

**ORGANIC
ELECTRODE
PROCESSES**

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FOREWORD

IN 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,
Indiana, U.S.A.
March 1957.

AUTHOR'S PREFACE

DURING 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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INTRODUCTION

*For out of olde fildes, as men seith,
Cometh al this newe corn fro yeer to yere
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

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GENERAL CONSIDERATIONS

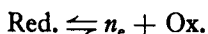
(1) POLARIZATION

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).

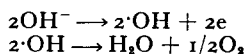
The term "decomposition potential" refers to that potential at which appreciable current begins to flow through the solution, accompanied by hydrogen evolution at the cathode and oxygen evolution at the anode. The reason given by LeBlanc for the "decomposition potential" being the same in different solutions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

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 1: 3
Cathodic and Anodic Electrode Overpotentials

	Hydrogen Overpotentials (In N.H ₂ SO ₄)	Oxygen Overpotentials (In N.KOH)
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).

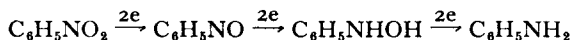
The electrodes used for electrolytic oxidations are somewhat more limited because it is difficult to obtain a stable anode potential with many electrodes in the presence of a depolarizer. The potential generally rises rapidly from the low value, at which the anode dissolves, to the high value for passivity 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

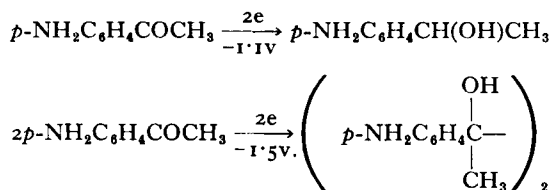
amount is low. This also holds for anodes of cobalt and nickel provided high current densities are used. At still higher current densities iron can be utilized. However, once this metal has become passive it is then possible to use the electrode at low current densities. Lead can also be used in acid 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:

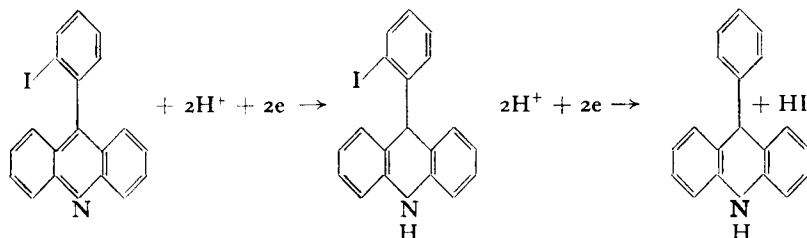


Each of these steps is controlled by the potential at the cathode surface. It has also been demonstrated that *p*-aminoacetophenone can be reduced at a mercury cathode to either the hydrol or the pinacol, depending upon the potential at the mercury cathode (5), thus:



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. ²
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).

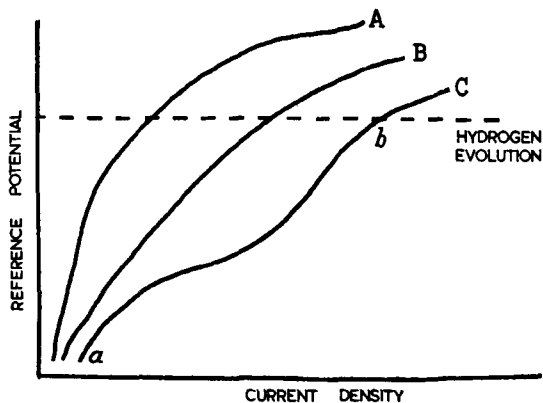


FIG. 1:1. *Reference Potentials in Cathodic Reductions.*

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