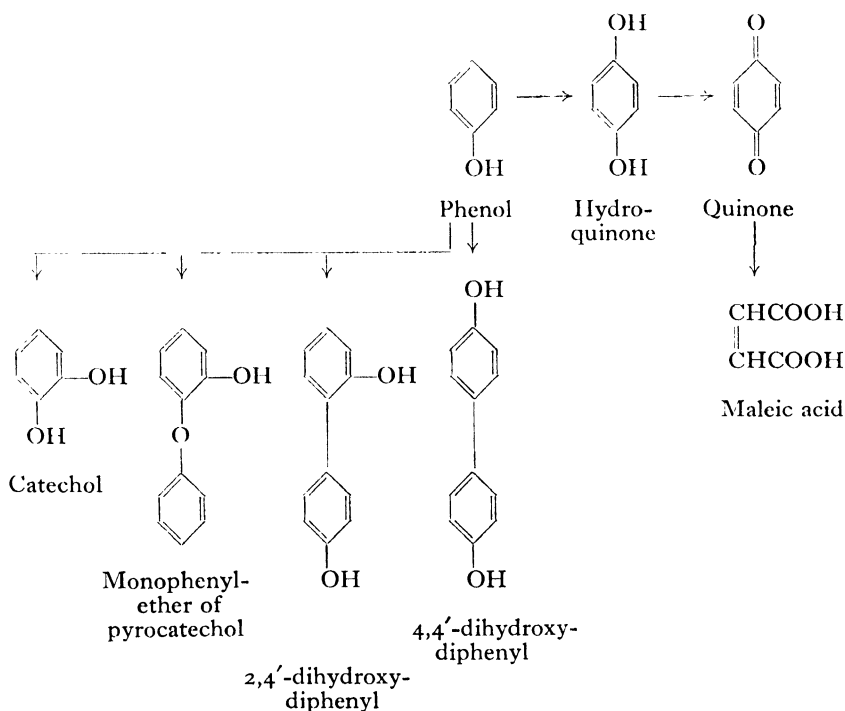
The electrolytic oxidation of anthracene to anthraquinone is of considerable importance, as the latter compound is an intermediate in the production of alizarin (66). The oxidation of a suspension of anthracene occurred with approximately 50 per cent efficiency when the reaction was performed at a platinum anode at 40° C., with current densities of from 0.01 to 0.03 amp./cm.<sup>2</sup>, in an acetone-sulphuric acid medium. The efficiency of this process was increased to more than 80 per cent by the addition of small quantities of either cerium, chromium, or manganese salts, which served as oxygen carriers. Similar results have also been obtained with a lead dioxide anode and a 20 per cent sulphuric acid medium (67). Phenanthrene, upon oxidation in the presence of an oxygen carrier, will yield phenanthraquinone, which, on further oxidation, will yield diphenic and benzoic acids (68) (p. 131).

As previously shown in the discussions on benzene oxidation, hydroxylated intermediates are formed prior to the quinone type compounds. It was found that when phenol was oxidized at a lead dioxide electrode in a sulphuric acid medium, diphenyl compounds, probably attributable to free-radical formation, were also formed. As a result of

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the various investigations (69) the following is the reaction process involved in the oxidation of phenol.

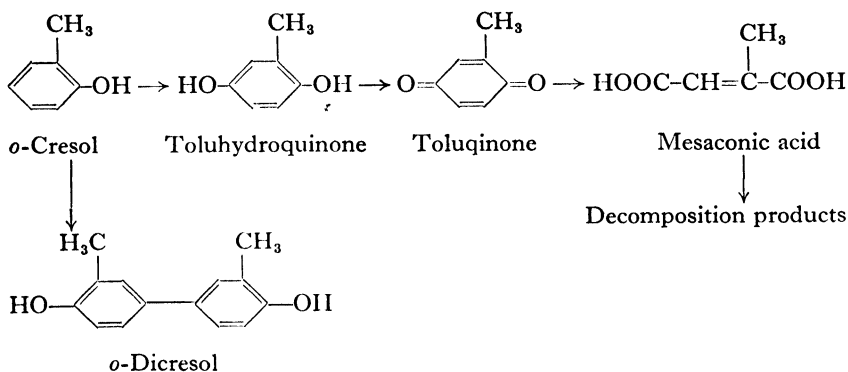


One group of investigators demonstrated that the nature of the products obtained in the oxidation of phenol depends to a great extent on the current density used (70). This being the case, it is not unreason-

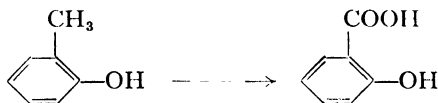
## ORGANIC ELECTRODE PROCESSES

able to assume that the reaction path is dependent on the potential at the electrode surface.

The anodic oxidation of *o*-cresol at a lead dioxide electrode in a sulphuric acid medium results in the formation of the following products (71):



It is claimed (72) that anodic oxidation of *o*-cresol in a concentrated alkali hydroxide at a lead or copper anode will give a good yield of salicylic acid.



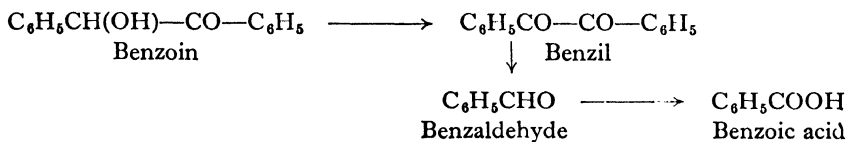
Benzyl alcohol in an aqueous sodium carbonate medium at a platinum anode will give a high yield of benzoic acid (73). However, at a nickel anode in a sodium benzenesulphonic acid medium, a mixture of benzaldehyde and benzoic acid is obtained (74), which is what might be expected of this lower potential anode. As it is known that benzaldehyde is quite susceptible to air-oxidation, it may be in this instance that the acid obtained is a result of air-oxidation, and not a direct consequence of the electrolysis.

### (a) Aromatic Aldehydes and Ketones

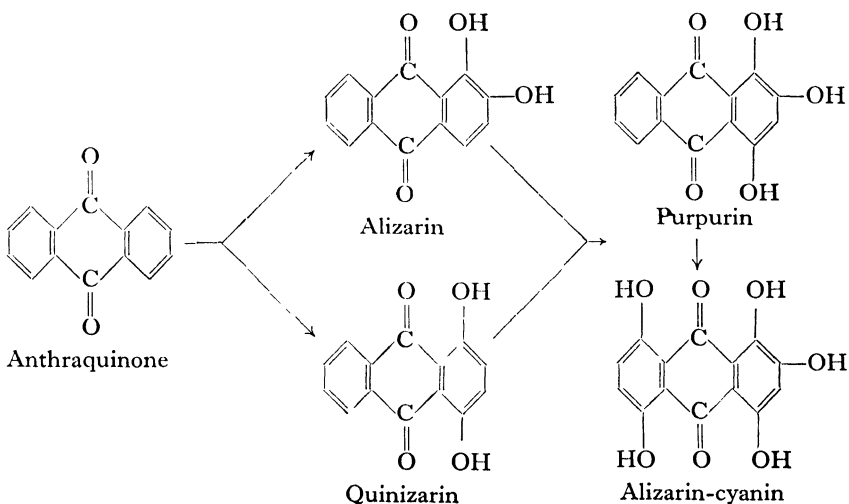
The anodic oxidation of aromatic aldehydes and ketones offers generally a synthetic route of little interest. Benzaldehyde can be oxidized almost quantitatively to benzoic acid, utilizing a copper oxide

## ANODIC OXIDATION

anode and an aqueous sodium benzenesulphonic acid medium (75). In an acetone-sulphuric acid medium, benzoin is oxidized in a stepwise manner according to the following scheme (76):



This oxidation, when performed in an alcoholic-sodium hydroxide medium, yields only a small quantity of benzoic acid. In this instance the poor yield can possibly be attributed to the reactivity of the carbonyl groups in a basic medium, with resultant formation of condensation products. In an alcoholic-hydrochloric acid medium an excellent yield of benzil is obtained (77). Of interest is the oxidation of anthraquinone to give a mixture of alizarin and quinizarin in 90 per cent yield, when the electrolysis is performed at a platinum anode in a concentrated sulphuric acid medium. In addition there are obtained smaller quantities of further oxidation products such as purpurin and alizarin-cyanin (78).

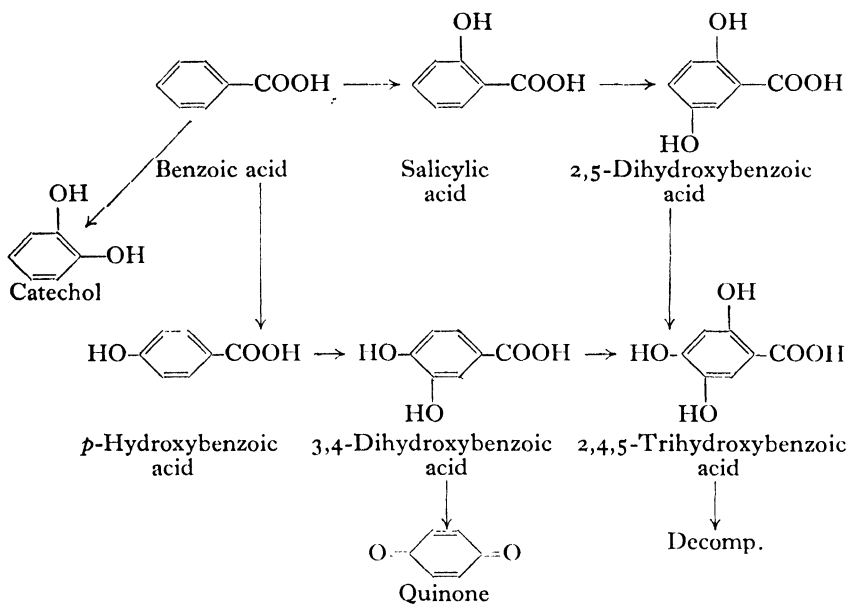


### (b) Aromatic Carboxylic Acids

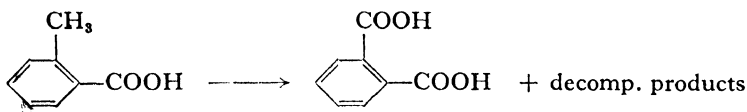
As in other types of aromatic compounds discussed, the initial step in the anodic oxidation of an aromatic acid is the introduction of a

hydroxyl group, either *ortho* or *para* to the carboxyl group. This is followed by further hydroxylation, with eventual decomposition upon too prolonged an exposure to electrolysis.

The oxidation of benzoic acid at a platinum anode in a dilute sulphuric acid medium illustrates the aforementioned (79):



The reports indicate that the isolation of any one particular compound is not large enough to make this an interesting preparative method. Of passing interest is the anodic oxidation of *o*-toluic acid at a lead dioxide anode in an acetone-sulphuric acid medium to yield approximately 5 per cent phthalic acid, plus a considerable quantity of decomposition products (80):

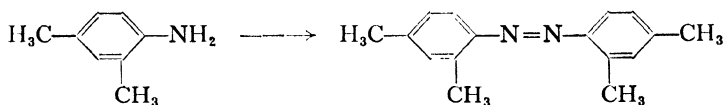


Similar conditions of electrolysis, when used on *p*-toluic acid, result in approximately 14 per cent terephthalic acid (81).

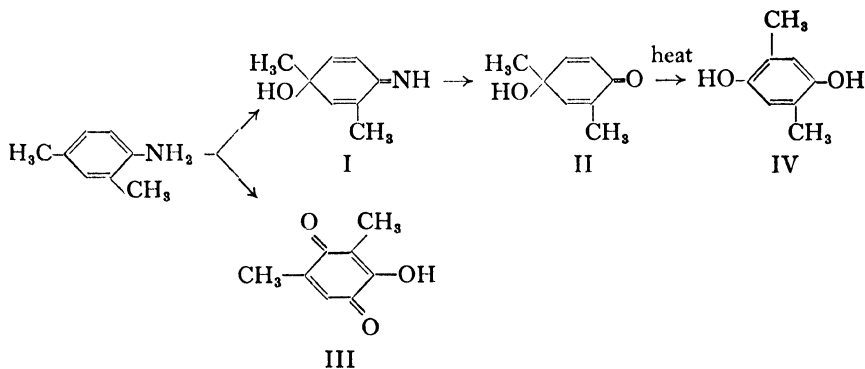
## (c) Miscellaneous Aromatic Oxidations

The electrochemical oxidation of a methyl group attached to an aromatic nucleus is considerably facilitated by the presence of a cyano-group in the molecule. Thus ortho-, meta-, and para-tolunitrile when oxidized at a lead dioxide anode in a sulphuric acid or acetone-sulphuric acid medium will give the respective cyanobenzoic acid in yields of 6.2 per cent, 28 per cent, and 37 per cent respectively. In addition, the para-tolunitrile also yields approximately 8 per cent of terephthalic acid (82).

Primary aromatic amines, when subjected to anodic oxidation, generally yield imines or azo compounds, depending on conditions of electrolysis. Thus the electrolytic oxidation of asymmetric *m*-xylylene at an iron anode in an alcoholic potassium hydroxide medium will yield azo-*m*-xylene (83):

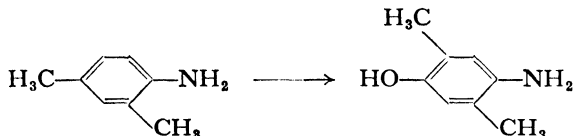


Utilizing a lead dioxide or a platinum anode and a dilute sulphuric acid medium the products obtained consist of approximately 50 per cent imino-2,4-dimethylquinol (I), 20 to 30 per cent 2,4-dimethylquinol (II), and a small quantity of 3-hydroxy-2,6-dimethylbenzoquinone-(1,4) (III). If elevated temperatures are used, the major product obtained is *p*-xyloquinone (IV), thus (84):



In a concentrated sulphuric acid medium the amino group is

apparently unaffected, with the major product being 4-amino-2,5-xyleneol:

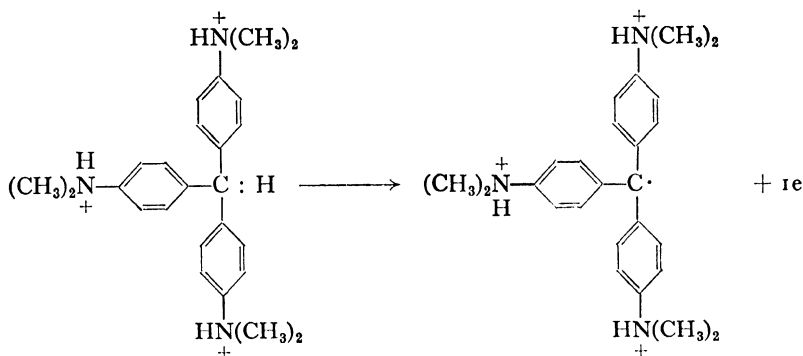


The secondary and tertiary amines are not as vulnerable to attacks as are the primary amines. The electrolytic oxidation of such compounds has been of interest in the dye-stuff industry. The anodic oxidation of the leuco-base of malachite green to malachite green has been accomplished, using a nickel anode in a dilute sulphuric acid medium containing a catalytic quantity of uranyl sulphate as an oxygen carrier (85):



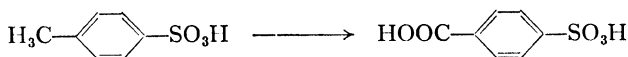
It might be of interest to mention that one investigator (86) has developed a method in which the leuco-base was impregnated into the cloth fibres and then submitted to anodic oxidation. The leuco-base of brilliant green has also been oxidized anodically by pressing the reduced form of the dye into the pores of a carbon anode and performing the electrolysis in an aqueous sodium sulphate medium (87). There is no doubt that the oxidation of the leuco-bases proceeds through a free-radical mechanism. This was demonstrated chemically by Michaelis *et al.* (88), who demonstrated that organic dyestuffs undergo a two-step oxidation. The first is the half-oxidized form or free radical, and the second is the completely oxidized or quinoid form. These investigators also found these changes to be *pH* dependent. This phenomenon was also found to be the same at an electrode surface. Investigations at a rotating platinum micro-electrode showed that when the leuco-bases of either crystal violet or malachite green are subjected to electrolysis in a strongly acidic aqueous hydrochloric acid medium, only a one-electron change occurred. The product in the case of the leuco-base of crystal violet gave every indication of being the free-radical tris-(*p*:*p*':*p*"-dimethylamino)triphenylmethyl trihydrochloride, thus (89):

ANODIC OXIDATION

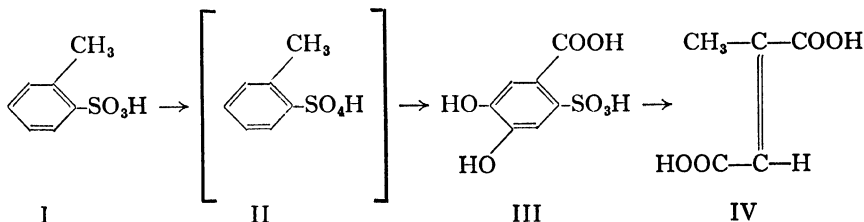


It is very possible that the free radical obtained could not be further oxidized to the quinoid form at the low *pH* used in the investigation. All the nitrogens were in the ammonium ion form, and thus the lower oxidation state was stabilized. However, as soon as the *pH* was raised, the free radical oxidized readily in the presence of air to the quinoid form. This indicates that under less acidic conditions the unshared pair of electrons from one of the nitrogen atoms was made available for contribution to the formation of a quinoid form, thus permitting a higher state of oxidation.

The toluenesulphonic acids are readily oxidized anodically at a lead dioxide electrode, to yield a sulphobenzoic acid. Thus *p*-toluenesulphonic acid, when subjected to electrolysis in a 20 per cent sulphuric acid medium at 50° to 60° C., results in a 30 per cent yield of *p*-sulphobenzoic acid, plus quantities of other degradation products (90):

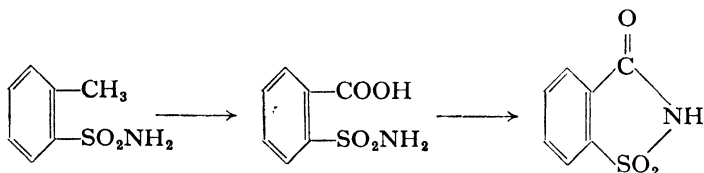


Anodic oxidation of *o*-toluene sulphonic acid (I) is claimed to give a per-acid intermediate (II), which then is further oxidized to a hydroxylated carboxylic-sulphonic acid, 3,4-dihydroxy-6-sulphobenzoic acid (III), and finally to mesaconic acid (IV) (91):



## ORGANIC ELECTRODE PROCESSES

In connection with the oxidation of toluene sulphonic acids it might be of interest to briefly discuss the anodic oxidation of *o*-toluene-sulphonamide to saccharin. In this process the sulphonamide is oxidized to the *o*-carboxyl-sulphonamide, which then loses a mole of water to form the saccharin:



The first reported process (92) utilized a 10 per cent solution of sodium *o*-toluene-sulphonamide in a 2 per cent solution of sodium hydroxide at current densities of 0.5 to 0.9 amp./cm.<sup>2</sup>. As other conditions were not specified, the validity of this method was questionable. Subsequent investigation, however, demonstrated that oxidation of *o*-toluene-sulphonamide could readily be accomplished using a platinum anode in a 2N sodium carbonate medium at a temperature of 60° C. (93). In this process it was found unnecessary to use a membrane to separate the anolyte from catholyte if a lead cathode were used. This procedure was reported to result in a 40 per cent yield of saccharin. Addition of an oxygen carrier resulted in an increase to a 75 per cent yield (94). Thus with the attainment of such satisfactory yields the preparation of saccharin by an electrolytic process has become a practical procedure.

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- (2) Moser, *op. cit.*, p. 65
- (3) D.R.P., 274032, 1911; Askenasy, Leiser and Grünstein, *Z. Elektrochem.*, 1909, **15**, 846; *Trans. Amer. electrochem. Soc.*, 1924, **45**, 129.
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## ANODIC SUBSTITUTION

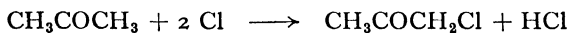
ANOTHER phase of electro-organic chemistry that has been studied, but not as extensively as electrolytic oxidations and reductions, is the process of anodic substitution. However, there are certain fundamental factors which are understood to be intimately related to these processes. Firstly, in anodic substitution there is no net change in electrons in the substitution product. Secondly, the hydrogen atom in the molecule is replaced by another atom or group, such as a halogen atom or nitro group, which has been freed from the solution by the electrolytic process. There are generally considered to be three processes by which such a substitution may occur. The first may be due to oxidation of a substance in solution to yield an active agent which attacks the organic compound. This type of process would be essentially electro-chemical in nature, and may be affected by the anode potential, current density, and electrode material. In this instance, too, the compound should behave as a typical depolarizer, by lowering the anode potential, and the products obtained may differ from those obtained by ordinary chemical methods. The second process would be analogous to a chemical reaction, with the current merely functioning as a release mechanism for the substituting agent from a solution of one of its compounds. Thus, for example, the liberation of bromine from a solution of a bromide salt is only dependent on the passage of current as a generating agent, and generally its ability to act as a substituting agent is independent of the anode potential and the electrode material. The net result in this instance would be essentially the same as if bromine gas were bubbled through a solution of the organic compound. A third process associated with the substitution reaction may be related predominantly to the concentration of an active specie at the anode surface, which enables substitution to occur where, under ordinary conditions of concentration, such a reaction would not result. To

illustrate this point we can consider a suspension of naphthalene in a dilute aqueous solution of nitric acid. Under ordinary circumstances no noticeable reaction results. However, with the passage of an electric current, nitro-naphthalene is obtained at the anode. This end result can be attributed not to the discharge of the nitrate ions at the electrode, but to the large concentration of these ions at the electrode surface. In this instance the factors generally associated with an anodic oxidation or a cathodic reduction, i.e. electrode potential and electrode material, would be of minor consequence as compared to the current density and the diffusion coefficient of the organic compound subjected to anodic substitution.

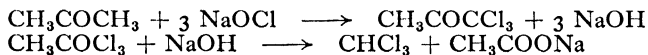
### (1) ANODIC HALOGENATION

It might be desirable, before discussing the reactions themselves, to briefly outline some aspects of anodic halogenation. If a halogen solution is subjected to electrolysis at an electrode such as platinum containing a trace of iridium or rhodium to render the electrode inert to the corrosive action of free halogen, the liberation of halogen will occur generally at the decomposition potential of the halogen in solution. Thus, the liberation of iodine, bromine, and chlorine should occur at a potential of about 0.52, 0.94, and 1.31 volts respectively. However, if there is present in solution a depolarizer which is capable of reacting with the halogen being liberated, the potential for halogen liberation will be somewhat lower. With the proper regulation of the anode potential, there is, in most instances, little danger of obtaining a mixed reaction. Although several values have been obtained for the decomposition potential of water, a steady evolution of oxygen and hydrogen is only obtained at about 1.7 volts. At this potential the hydroxyl ions are discharged at the anode with the formation of water and the evolution of gaseous oxygen. However, there is always the possibility that the substance being subjected to anodic substitution may also be a satisfactory oxygen depolarizer, with the final result a product which has undergone both anodic oxidation and substitution. If the anodic substitution is performed in a basic medium there is a certain degree of polarization which leads to oxygen evolution, with the result that the product obtained is a consequence of dual action. This is especially so in instances in which the organic depolarizer is not present in sufficient quantity to react immediately with the liberated halogen. In this situation the halogen reacts with the hydroxyl ion to form a hypo-

halogen acid (HOX) which can act both as a halogenating agent and an oxidizing agent. This is especially true in a concentrated basic medium where the oxygen potential is quite low, and therefore the halogen liberated readily forms hypohalous ions. An example of the different action in acid and alkaline solution is found in the electrolysis of solutions of acetone. In a dilute hydrochloric acid medium, monochloroacetone is obtained.



In an alkaline medium the reaction does not stop at the monohalogen substitution product, but continues on to form a trihalogen derivative, thus:

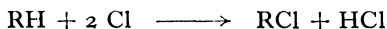


Therefore, before attempting an anodic halogenation, considerable thought should be given to the experimental condition prior to onset of an investigation.

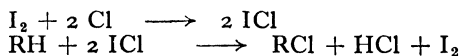
#### (a) Chlorination

The addition of chlorine to organic depolarizers has been the subject of detailed investigation by a number of workers (1). As a result of their experimental findings it is possible to elucidate three different mechanisms which may serve to explain the process of anodic chlorination which results from the conversion of chlorine ions to atomic chlorine.

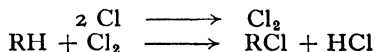
The first mechanism proposed is that the liberated chlorine reacts directly with the organic compound in the following manner:



In the second instance, if a carrier such as iodine were added to the electrolysis medium the reaction would proceed in the following way:



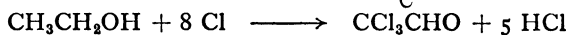
Lastly, the chlorine atom might combine with another of its kind to form gaseous chlorine, which would then react to yield the halogenated compound:



It may well be that in the first two proposed mechanisms the anode potential will be lowered. However, in the last mentioned instance, the

addition of the organic substance should have no effect on the anode potential. Therefore, this process will be essentially comparable to a chemical addition of chlorine gas to a solution of the organic compound. Unfortunately, though we may theorize in subsequent discussions, there are to date no clear cut examples which would definitely prove an anodic chlorination to be purely electrochemical in nature.

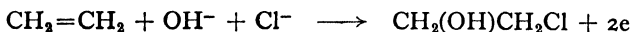
The first record of the introduction of a halogen in place of hydrogen was reported as far back as 1830 by Lüdersdorf (2), who electrolysed a mixture of ethyl alcohol and concentrated hydrochloric acid, with the resultant separation of a heavy oily layer possessing a sweet ethereal odour. This product was probably chloral, whose commercial preparation from ethanol has been reported (3), using a carbon anode and an aqueous hydrochloric acid or potassium chloride medium at a temperature of 100° C. The chloral distills off, thus preventing its further oxidation. More recently the preparation of chloral with a 61 per cent efficiency was reported (4), using aqueous potassium chloride as the anolyte, a carbon anode, a copper cathode, a current density of 0.08 amp./dm.<sup>2</sup>, and a temperature of 70° to 80° C. A subsequent group of investigators (5) found they were unable to obtain the efficiency claimed by the previous investigator (4) and, therefore, conducted a more systematic study on the preparation of chloral using a porous carbon tube as an anode, a copper cathode and various chloride media. They pointed out that the reaction involves the simultaneous anodic oxidation of alcohol and substitution of chlorine, thus:



These, as well as the previously mentioned investigators, also reported the complication of the over-all reaction process by the possible side reactions which yielded chloral alcoholate, monochloroacetic acid, ethyl acetate, monochloroacetaldehyde hydrate and its alcoholate, and chloroether. The last three named compounds were considered to be intermediates in the production of chloral. According to their findings they concluded that a viscous solution of calcium chloride, plus a catalytic quantity of cyanuric acid at reflux temperature gave best results. An excessive amount of water in the medium caused a decrease in yield. Additional findings showed that platinum was a more effective anode than carbon, with the maximum current efficiency obtained being 61 per cent. They claimed from the results obtained that the anode potential is the main controlling factor in the process. However, the

experimental evidence presented does not quite substantiate this claim.

Another interesting chlorine derivative of alcohol is ethylene chlorohydrin, which is obtained by passing ethylene into the anode compartment of an electrolysis cell in which chlorine is being liberated, as a result of the electrolysis of either an aqueous hydrochloric acid or sodium chloride solution. The reaction is performed at a temperature of 100° C., with improved yields being obtained by the addition of catalytic amounts of either charcoal or platinum black (6). Recently a group of investigators (7) conducted detailed studies on this particular reaction, using porous carbon tubes as anodes, and a sodium chloride solution as the electrolyte. They report that in this reaction both ethylene chlorohydrin and ethylene glycol are produced, the yields depending on the experimental conditions. The over-all reaction involves essentially a simultaneous oxidation and chlorine addition:

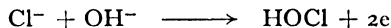


The conditions resulting in the optimum yield of ethylene chlorohydrin (84 per cent) involved the use of a 10 per cent solution of sodium chloride, a flow rate of 5.55 litres of ethylene/hour/dm.<sup>2</sup> of anode surface, and a current density of 2.25 amp./dm.<sup>2</sup> at a temperature of 1° C. At a temperature of 90° C. the recorded yield dropped to 1 per cent. At this temperature the quantity of glycol obtained amounted to 17 per cent, whereas at 1° C. a 5 per cent yield of glycol was obtained. The evidence presented indicates that a higher electrode potential is necessary in order to obtain the optimum yield of ethylene chlorohydrin. Lower electrode potentials favour the formation of ethylene glycol. In this instance it appears that ethylene is a better depolarizer for oxygen than for chlorine; thus the reason for oxidation of ethylene to its respective glycol at the lower potential.

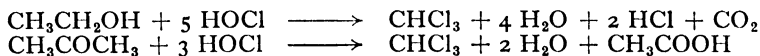
The early methods for the preparation of chloroform which involved the electrolysis of a dilute alkaline chloride solution resulted mainly in the oxidation of the alcohol, with the chloroform obtained being a minor side product (8). These results are not unexpected in view of the considerably lower oxygen liberation potential in an alkaline medium as compared to that in an acidic medium. Some improvement in yield was obtained using an aqueous calcium chloride medium at a current density of 0.08 amp./cm.<sup>2</sup>, and a temperature of 50° to 70° C. (9). In this manner the alkalinity of the medium was controlled as a result of the precipitation as calcium hydroxide. However, there is disadvantage

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here, too, in the fact that the calcium hydroxide tends to occlude the passage of current by plating on the electrode. One investigator (10) conducted quite an extensive survey of the conditions necessary to obtain chloroform by electrolysis. Utilizing a platinum anode, a current density of approximately 1 amp./cm.<sup>2</sup>, and Roush neutralization cathode (11), and an electrolysis medium containing a 20 per cent solution of potassium chloride, yielded chloroform with current efficiencies from 65 to 75 per cent. This method was satisfactory for the conversion of both ethanol and acetone. However, when ethanol was being converted it was possible to utilize temperatures of approximately 30° C., whereas with acetone, a temperature of 15° C. was found more desirable. Feyer further found that a current efficiency as high as 95 per cent from ethanol or acetone is possible, if a nickel or copper electrode, which is first etched by nitric acid, is used as the cathode in an aqueous calcium chloride medium. The calcium hydroxide which formed on this type of cathode did not cause occlusion of the electrode surface, with the result that the resistance to the passage of current remained low. We may look upon the general reaction in the following manner. The initial step can be considered electrochemical, thus:



The hypochlorite formed reacts chemically with the ethanol or the acetone to yield the desired compound in the following manner:



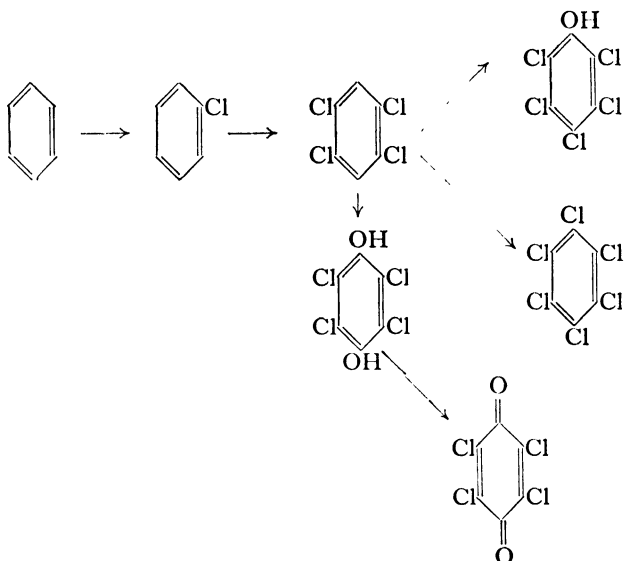
A number of other modifications in the electrolyte have been reported (12), but without any advantage over that discussed previously. Propyl alcohol, as well as methyl ethyl ketone, when subjected to electrolysis in a calcium or potassium chloride medium, reportedly also yields chloroform (13). Electrolysis of acetone in a concentrated hydrochloric acid medium, utilizing a platinum anode and a membrane to separate the anode and cathode compartments, results in satisfactory yields of chloroacetone (14). Propionic acid under similar conditions will yield predominantly  $\beta$ -chloropropionic acid, with a small quantity of  $\alpha$ -chloropropionic acid (15).

In studies on the anodic halogenation of aromatic compounds it was thought that it might be much easier to distinguish the electrochemical halogenation process from the purely chemical one. However, the

results are such that here, too, there is available no clear picture from which one can form a definite opinion concerning the process involved. When dealing with a suspension of the organic compound to be substituted, there is very little likelihood of a true electrochemical process. The anodic chlorination of benzene was first attempted on a suspension in concentrated hydrochloric acid, from which was obtained a small quantity of an oily chlorinated product, with the balance of the material being unchanged benzene (16). This investigator found that the addition of iodine did not improve the experimental results. However, subsequent research (17) showed, for example, that when benzene was electrolysed as a suspension in aqueous hydrochloric acid, especially in the presence of a carrier such as iodine, chlorobenzene was obtained with efficiencies as high as 75 per cent. A group of Indian investigators (18) found they were able to obtain current efficiencies as high as 89 per cent utilizing a porous carbon anode, a medium consisting of benzene in a hydrochloric acid-monochloroacetic acid solution, a current density of 4.3 amp./dm.<sup>2</sup>, a temperature of 38° C., and a catalytic amount of cyanuric acid. These results cannot, however, be attributed to an electrochemical phenomenon, as it is possible to obtain almost as satisfactory yields by direct chemical chlorination of benzene. If one were to obtain an appreciable amount of a further chloro-substituted benzene, then this might be considered an electrochemical process. Van Name and Maryott (19) made a careful study of the effects of anodic electrolysis of benzene in an acetic acid-lithium chloride medium, and in an ether-zinc chloride medium, using graphite as electrodes. The results obtained were very discordant, which made impossible any conclusion as to whether the process which yielded various chlorobenzenes was strictly anodic. A subsequent investigation on the anodic substitution of benzene by another group of workers (20) claimed that the contradictory results obtained by the previous investigators could be directly attributed to the non-homogeneity of the benzene in the electrolyte. The results obtained from electrolysis of benzene in a glacial acetic-hydrochloric acid medium left no doubt in these authors' minds that the processes which yielded the different chloro-substituted products under varying current density conditions were electro-chemical in nature. Utilizing suitable conditions it was possible to achieve maximum chlorination, although the products obtained were always somewhat contaminated by quantities of oxidation products. In addition to chloro-, *p*-dichloro-, *sym*-tetrachloro-, and hexachlorobenzene, such

## ANODIC SUBSTITUTION

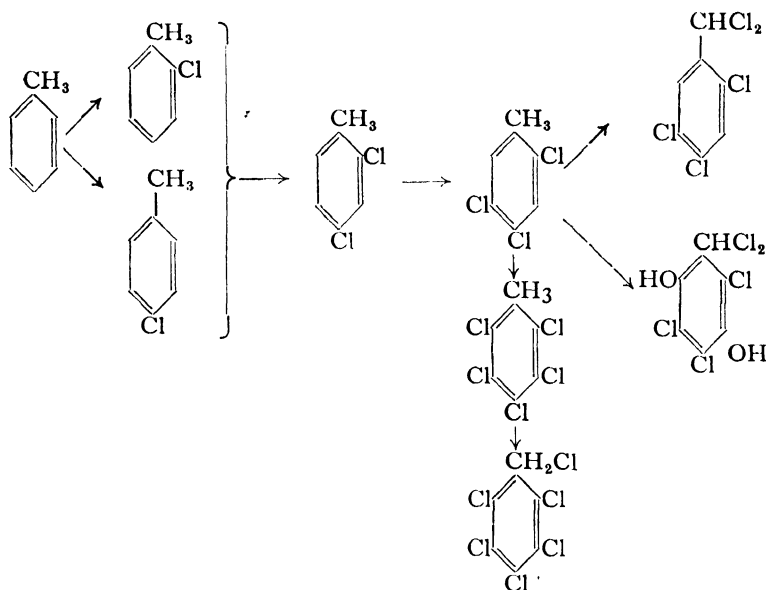
oxidation products as pentachlorophenol and chloranil were obtained, according to the following scheme:



It was found that platinum was the most suitable electrode material for the chlorination. With magnetite and carbon anodes, lower efficiencies and considerable oxidation of the depolarizer were obtained; at the platinum anode, the higher current densities resulted in excellent conversion to the hexachlorobenzene. If the current density was maintained below 0.26 amp./cm.<sup>2</sup>, it was not possible to demonstrate the presence of the highly chlorinated product. In addition to the necessity for high current densities, it was also desirable to perform the electrolysis at elevated temperatures and a low concentration of benzene, to obtain the maximum conversion to the hexachlorinated product.

The anodic electrolysis of a hydrochloric acid suspension of toluene at a platinum electrode and room temperature will yield a mixture of approximately 70 per cent *o*-chlorobenzene, and 30 per cent *p*-chlorobenzene (21). If this reaction is performed at reflux temperature and at a carbon anode, the major product is *p*-chlorobenzene, with only a small quantity of the *o*-chloro-substitution product (22). The results obtained in these electrolyses are indicative of an electrochemical process, for, if the substitution were performed utilizing gaseous chlorine

under almost identical conditions, the main product obtained, benzyl chloride, would be a consequence of substitution on the methyl group. The anodic substitution of toluene by chlorine was also investigated in an acetic-hydrochloric acid medium (23), with the results obtained being represented by the following scheme:



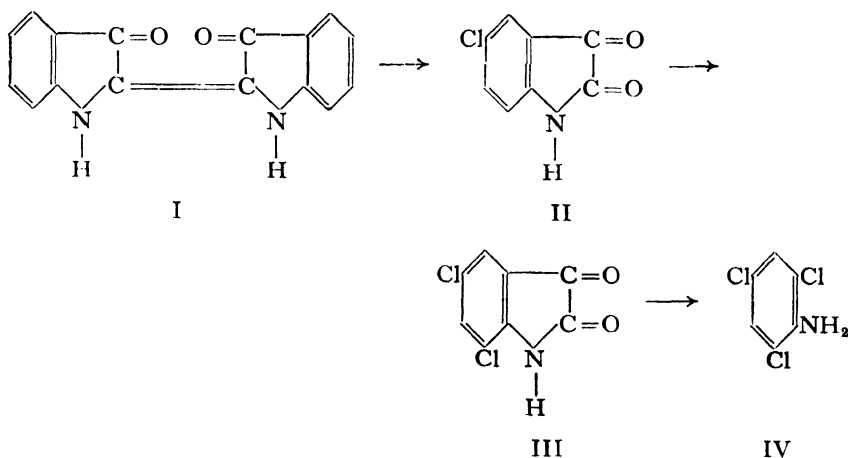
This process also appears to be a true electrochemical one, at least partly, for the methyl group is not substituted with the halogen until the 2,4,5-trichlorotoluene is formed.

The anodic substitution, by chlorine, of such compounds as cyclohexanone, benzophenone, acetophenone, and propiophenone in an acetic-hydrochloric acid medium has been investigated (24), with the resultant formation in each instance of a monochloro-substituted product. Cyclohexanone and benzophenone yielded a monochlorocyclohexanone and a monochlorobenzophenone respectively, with the position of the chlorine not being established. The acetophenone and propiophenone substitutions occurred on the aliphatic portion of the molecule, the former compound yielding  $\omega$ -chloroacetophenone and the latter a mixture of  $\alpha$ - and  $\beta$ -chloropropiophenones.

The substitution of chlorine in aromatic amines is generally accom-

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panied by some oxidation. Initial studies on the electrolysis of aniline, under conditions which were not too carefully controlled, resulted in the isolation from the hydrochloric acid reaction medium of aniline black or chlorinated aniline and chlorinated quinone (25). A more recent study (26) indicated that, if conditions were carefully controlled, it was possible to obtain a certain degree of selectivity in the substitution process. Thus, using a carbon anode, a concentrated hydrochloric acid medium and low temperatures, it was possible to obtain a satisfactory yield of the 2,4,6-trichloroaniline. At a temperature of 35° to 40° C. in a 10 per cent hydrochloric acid medium, the major product isolated was the tetrachloroquinone. A more concentrated hydrochloric acid medium, i.e. 20 per cent, and a temperature of 5° to 50° C., resulted in the formation of 2,4,6-trichloroquinone. Thus it appears that under conditions in which the hydroxyl ion might be considered to be at a minimum, that is in the concentrated hydrochloric acid medium, the anodic oxidation process is comparatively a minor one. It has also been reported (27) that the anodic substitution of indigo (I) by chlorine, using a concentrated hydrochloric acid medium, is accompanied by an oxidation process which results in the formation of chloroisatin (II), dichloroisatin (III), and trichloroaniline (IV):

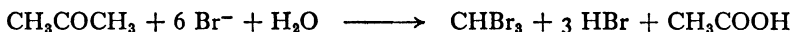


### (b) Bromination

The early attempts to prepare bromoform by anodic substitution of ethanol in an aqueous potassium bromide-sodium carbonate medium resulted only in the oxidation of the alcohol to acetaldehyde and acetic

## ORGANIC ELECTRODE PROCESSES

acid, and finally to carbon dioxide and water. This can be attributed to the greater ease of oxidizability of the bromide ion to bromate, which in turn reacts with the alcohol under these experimental conditions (28). Utilizing a sodium bromide-calcium bromide medium results in the formation of some bromoform, but in this instance, too, the major process is the oxidation of the alcohol (29). The results obtained with acetone, however, are considerably better. The electrolysis can be performed at a platinum anode, in a cell containing a diaphragm to separate the anode and cathode compartments. The anolyte consists of 10 ml. acetone and 2½ gm. of potassium bromide in 75 ml. of water. During the course of the electrolysis, which is performed at current densities of 0.02 to 0.04 amp./cm.<sup>2</sup>, sodium carbonate is added from time to time to compensate for the acid formed. This process results in almost a quantitative yield of the desired product, according to the following equation (30):



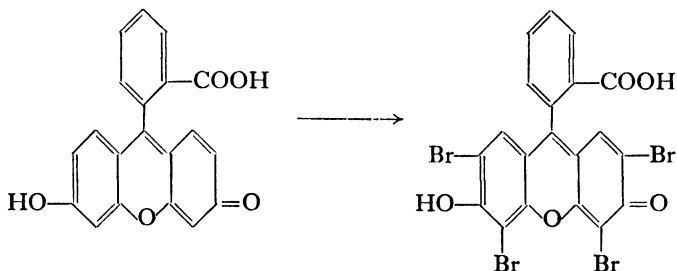
It has also been reported (31) that this process can be successfully accomplished without the use of a diaphragm, provided that the alkali formed at the cathode is neutralized by addition of carbon dioxide to the medium, and that the reduction of the acetone at the cathode is prevented by addition of a substance such as chromate ion, which is more readily reduced. Such a process involved the electrolysis of an aqueous solution containing 140ml. acetone, 385 gm. potassium bromide, and 2.1 gm. of potassium chromate per litre. The current efficiency in this instance is approximately 90 per cent at a current density of 0.07 amp./cm.<sup>2</sup>.

Unfortunately little work has been done on the anodic bromination of the aromatic nucleus. Some studies have been carried out on the anodic substitution of benzene as a suspension in an aqueous hydrobromic acid solution, using either a platinum or carbon anode (32). The maximum efficiency (23 per cent) for the conversion to bromobenzene is attained if an iron carrier is used in the process. As this product can be obtained in the same yield by passing bromide gas through a solution of benzene, it is highly questionable that this can be considered a true electrochemical process. The electrolysis of toluene in a hydrobromic acid medium at either a carbon or platinum electrode results in substitution in the nucleus, to give bromotoluene. However, this result is obtained only if the electrolysis cell is kept in

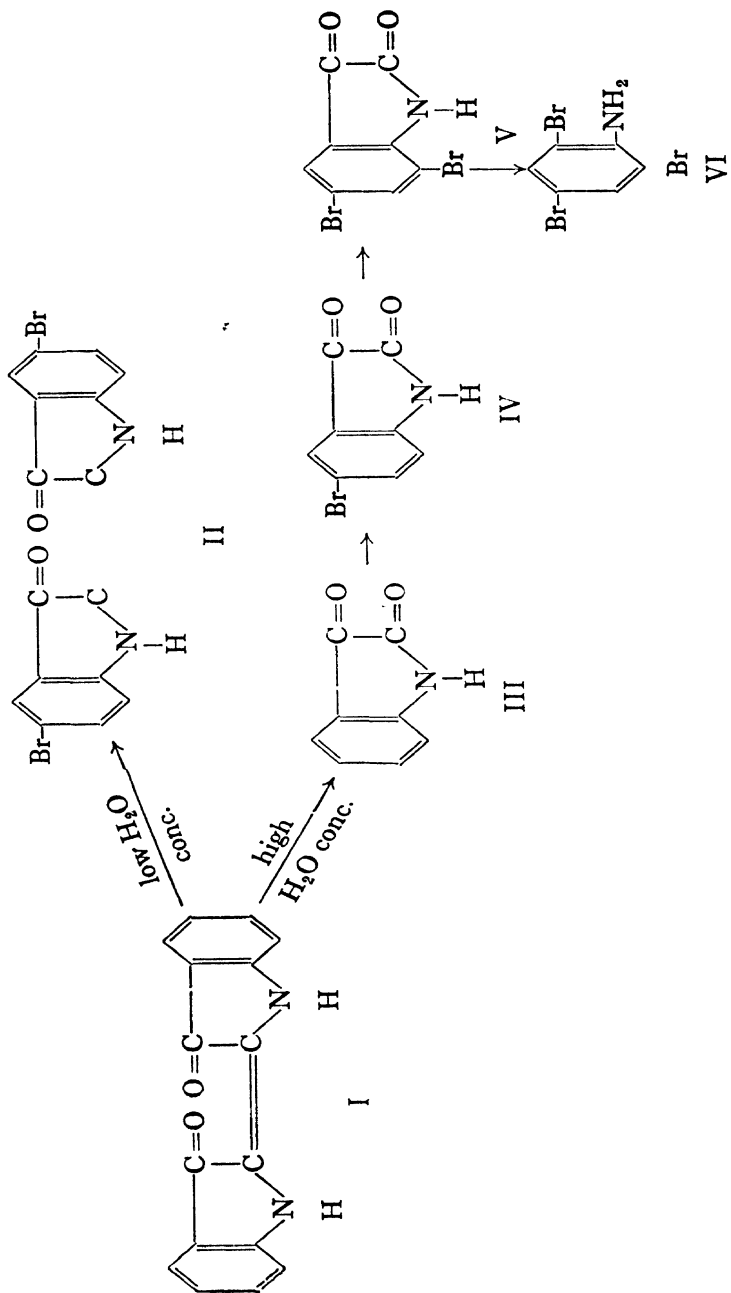
## ANODIC SUBSTITUTION

the dark during the course of the reaction. If the same reaction is performed in bright light the final product is benzyl bromide (33). Here too it is quite questionable whether or not this is a direct electrochemical process. A certain amount of bromination of benzene and toluene also occurs when the molecular compounds  $\text{AlBr}_3 \cdot 3\text{C}_6\text{H}_6$  and  $\text{AlBr}_3 \cdot 3\text{C}_7\text{H}_8$  are electrolysed (34). The products obtained as a result of electrolysis of phenol in a hydrobromic acid medium depend to a great extent on the concentration of acid used. In a relatively low concentration medium, e.g. 1 N, the primary process is oxidation of the phenol, probably due to the greater ease with which phenol acts as an oxygen depolarizer as compared to its action on bromine. However, if a 4 N acid solution is used, a 20 per cent yield of *p*-bromophenol is obtained, due to the fact that the bromine potential is lowered sufficiently for oxidation to be somewhat inhibited (35). This investigator reports that the phenol had a definite depolarizing action, which resulted in a depression of the anode potential. Similar results were obtained upon anodic chlorination of phenol in a hydrochloric acid medium. Low concentrations of phenol in the 4 N hydrobromic acid medium results in the formation of 2,4,6-tribromophenol as one of the reaction products (36).

Aniline, when subjected to anodic bromination in an aqueous hydrobromic acid medium, yields, in addition to oxidation products, an appreciable quantity of 2,4,6-tribromoaniline (37). The accompanying oxidation can probably be attributed to the fact that the decomposition potential of bromine is quite close to the oxidation potential for aniline under the experimental conditions used. Of interest is the reported preparation of eosin by electrolysis of fluorescein in an aqueous potassium bromide medium (38), thus:



As mentioned previously, the inhibition of oxidation during the bromination of phenol can be accomplished by utilizing a high concen-

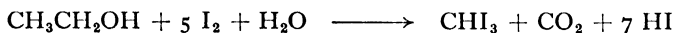


tration of bromide in the medium. This factor has been utilized in the preparation of 5,5'-dibromoindigo (II), with excellent yields, by anodic substitution, of indigo (I), at a carbon anode in a 51 per cent hydrobromic acid medium at a temperature of 20° to 22° C. (39). If the water concentration is increased the oxidative process accompanies that of bromination, as indigo is also a good oxygen depolarizer, with the net result being the formation of 5-bromoisatin (IV), 5,7-dibromoisatin (V), and 2,4,6-tribromoaniline (VI). Under these conditions oxidation of the indigo to isatin (III) probably precedes the halogenation (p. 154).

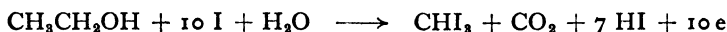
In the reaction in which indigo is subjected to anodic chlorination, (p. 151) the potentials for oxidation and chlorination are so close that the formation of 5,5'-dichloroindigo is almost impossible. It has also been reported that satisfactory yield of the dibromoindigo can be obtained by utilizing a nonaqueous medium consisting of pyridine dihydrobromide in nitrobenzene (40). As dibromoindigo can be obtained by chemical means, this initial bromination cannot be looked upon as a primary electrochemical reaction. In fact the only possible electrochemical process which may be considered a primary one in this instance is not that of halogenation, but of oxidation.

### (c) Iodination

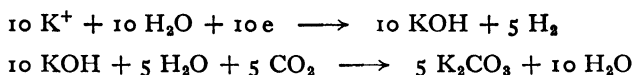
Probably the most outstanding example of the application of anodic iodination is in the preparation of iodoform. This compound can be prepared chemically by the action of iodine on an aqueous solution of alcohol or acetone, in the presence of a base, according to the following equation:



From this equation it can be seen that 70 per cent of the iodine is not used in the process. This iodine must be recovered by use of a chlorine or hypochlorite solution which oxidizes it again to the free iodine required in the process. Thus the practicality of this process is questionable. In the electrolytic process the medium consists of an alkaline solution of the alcohol containing potassium iodide. The passage of current serves merely to liberate the iodine ions at the anode, as potential measurements indicate that the alcohol is not a depolarizer in these circumstances (41). The net anodic reaction can be assumed to be the following:

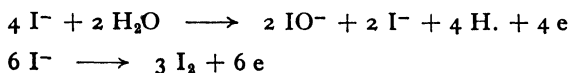


and the cathodic reaction:



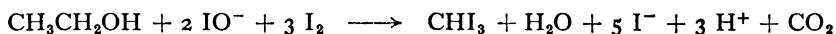
The potassium iodide, which forms as a result of neutralization of the hydriodic acid by the potassium hydroxide, is again electrolysed to free iodide ions, thus making the process somewhat continuous, until all the iodide is exhausted. The electrolytic preparation of iodoform has been the subject of some very comprehensive investigations dating back to patents issued to the Schering Co. in 1884 (42). As a result of subsequent investigations (43) the factor which has been found most critical in the process is the pH of the medium. It has been found that the optimum condition for the formation of the iodoform is the presence of a quantity of hypiodite ion, which of necessity requires slightly alkaline conditions (44). Conditions which result in too high a hydroxyl-ion concentration cause decomposition of the hypiodite ion to the iodate, with resultant decreased efficiency for iodoform production. The optimum degree of alkalinity is usually achieved by use of a potassium carbonate medium. In addition to this factor it has been found that the efficiency of the process is enhanced by use of elevated temperatures, high concentrations of alcohol and iodide, and low concentrations of carbonate and current density (45). Utilizing the conditions in which the electrolysis is performed at a platinum anode at a current density of 0.01 to 0.02 amp./cm.<sup>2</sup>, on a solution containing, per 100 ml. of water, 10 gm. of ethanol, 5 gm. of sodium carbonate, and 17 gm. of potassium iodide at a temperature of 60° to 70° C., results in efficiencies as high as 98 per cent (46). The process can be made almost continuous by adding further quantities of ethanol and potassium iodide, and removing the relatively pure iodoform, which precipitates as the electrolysis proceeds.

It might be of interest to briefly discuss the reactions which may occur at the anode, as a result of this electrolytic process. As indicated earlier, ten iodide ions take part in the reaction with the ethanol to form the iodoform. As a certain amount of hypiodite is required for the process we may consider the initial reactions at the anode to be the following:

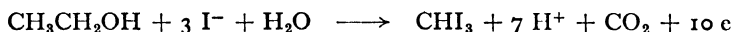


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This electrochemical process is followed by a reaction of the ethanol with the electrolysis products, thus:

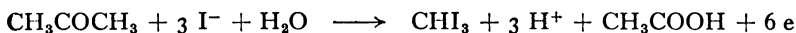


with the overall reaction being:



The above equations show that the total reaction requires ten atoms of iodine, with seven of these being used to form seven equivalents of acid. Of the ten equivalents of alkali produced at the cathode, seven are used to neutralize the acid and two are used to neutralize the carbon dioxide formed. This leaves an excess of one equivalent of alkali, which will increase the concentration of hydroxyl ions to such an extent as to cause the hypiodous acid to react to form increasing amounts of iodate, with the consequential decrease in iodoform production efficiency. This free alkali is removed by passage of a slow stream of carbon dioxide gas in the vicinity of the cathode. The amount is regulated so that the alkali is converted to the carbonate, as indicated by the presence of an amber yellow colour in the electrolyte.

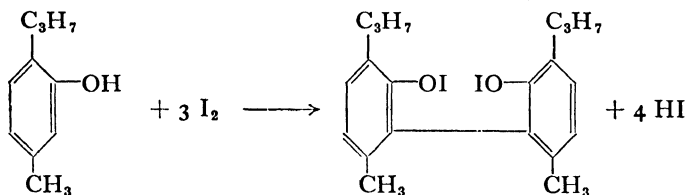
According to the Schering patents (42) for the preparation of iodoform from ethanol, acetone may replace the latter in the process. The details are not given, but the reaction probably proceeds according to the following scheme:



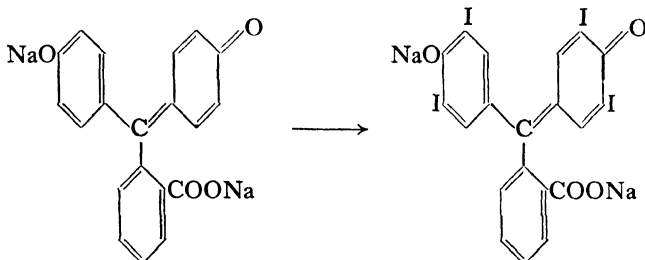
The use of acetone in place of alcohol has the advantage in that it requires only 60 per cent of the energy required for ethanol to produce the iodoform. In actual practice however, this process has a number of disadvantages. The control of alkalinity is more difficult, since of the six equivalents liberated at the cathode only four are used up at the anode. In addition this alkalinity factor is more critical with acetone, as this substance tends to form condensation products in a basic medium. Therefore it is absolutely essential that the reaction medium be kept almost neutral during the electrolysis, either by the addition of small quantities of iodine (47) or acetone (48). Another method which has been suggested as being better is the use of the "Roush neutralization cathode" (11), in which two cathodes are utilized. One of these is enclosed in a porous diaphragm cup and, by utilization of proper resistances, the amount of current to each cathode is controlled. As

a result the alkali liberated at the enclosed cathode does not mix with the bulk of the solution, and that amount liberated at the other cathode can be so regulated as to be sufficient to neutralize the acid formed at the anode. Utilizing this procedure it is possible to obtain a current efficiency of 95 per cent for the production of iodoform.

Attempts to iodinate benzene by electrolysis in a hydriodic acid medium have yielded negative results (31). Phenol also will not respond to iodination under these conditions. However, if the reaction is performed in an alkaline medium, the hydrogen of the phenolic group is replaced by iodine to yield the iodoxy-derivative (35). Thymol, when electrolysed in an alkaline potassium iodide solution, yields the dithymoldiiodide which has been used as an antiseptic (49).

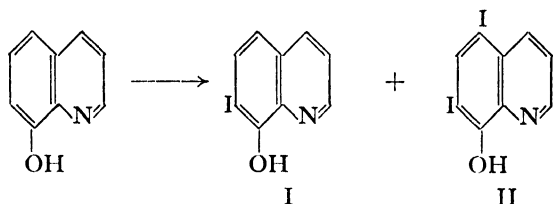


Phenolphthalein, when iodinated under similar conditions, is not attacked at the hydroxyl hydrogen, as is the case with thymol, but instead is substituted on the ring to yield tetraiodophthaleine (50):



This has also been found to be the case with fluorescein, whose product, as a result of electrolysis, is the tetraiodofluorescein (51). It has also been reported that 2-amino pyridine can be electrolysed to the 2-amino-5-iodopyridine in an aqueous methanolic potassium iodide medium (52). Satisfactory yields are obtained if the temperature is maintained between  $0^\circ$  and  $5^\circ$  C. Electrolysis of 8-hydroxyquinoline in an aqueous sodium carbonate-potassium iodide medium at a platinum anode results in a mixture of 7-iodo-(I) and 5,7-iodo-8-hydroxy quinoline (II) (53).

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### (d) Fluorination

The investigation and application of anodic fluorination has its origin in the relatively recent experimental work of Simons and his co-workers (54). In the electrochemical method for the preparation of fluorocarbons, elementary fluorine is neither produced nor employed in the preparation. The chemical methods involved the use of elementary fluorine, which was reacted directly with the hydrocarbon, or used in the preparation of intermediate metal fluorides such as cobaltic fluoride and silver fluoride (55).

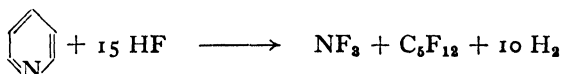
The general technique for performance of the electrochemical process consists of passing an electric current through a one-compartment cell containing an electrically conducting solution of hydrogen fluoride and the organic compound to be subjected to anodic fluorination. The cell is constructed of any material, such as iron and copper, which is resistant to attacks by hydrogen fluoride. These same conductor materials may be used as cathodes as well as nickel, which is also used as an anode in this process. No corrosion of the electrodes occurs if the applied voltage is kept below that which will cause the liberation of elementary fluorine. The preferred voltage for the process is generally between 5 and 6 volts, at a current density of approximately 0.02 amp./cm.<sup>2</sup>. Temperatures are kept low to prevent escape of the hydrogen fluoride. Utilizing this technique, various types of organic compounds such as carboxylic acids, alcohols, ethers, amines, hydrocarbons, etc., have been successfully fluorinated. The carboxylic acids yield saturated fluorocarbons corresponding to the hydrocarbon radical, in addition to large quantities of the hydrogen-containing product.

Acetic acid, when subjected to anodic substitution in the hydrogen fluoride medium, yields, in addition to carbon dioxide and hydrogen, a mixture of carbon tetrafluoride and fluoroform in a ratio of about two to one. Acetyl fluoride requires the addition of sodium fluoride to the medium to overcome the solution resistance brought about by the reaction with hydrogen fluoride to yield the poor conductor, acetyl

fluoride. Using these modified conditions results in the formation of equal quantities of fluoroform and carbon tetrafluoride. Acetone will also yield equal quantities of fluoroform and carbon tetrafluoride upon electrolysis in a hydrogen fluoride medium.

Propionic acid will yield  $C_2F_5H$  and butyric acid quantities of  $C_3F_6H_2$  and  $CF_7H$ . Some of the oxygen-containing organic substances yield quantities of  $OF_2$ , particularly if water is present in the medium. Many nitrogen-containing starting materials will yield a quantity of  $NF_3$ . Under certain conditions carbon dioxide, and to a lesser extent carbon monoxide, may be obtained as a result of the electrolytic process. In some cases fluorinated resins are formed but, as these are generally soluble in the medium, they do not interfere with the isolation of the products. The product in greatest amount is usually that containing the same number of carbon atoms as the starting material. On occasion, products will be obtained which contain either a larger or lesser number of carbon atoms.

Electrolysis of pyridine results in the formation of nitrogen trifluoride and perfluoropentane, thus:



In addition to the major reaction products a small quantity of 2-fluoropyridine was also isolated from the reaction medium. Under similar conditions of electrolysis quinoline yielded a quantity of nitrogen trifluoride and a compound  $C_9F_{18}$ .

Normal propyl alcohol and normal amyl alcohol were found to yield mixtures of fluorinated products which could be fractionated by distillation. The normal amyl alcohol was found to yield such products as  $CF_4$ ,  $CF_3H$ ,  $C_2F_6$ ,  $C_4F_{10}$ , and  $C_5F_{12}$ . The last two products, perfluorobutane and perfluoropentane, were the major fluorinated products.

Anodic fluorination of the olefins, when attempted in the anhydrous hydrogen fluoride medium, results in addition of hydrogen fluoride to the double bond with subsequent polymerization of the olefin, which in many cases is quite undesirable. This polymerization can be minimized to a great extent by performing the reaction in a glacial acetic acid-potassium hydrogen fluoride medium. The cell used is divided by a diaphragm to separate the anode from cathode. In this manner the organic fluoro-carbon is prevented from coming in contact with the

## ANODIC SUBSTITUTION

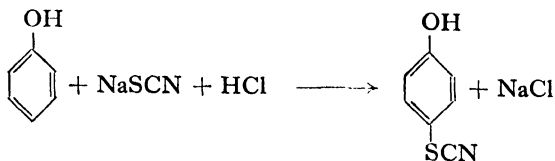
cathode, where it is suspected that the polymerization reaction is instigated. Using this method it was possible to obtain a 70 per cent yield of 1,1-diphenyl-1,2-difluoroethane from the respective stilbene (56):



The mechanism of anodic fluorination is suspected to be very similar to that of other types of anodic halogenation (57). However, considerable work will have to be published before any final conclusions can be arrived at concerning the general applicability of this anodic process to the fluorination of organic compounds.

### (2) ANODIC THIOCYANATION

It has been demonstrated that electrolysis of thiocyanate salts in the presence of organic compounds in the anode chamber of a cell generally results in satisfactory yields of the organic thiocyanate. In this manner, many derivatives of phenol, and of primary, secondary, and tertiary aromatic amines can be obtained. For example, phenol, when subjected to anodic substitution at a graphite electrode at current densities of 0.03 to 0.04 amp./cm.<sup>2</sup> in a sodium thiocyanate-hydrochloric acid medium at a temperature of 0° to 5° C., yields the respective thiocyanate (58):



Under similar conditions the thiocyano derivatives have been obtained from carvacrol, *o*-, *m*-, and *p*-cresols, thymol, and guaiacol (59). As previously mentioned, aromatic amines also respond to anodic thiocyanation. Thus aniline yields 4-thiocyananiline, *N*-methylaniline the 4-thiocyano-*N*-methylaniline, and *N,N*-dimethylaniline the *N,N*-dimethyl-4-thiocyananiline (60). Electrolysis of *o*- and *m*-toluidine results in substitution of the thiocyanate para to the amino group to yield respectively 2-methyl-4-thiocyananiline and 3-methyl-4-thiocyananiline (58). The electrochemical thiocyanation of the aromatic amines is of great interest because these thiocyano derivatives are readily converted to the respective aminobenzthiazoles, which have

been found useful as intermediates in the synthesis of dyestuffs, sensitizers, pharmaceuticals, and moth-proofing agents. To illustrate the process, we may consider the preparation of 2-amino-6-methylbenzothiazole, which involves the intermediate thiocyanation of *p*-toluidine. The anolyte was a solution of 1.5 gm. of *p*-toluidine, 3.2 gm. of ammonium thiocyanate, and 2 ml. concentrated hydrochloric acid in 35 ml. aqueous alcohol. After the passage of 2 amp. hr. of electricity at a current density of 0.03 to 0.04 amp./cm.<sup>2</sup>, the electrolyte was diluted with water. A heavy oily layer, which was essentially the thiocyanotoluidine, formed. This was not isolated, but instead the mixture was boiled under reflux for a period, to accomplish the rearrangement to the respective benzothiazole. Utilizing these conditions, other benzothiazoles, namely 2-amino-6-methoxy-benzothiazole, 2-amino-6-ethoxybenzothiazole, and 2-amino-6-carboethoxy-benzothiazoles were also prepared (61).

### (3) ANODIC NITRATION

Earlier in this chapter it was pointed out that electrochemical nitration is the result of an increase in concentration of nitrate ions at the electrode surface, which results in the formation of the desired nitration product. This type of reaction is especially advantageous in cases in which a high concentration of nitric acid in the bulk of the solution would result in decomposition, either of the starting material or of the product. Thus it is possible to use a dilute solution of nitric acid which would have no effect on the substances in solution. Relatively high current densities would seem to be desirable in this process as they would result in an increase in the concentration at the anode surface. However, too high a current density may counteract this condition, due to dispersion of this concentration state by oxygen evolution.

One of the earliest applications of this process was in the nitration of naphthalene, in which a suspension of this compound in dilute nitric acid yielded the respective mono- and di-nitronaphthalenes (62). A subsequent group of investigators (63) concluded from their experiments, which were performed at a current density of 0.3 amp./cm.<sup>2</sup> and a temperature of 95° to 98° C., that the reaction was not a result of increased concentration of nitrate ions at the electrode surface, but of local heating at the anode from the oxidation reactions taking place therein. This concept, however, is contradicted to some extent by the results of another group of investigators (64), who found that a suspen-

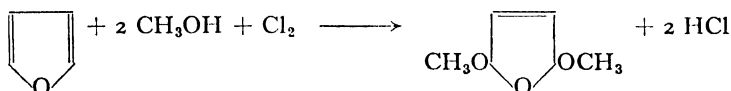
## ANODIC SUBSTITUTION

sion of naphthalene could be nitrated electrolytically using a current density of 0.2 amp./cm.<sup>2</sup>, while maintaining the temperature below 45° C. These investigators found that, although there was a relative increase in nitric acid concentration in the bulk of the solution which was, however, insufficient to accomplish the nitration, the reaction did occur within the highly concentrated diffusion layer at the electrode surface.

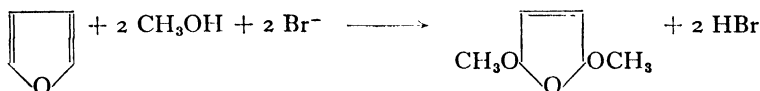
The process of anodic nitration has also been utilized for the preparation of nitrocellulose [C<sub>6</sub>H<sub>7</sub>O<sub>5</sub>(NO<sub>2</sub>)<sub>3</sub>], nitrobenzene, nitrotoluene, nitro-*m*-xylyl, and nitroglycerin (65).

### (4) ANODIC ALKOXYLATION

If furan is treated with a methanolic solution of chlorine or bromine, the addition of two methoxyl groups occurs, with the net result being the formation of 2,5-dimethoxy-2,5-dihydrofuran (66):



As the product obtained by the chemical method is often contaminated with a small quantity of halogen-containing impurity, the stability of the acid-sensitive dimethoxydihydrofuran is not too great. An electrolytic method has been developed which is superior to the chemical method, in that a halogen-free reaction product is obtained (67). The furan is mixed with a methanolic solution of ammonium bromide and the solution subjected to electrolysis at a temperature of approximately -14° C. using a nickel cathode and a platinum anode. During electrolysis, ammonia and hydrogen are liberated at the cathode; at the anode the bromine which forms reacts with the methanol and the furan to give the desired compound, thus:



The hydrogen bromide reacts with the ammonia being liberated at the cathode to regenerate the ammonium bromide required in the process. With the electrolytic method the investigators obtained a 73 per cent yield of the dimethoxydihydrofuran and a current efficiency of 86 per cent. This method has been applied to the methoxylation of such

furans as 2-methyl furan, furfuryl alcohol, and furfuryl acetate, with the final products being the respective 2,5-dihydro-2,5-dimethoxyfuran in each case (68). Ethoxylation of the furans has also been accomplished by using ethanol instead of methanol in the process. The result is the formation of 2,5-diethoxy-2,5-dihydroxyfuran from furan (69).

A more recent investigation (70) showed that it was unnecessary to include a bromide salt in the reaction medium. The same reaction, that is the anodic methoxylation of furan, can be accomplished by utilizing a medium of sodium hydroxide and methanol. Thus all possibilities of destruction of 2,5-dihydro-2,5-dimethoxyfuran by halogen are eliminated.

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*This is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning.*

WINSTON CHURCHILL.

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