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ELECTROCHEMICAL REDUCTION OF ISOMERIC ORGANIC BROMIDES

by

Ronald Raymond Carlton

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Head of Major Department

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TABLE OF CONTENTS

INTRODUCTION

Electrochemical reduction at a dropping mercury cathode is known as polarography. Since the invention of this technique by Heyrovsky in 1922 (20), a large body of knowledge about it has developed. A substantial part of this knowledge deals with the electrochemical reduction of organic compounds. Polarography provides an ideal method for the quantitative measurement of reducible organic compounds and fortunately, the validity of such analytical methods can be established simply, although only empirically.

The initial result of the polarographic technique is a polarogram which is a plot of current versus the voltage applied to a dropping mercury cathode and a mercury-mercurous chloride anode. Reduction occurs at a particular potential of the dropping mercury cathode for a given reducible species and causes an increase in current. This increase in current is designated the polarographic wave where the height of this wave, called the limiting or diffusion current, is a linear function of the concentration of the reducible species. This linear relationship can often be proved easily by constructing a calibration curve using solutions of known concentration and is particularly useful for quantitative analysis. Far more difficult problems arise in attempting to establish theoretical relationships between the magnitude of the current, the concentration of the reducible species and the physical characteristics of the dropping mercury cathode.

Even greater difficulties arise in attempting to establish the chemistry involved in the reduction reaction and in elucidating the mechanism of the reaction.

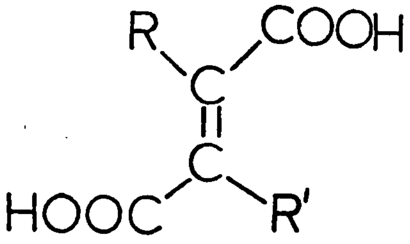
The course of a reaction at an electrode is usually complex. Electron transfer from the electrode to a species in solution or one adsorbed on the electrode is involved and occurs in the interfacial region between the bulk of the solution and the electrode, an area known as the electrical double layer. Thus, electrochemical reactions are heterogeneous.

The electrochemical reduction of organic compounds is especially complex, and in particular, the reduction of organic halides has been difficult to unravel. According to Elving (11), the disputes that have arisen in this field result from accepting generalized mechanisms that are based on data for too few compounds, failure to identify the reaction products and neglect of the kinetics involved. The basic questions that must be answered to elucidate the complete mechanism of the electroreduction of an organic compound are:

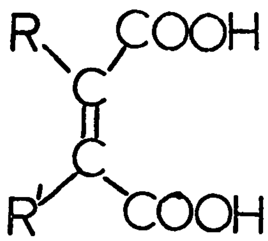
1) What is the orientation of the molecule when electron transfer occurs?
2) In what form is the electroactive species?
3) How does electron transfer occur?
4) How do steric requirements of the molecule affect the electron transfer and the reduction products?

These four questions are interdependent. The orientation of the molecule at the electrode surface at the time of electron transfer will be dependent on the steric requirements of the electroactive species. For example, in an organic bromide, the bromine atom is quite large compared to other typical substituent groups (i.e., hydrogen, methyl) and by comparison, sweeps out a considerable volume of space on approaching the electrode. In view of this difference in size, the preferred orientation of the carbon-bromine bond may be that with carbon or one in which bromine makes the closest approach to the mercury cathode. Oddly enough, there is sharp disagreement over the answer to this seemingly straight forward question. For, in addition, the substituents on adjacent carbons will have an affect on the orientation of the carbon-bromine bond. The form (i.e., carbonium ion, R^+, carbanion, R^-) of the electroactive species is determined by steric requirements. For instance, the possibility for dissociation of the carbon-bromine bond into a carbonium ion and a bromide ion is a function of the orientation of the molecule. Finally, the mode of electron transfer is influenced by the orientation and form of the electroactive species. Thus, it becomes readily apparent that steric factors play an important role in the electrochemical reduction of organic bromides.

The present work is an attempt to gain an insight into the role of structure and steric requirements in electrode reductions by determining the sequence of chemical and electrochemical reactions involved in the reduction of geometrical isomers of the type I and II:



I



II

in which R is either hydrogen or methyl and R' is either hydrogen or bromine. These compounds possess two possible reducible sites. The first site is the reduction of the double bond, a reaction represented in the following manner:

$$\mathrm{RCH{=}CHR'} + 2e^- + 2H^+ \longrightarrow \mathrm{RCH_2CH_2R'} \qquad (1)$$

The second site is the reduction of the carbon-bromine bond (termed bond fission by some authors) and is represented by the following reaction:

$$\mathrm{RCHR'Br} + 2e^- + H^+ \longrightarrow \mathrm{RCH_2R'} + Br^- \qquad (2)$$

The effect of cis-trans isomerism and steric arrangement of R and R' on the electrochemical behavior were studied. Polarography, chronopotentiometry and controlled potential electrolysis techniques were employed in the study.

REVIEW OF LITERATURE

Polarography (21, 26, pp. 298-325; 29, pp. 234-266, 450-483) involves the use of a mercury drop as an electrode (dropping mercury electrode or DME) which grows in size while hanging for a few seconds at the orifice of a glass capilliary. Depending on the height of the mercury reservoir connected to the capilliary, the mercury sphere finally drops away from the capilliary. In a polarographic run, the mercury electrode will be immersed in a deaerated solution containing an electroactive species. During the time the mercury drop is hanging from the capilliary orifice a potential may be applied to the mercury drop cathode to reduce the electroactive species by transferring one or more electrons from the cathode to the material in the vicinity of the electrode. The electrode is immediately renewed by a new, growing drop. The continuously renewed surface of the mercury is the unique feature of this electrode for with it, current-voltage curves of high reproducibility are obtained. Each succeeding portion of the curve is independent of the electrolysis occurring on the previous drop.

Mass transfer of the electroactive species to the electrical double layer is by diffusion; all sources of mechanical stirring are avoided if possible and a supporting electrolyte of sufficiently high concentration (0.1-1.0 M) is present to carry the current. Otherwise, the electroactive species would transport the current, and in doing so, would migrate and complicate the picture. As the applied potential is increased above the decomposition potential of the electroactive species an increase in current results as the species undergoes reduction; the concentration of the reducible species at the electrode surface decreases. The reducible species diffuses into the boundary layer until an equilibrium condition is reached in which the electroactive species is reduced as rapidly as it diffuses to the electrode surface. The concentration at the electrode sinks to a minimal value which remains practically constant with still further increases in potential. The rate of diffusion transfer is dependent on the difference in concentration between the electrode surface and the bulk of the solution and on a proportionality constant called the diffusion coefficient which is a value characteristic of the species in question. Therefore, the current rises in a given potential range and reaches a limiting value, giving rise to an S-shaped curve. The current which passes depends on several factors the effects of which are given by the Ilkovic equation (21):

$$i_d = 706nD^{1/2}Cm^{2/3}t^{1/6} \qquad (3)$$

in which i_d is the instantaneous diffusion current in microamps, n is the number of faradays of electricity passed per mole of chemical reduced (number of electrons involved in the reaction), D is the diffusion coefficient of the species in cm^2/sec., C is the concentration in millimoles/liter, m is the rate of mercury flow from the DME in mg./sec. and t is the drop time of the DME in seconds.

The potential at which the concentration of the reduced species is equal to the concentration of the oxidized species in the diffusion layer is called the half-wave potential ($E_{\frac{1}{2}}$); it falls at the point of inflection of the S-shaped curve. Half-wave potentials are independent of concentration and depend only on the nature of the reducible species and the composition of the supporting electrolyte. The potential E at any point on the polarographic wave is given by the Nernst equation:

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln\left[(i_d - i)/i\right] \qquad (4)$$

in which R is the gas constant, 8.314 volt-coulombs/deg., T is the temperature in degrees Kelvin, n is the number of electrons involved in the electrode reaction, F is the value of the faraday, 96,493 coulombs, i_d is the limiting current, and i is the current at any time during the polarographic wave. Substituting in the values for R, T and F and converting to logarithms of base ten, Equation 4 reduces to:

$$E = E_{\frac{1}{2}} + \frac{0.059}{n} \log\left[(i_d - i)/i\right] \qquad (5)$$

at 25° C. A plot of E versus $\log\left[(i_d - i)/i\right]$ yields a straight line with a slope of 0.059/n, provided the reduction proceeds reversibly. (In a strict thermodynamic sense, no reaction that is proceeding at anything greater than an infinitesimally slow rate is truly "reversible". However, in many cases the overpotential required to sustain a reaction is so small that Equation 5 holds within a small experimental error. This is what is meant by "reversible" in ordinary polarographic parlance). A linear log plot with the proper theoretical slope is generally, although not universally accepted, as a criterion of reversibility. With irreversible reactions, the plot is not a straight line, or the slope is less than that predicted by Equation 5. Inspection of the polarographic wave of an irreversible electrode reaction shows that the wave rises less steeply than for a reversible reaction.

For those polarographic reductions which cannot be labeled as reversible because the slope of the log plot deviates grossly from the theoretical slope, another concept is introduced called the transfer coefficient represented by the Greek letter alpha (α). The wave equation for irreversible systems then becomes:

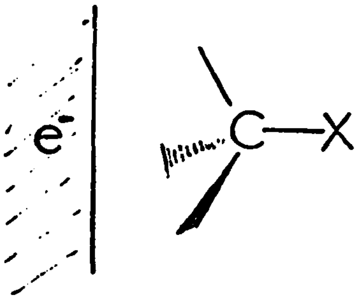
$$E = E_{\frac{1}{2}} + \frac{0.059}{\alpha n} \log \left[(i_d - i)/i \right] \qquad (6)$$

The significance of alpha is best seen from a thermodynamic consideration of the electrode process. As the potential of the dropping mercury cathode is made more negative by an increment ΔE, the Gibbs free energy change, ΔF, is equal to $-nF\Delta E$. In a truly reversible system all of this energy is used to increase the rate of the cathodic reaction, i.e., to do work in the form of transferring an electron from the cathode to the electroactive species. However, for nonideal systems a certain amount of this energy is expended to raise a molecule of the reactant to an activated state. The amount of energy consumed is termed the free energy of activation. Alpha then, is that fraction of the change ΔE in the electrode potential that remains and acts to increase the rate of the cathodic reaction. As the energy barrier for electrode reactions increases (reaction becomes more irreversible), the less of the total energy is put to use in transferring the electron. The net result is that it takes more negative potentials to do the same amount of work as for an anologous reversible system. Hence, the polarographic wave is drawn out over a wider range of potential.

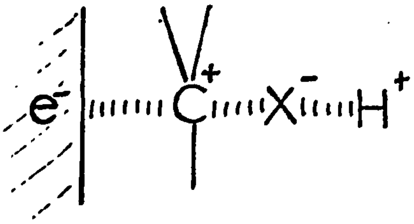
The value of alpha is less than unity and the more irreversible the electrode reaction, the smaller the value. The magnitude of the transfer coefficient for a given electrode reaction is a characteristic of the electroactive species. Therefore, the value of the transfer coefficient of an electrode reaction is of more than routine curiousity since a comparison of the value of alpha for a particular species with that of another slightly different species, may provide information that will help in elucidating the mechanism of the electroreductions.

General mechanisms for the reduction of organic halides

Von Stackelberg and Stracke (44) proposed the first general mechanism for the reduction of organic halides, a reaction which involves the addition of two electrons and a proton and the removal of the bromine as an anion. The rate determining step was believed to be the addition of the first electron with all subsequent chemical and electrochemical steps being very fast. However, experimental data has accumulated since the Von Stackelberg and Stracke work which can not be interpreted in terms of the mechanism proposed. Elving (11) considers the general mechanism to be a nucleophilic displacement on carbon, the reducible species diffusing toward the electrode with the carbon foremost and the halogen following, the carbon-halogen bond being more or less perpendicular to the electrode.



Electrostatic repulsion causes elongation of the carbon-halogen bond producing a transition state represented in the following way:



At this point there are two alternatives, the first being a diffusion away from the electrode to reform the bond. The second alternative is further diffusion towards the electrode which breaks the bond forming an incipient carbonium ion and bromide ion. This would be followed by an immediate transfer of one electron to form a free radical or of two electrons to form a carbanion. The various organic reaction mechanisms can be expressed by one of three general approaches in terms of homogeneous reaction kinetics.

1) S_N1-like:

$$R\text{-}X \longrightarrow R^{+} + X^{-} \tag{7}$$

$$R^{+} + 2e^{-} \longrightarrow R^{-} \tag{8}$$

$$R^{-} + H^{+} \longrightarrow R\text{-}H \tag{9}$$

2) S_N2-like:

$$R\text{-}X + 2e^{-} \longrightarrow R^{-} + X^{-} \tag{10}$$

$$R^{-} + H^{+} \longrightarrow R\text{-}H \tag{11}$$

3) Free radical:

$$R\text{-}X + e^{-} \longrightarrow R\cdot + X^{-} \tag{12}$$

$$R\cdot + R\cdot \longrightarrow R\text{-}R \tag{13}$$

$$R\cdot + e^{-} \longrightarrow R^{-} \tag{14}$$

$$R^{-} + H^{+} \longrightarrow R\text{-}H \tag{15}$$

The possibility of chemical reactions prior to electron transfer can be represented by the reaction

$$R\text{-}X + Hg^{\circ} \longrightarrow R\text{-}Hg\text{-}X \tag{16}$$

The mercury compound may be an adsorbed species or exist in solution. Its presence does not necessarily constitute a case for non-reversibility or kinetic complication since the organomercural bromide may behave ideally in the subsequent electron transfer steps which may proceed by one of the above mechanisms.

In terms of homogeneous reaction kinetics, an S_N1 mechanism refers to a nucleophilic substitution at a carbon atom that is kinetically first order. The driving force for the reaction is believed to be the tendency of the reaction medium to solvate or combine with the departing group so as to leave a solvated carbonium ion, R^+. The carbonium ion can then react with another anion in solution, approaching the ion either from the same side as the departed anion or from the side opposite to the leaving group. The direction of approach of the entering group is dependent on such factors as the stability of the carbonium ion, steric arrangement and the nature of the solvent media. A homogeneous S_N2 mechanism is a nucleophilic substitution that is kinetically second order. It is generally agreed that the S_N2 reaction proceeds by the attack of the anion at the side of the carbon opposite to that at which the halide is attached. The S_N2 reactivity of a compound is very much dependent on the steric hinderance the substituents present to the entering anion and, in general, steric factors are much more important in an S_N2 mechanism than in an S_N1 mechanism.

By analogy, the dissociation step (Reaction 7) in the S_N1-like mechanism for an electrode reaction is due to the electrical field (electrode potential) to form the carbonium ion. The electron then takes the role of the anion and the transfer is believed to be the potential determining step. A similar analogy for the S_N2-like mechanism can be made but with a carbanion, R^-, as the transient species.

The free radical mechanism was postulated by von Stackelberg and Stracke (44) for the polarographic reduction of organic halides. Although the free radical mechanism is listed as a separate mechanism, it should be recognized that free radicals can operate within the S_N1-like and S_N2-like mechanisms where one electron may be picked up in Reactions 8 and 10 to form the free radicals which can then undergo Reaction 5, or Reactions 14 and 15.

All electrochemical reductions of organic halides can be classified according to one or a combination of the above general mechanisms. The remainder of this chapter will be devoted to reporting the results and theories of other investigations with emphasis on answering the basic questions listed on page 2. In the interest of continuity, all pertinent chronopotentiometric and controlled potential electrolysis data reported in the literature are presented along with the polarographic data to support the author's theories and findings. The definite lack of such supporting evidence for organic halide reductions will be obvious. The historical background and description of the techniques are presented later.

Reduction of benzyl halides

Marple, Hummelstedt and Rogers (32) studied the reduction of benzyl halides and found that two waves occur for the iodide and bromide compounds. Adsorption of intermediate reaction products formed from the benzyl free radical was believed to be responsible for the unusual character of the first wave. Bibenzyl was isolated from controlled potential electrolysis of benzyl bromide, proof of the free radical nature of the reduction. Since the effect of bibenzyl on the surface tension of mercury is quite pronounced in the region where the first polarographic wave of the bromide is observed, adsorption of bibenzyl appeared to be the cause of the unusual shape of the first wave.

The polarographic reduction of the benzyl halides in acetonitrile and dimethylformamide was studied by Wawzonek and co-workers (47). Reaction of the iodide compound with mercury was proposed but the reduction products were not isolated nor identified by chemical means to verify this statement. The chloride was believed not to react with mercury, instead, the reduction appeared to involve a direct two-electron transfer to produce a relatively stable carbanion, an S_N2-like mechanism.

Diefenderfer (10) studied the benzyl halides using the chronopotentiometric technique and proposed that a chemical reaction between the compounds and mercury does indeed take place. The products proposed by Diefenderfer were not the same as those proposed by Wawzonek (47).

The polarography of para-substituted benzyl bromides in methyl alcohol solutions was studied by Klopman (25) who did not observe any reaction with the mercury cathode. Controlled potential electrolysis of p-nitrobenzyl bromide gave only 4,4'-dinitrobibenzyl. The isolation of only one product that must occur through dimerization is strong evidence of a free radical mechanism. Streitwieser and Perrin (41) have also presented evidence that the transition state for the polarographic reduction of substituted benzyl chlorides possesses considerable radical character.

In summary, there is disagreement as to the nature of the reduction of benzyl halides. Evidence has been presented supporting both free radical and carbanion type mechanisms. However, it appears that the mechanism depends somewhat on the halide under investigation. The bromide and iodide compounds are reported to undergo free radical reductions while there is conflicting evidence for benzyl chloride. The isolation and identification of dimers as reduction products favor the free radical mechanism. Strong support is given for a chemical reaction occurring between organic halides and mercury (page 11, Reaction 16). Once again, the possibility of such a reaction seems to depend on the halide, the iodide and bromide compounds tend to react with mercury while the chloride does not. One author even indicates that substitution on the benzene ring by some functional group may, in some way, influence the conditions which control the reaction of benzyl halides with mercury.

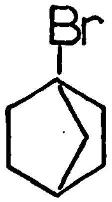
Reduction of alkyl and cycloalkyl halides

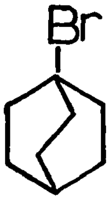
Von Stackelberg and Stracke (44) postulated the free radical mechanism for the polarographic reduction of alkyl halides. In general, the reductions were found to be independent of pH. The products isolated from the controlled potential electrolyses were the corresponding alkanes. They found little or no evidence of dimerization. The rate controlling step was the pick up of the first electron with all subsequent chemical and electrochemical steps being rapid. Lothe and Rogers (31) studied the polarographic reduction of carbon tetrachloride and agree with von Stackelberg and Stracke's findings.

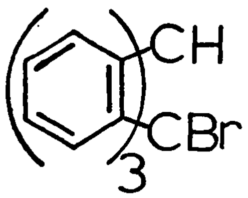
Lambert and Kobayashi (28) quantitatively correlated polarographic half-wave potentials with homogeneous S_N2 reactivity for a series of alkyl bromides with increasing substitution on the bromine bearing carbon. For example, the $E_{\frac{1}{2}}$ values for methyl, ethyl, isopropyl and tertiary butyl bromides follow the same general trend as the S_N2 reactivity for these compounds, even to the point of reflecting the apparent change in kinetics to an S_N1 mechanism for the tertiary compound. The switch in kinetics is brought about by the steric hinderance of the three methyl groups of the tertiary compound. Comparison of half-wave potentials for the cycloalkyl bromides with their relative substitution rates illustrates even more the importance of steric factors in organic polarographic reductions.

Lambert concurs with Elving that the halogen orientation is away from the electrode with a displacement on carbon as the mechanism regardless of whether the reaction proceeds S_N2-like for the simple alkyl bromides or S_N1-like for the more hindered cyclic compounds. The reduction of highly hindered compounds such as 1-bromo-2,2,2-bicyclooctane (see center structure below) are thought not to proceed by an S_N2-like process. This is supported by the fact that the ease of reduction of a series of similarly bridged-type structures follows the ease of their carbonium ion formation in solvolysis reactions (27).

Sease and co-workers (40) also investigated the reduction of bridgehead halogen compounds of the type:







They propose that the cage structure would make it impossible for the rear of the carbon-halogen bond to approach a mercury cathode and thus exclude the back side attack on carbon. Sease proposes that the mechanism is a displacement on bromine to give a free radical plus the liberation of bromide ion. This mechanism requires a transfer of an electron through the bromine atom from the cathode to the carbon atom. It was suggested that perhaps all halide reductions occur with an initial attack on the halogen atom. In reply, Lambert and co-workers insist that work in their laboratories with bridgehead and highly hindered organic halides indicate that the electrochemical reduction results give support to their use of Elving's basic mechanism. They propose that as the organic halide diffuses into the vicinity of the electrode, the bromine atom should be oriented away from the negatively charged electrode surface due to the electronegativity of the bromine atom. The electrostatic field should act to increase the polarization of the carbon-halogen bond. Depending on several factors[1], the actual potential determining step may involve direct ionization to form a carbonium ion and a bromide ion (S_N1-like), or add an electron to an antibonding orbital of carbon to form an "electrode complex" (S_N2-like). The argument supporting Elving's mechanism accommodates the postulation that steric interference by the cyclic structure hinders close approach of the back side of the carbon-halogen bond. This kind of orientation probably excludes the S_N2-like process. At the same time, steric effects should also decrease the polarizing influence of the electrical field on the bond. Therefore, since formation of neither an anion radical nor a carbonium

[1]a) Steric influences in the R of R-X.

b) Polar effects in R.

c) Resonance stabilization of groups in R.

d) Bond strength in R-X.

e) Nature of the supporting electrolyte.

ion can occur, reduction should not and indeed, does not take place at moderate potentials. However, if the electrode potential is made more negative, polarization increases and if allowed to proceed far enough, ionization might occur to form a carbonium ion. The potential at which ionization occurs might be expected to follow an order determined by the relative ease of carbonium ion formation of bridgehead compounds. Lambert did find that the reduction potentials follow such an order indicating that an ionic process of dissociation to carbonium ions may be the potential determining step.

Zavada and co-workers (49) have questioned the validity of any comparisons of homogeneous reaction kinetics with half-wave potentials. They report similar half-wave potentials for simple monobromides which have widely varying rates of homogeneous substitution and that such correlations, at best, are only superficial.

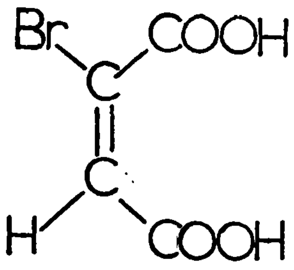
Annino and associates (1), in an effort to distinguish between a displacement on carbon and a displacement of halogen, investigated the stereospecificity of the reduction of carbon-halogen bonds at asymmetric carbon atoms in cyclopropyl halides. Their experimental results did not support an S_N2-like mechanism. The data did compare nicely with that from a zinc reduction technique used on the same compounds which is reported or believed to cause reduction by displacement on the halogen atom.

There is certainly a great deal of disagreement and conflicting data in the literature over the reduction of alkyl and cycloalkyl halides. Evidence is presented supporting both S_N1-like and S_N2-like mechanisms for identical compounds. No one reports the isolation of any dimerized reduction products which indicates that relatively stable free radicals do not play a major role in these reductions.

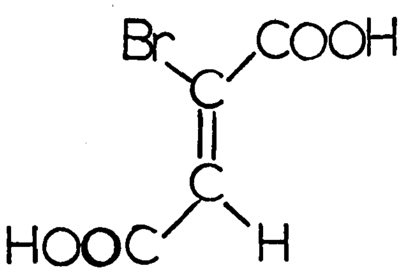
Reduction of allylic bromides

Although a major part of the foregoing literature report is concerned with compounds other than geometric isomers, the same problems are present when dealing with non-aromatic unsaturated compounds and cis-trans isomers. Kirrmann and Kleine-Peter (24) found that the polarographic reduction of allyl bromide gave first a kinetic wave followed by a normal reduction wave. The kinetic wave was believed to be due to the reaction of the bromide with the mercury electrode to give allyl mercuric bromide. Evidence of this was obtained by comparison of the half-wave potentials of the kinetic wave with the wave of known allyl mercuric bromide.

Elving and co-workers (14) studied the reduction of the cis and trans isomers, monobromomaleic acid (III) and monobromofumaric acid (IV). Further proof that free radicals of some definite stability can be produced in the reduction of organic halides is shown by the formation of the dimer, 1,2,3,4-butanedienetetracarboxylic acid from the electrolysis of monobromomaleic acid. Electrolysis of the trans isomer did not yield any dimer product.

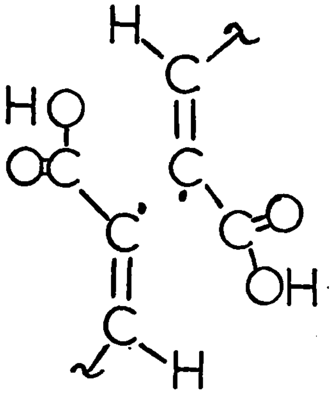


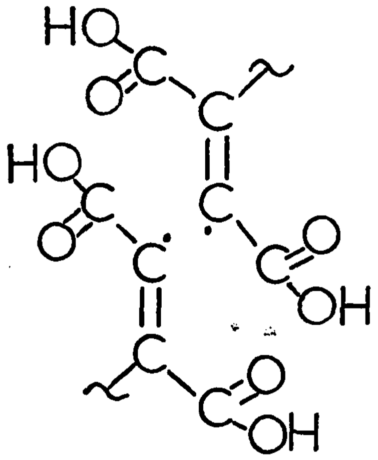
III



IV

Elving explains this as a result of stabilization of the cis intermediate through the interaction of the double bond with mercury at the electrode surface. An alternative explanation can be proposed. A specific orientation of the molecule at the electrode surface prior to electron transfer may be assumed. Since both acids have a planar structure, an S_N2-like orientation (carbon-bromine bond normal to the electrode surface) is unlikely. On the other hand, an orientation where the molecule is co-planar with the electrode surface appears very likely whether the compound is in the form of R-Br or R^+. This orientation should permit stabilization of intermediates of either cis or trans isomers through pi-bond interaction with the mercury surface. This explanation conflicts with Elving's theory which assumes that double bond mercury interaction stabilization alone accounts for the formation of dimers from the cis isomer. However, since free radical intermediates are not particularly stable, dimer formation must take place in the vicinity of the electrode surface where the radical is generated. Steric considerations can now be used to show that dimerization of the trans form is highly imporbable, or at least less likely to occur than for the corresponding cis isomer.





Dimerization of two cis free radicals requires the intimate interaction of a small hydrogen atom with a bulky carboxylic acid group. This is not a particularly strained system. During the dimerization of two trans free radicals, however, the interaction becomes more aggravated since it involves two large carboxylic acid groups.

Subtle modification of the electroactive species might be expected to give a considerable amount of information on the reduction mechanism of cis-trans isomers. For instance, if steric hinderance is one of the controlling factors in the reduction of organic halides, then replacing the hydrogen on the double bond in monobromomaleic acid and monobromofumaric acid with a methyl group (viz. 1-bromo-2-methylmaleic acid known as bromocitraconic acid and 1-bromo-2-methylfumaric acid known as bromomesaconic acid) would provide compounds for polarographic investigation which possess slightly greater steric requirements.

Bromocitraconic acid should not be able to approach or lie as flat on a mercury surface as monobromomaleic acid due to the added steric requirements of the methyl group. Accordingly, double bond interaction with the mercury electrode should be reduced (if it indeed occurs) and the amount of dimeric product should be less. In addition, geometric isomers can undergo cis-trans interconversion which would affect the amount of dimer formation. Cis-trans interconversion comes about as the result of the energy differences between the two isomers. For example, the trans isomer, monobromofumaric acid is more stable than the cis isomer because of the steric strain present in the cis molecule from the interaction of the two bulky carboxylic acid groups located on the same side of the double bond. There is a tendency for sterically hindered cis isomers to rearrange to the trans form to relieve the strain. For interconversion to occur, the pi-bond must be broken by some sort of induced electronic rearrangement to give a single bond. Free rotation about the single bond is then allowed to give the trans isomer which is locked into position by the reforming of the double bond. Electronic rearrangement, rotation and interconversion can probably occur during the electrode reaction and most likely occurs after electron transfer when the halide has split off as an anion. Any conversion of the cis isomer to a trans configuration would then reduce the amount of dimer product since the cis form is responsible for the dimerization reaction.

As the substituent on the carbon adjacent to the bromine bearing carbon increases in size, one would expect less energy differences between the cis and trans products. So a retention of the cis configuration would be expected for bromocitraconic acid compared to monobromomaleic acid during the electrode reaction. If this were true, then the dimer formation reaction would be favored which is a direct contradiction with the previous theory in which steric hinderance may produce conditions conducive to less dimer formation. It is difficult to decide which process will predominate during the electrode reaction and determine the configuration of the final reduction products.

In the reduction of trans isomers such as monobromofumaric acid and bromomesaconic acid, trans products should be the rule since there is no driving force for conversion to the cis isomer, and subsequently, little or no dimeric product should be found in the reduction products.

After reduction of the carbon-bromine bond in allylic bromides, the reduction of the double bond is possible to give the corresponding alkane. Double bond reduction is reported to occur at more negative potentials than the reduction of the carbon-bromine bond (14). The nature of double bond reduction for unsaturated C_4 dibasic acids has been reported (12,13,15,45). Polarographic reductions of compounds containing carboxylic acid groups are generally pH dependent. The polarograms will exhibit a characteristic wave splitting in a pH range near the pKa's of the acidic groups. In a solution buffered at a pH where both the undissociated acid form and the anionic form of the acid can exist, the undissociated acid molecule will undergo double bond reduction first to give the initial wave. The anionic form reduces at more negative potentials to give a second wave. Only one wave is oberved in strong acid and base solutions since only one form of the acid will exist in solution under these conditions.

Controlled Potential Coulometry

Although the Ilkovic equation can often be used to decide the number of electrons involved in the electrode reaction responsible for a polarographic wave, its use requires a knowledge of the diffusion coefficient of the electroactive substance. The lack of precise diffusion coefficient data under typical polarographic conditions makes it necessary to employ estimated or approximate values. This method of calculation becomes unreliable for systems of three or more electrons. Controlled potential electrolysis then becomes the method of choice for measuring the n-value for an electrode reaction.

A solution, corresponding in all respects to the solution used to record the polarographic wave, is electrolyzed exhaustively with a mercury pool electrode whose potential is controlled at a value corresponding to the diffusion current plateau of the polarographic wave. By carrying the electrolysis to completion on a known quantity of substance, the number of electrons is easily computed from the measured quantity of electricity passed. The quantity of material being oxidized or reduced at an electrode is directly proportional to the quantity of electricity passed as expressed in Faraday's Law. One faraday or 96,493 coulombs is required to electrochemically oxidize or reduce one gram-equivalent of a substance. The fundamental condition for coulometric analysis is that the electrolysis proceed with 100% current efficiency in order for Faraday's Law to be valid.

Coulometric analysis at controlled potential was orginated by Hickling (22) who determined cupric ion by measuring the quantity of electricity required for its complete reduction at a platinum cathode and determined iodide similarly by its oxidation at a platinum anode. Lingane (30) developed the method further and introduced the use of a mercury pool cathode which has certain advantages over the platinum cathode. The mercury cathode has a greater cathodic overvoltage than platinum, optimum control potentials are easily determined from polarographic data, and conditions for 100% current efficiency are generally more easily established with mercury than with platinum.

One of the classical examples of the application of controlled potential coulometry was the determination of the n-value for the reduction of picric acid, a trinitro phenolic compound. The number of electrons consumed per mole of picric acid was experimentally found to be 17 where in theory it should have required 18 electrons to reduce the three nitro groups to give 2,4,6-triaminophenol (30). The primary electrode reaction was then thought to involve a dimerization to give a substituted hydrazobenzene. However, Meites and Meites (33) found that in very dilute solutions the electrolysis gave an n-value of 18. This dependence on solution conditions becomes important when one is correlating n-values and reduction products for the purposes of elucidating reduction mechanisms.

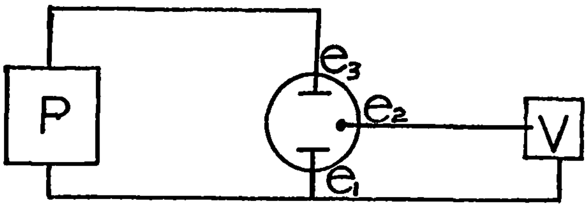
Wawzonek (46) reported that polarographic data do not always agree with the results obtained in a large scale electrolysis since the former technique requires diffusion controlled conditions while the latter technique is accompanied by vigorous stirring. As an illustration, benzenediazonium chloride gives two polarographic waves. The first wave is independent of pH and represents the one electron reduction of the ion to give a phenyl radical and a molecule of nitrogen gas. Large scale electrolysis with a controlled potential at the first wave gave products arising from the phenyl radical, phenylmercuric chloride and diphenyl mercury. The second wave is pH dependent and represents the reduction of the ion to phenylhydrazine. Large scale electrolysis at a controlled potential on the plateau of the second wave gave, however, products similar to those obtained by use of the of the potential of the first wave (2). Thus it appears that in those electrode reactions where free radicals are formed and dimerization can take place, the ultimate products from large scale electrolysis may be somewhat different from those formed at a dropping mercury electrode. The coulometric technique reliably establishes the n-value for the electrode reaction but identification of the reduction products give the n-value meaning.

Chronopotentiometry

Chronopotentiometry or voltammetry at constant current involves the measurement of potential, as it varies with time, across an electrolysis cell where the electrolysis is conducted at constant current (29, pp. 617-638). The solution is quiescent so that mass transfer is diffusion controlled. Migration of the reducible species is kept at a minimum by using a large excess of supporting electrolyte.

Electrolysis at constant current is the oldest voltammetric method with its origin traced to the work of Weber (48) reported in 1879. The technique was applied in the early 1900's by Sand (39) and Karaoglanoff (23) to the verification of Fick's first law of diffusion and the determination of diffusion coefficients. Butler and Armstrong (6) applied chronopotentiometry in the 1930's to the study of electrochemical kinetics. Gierst and Juliard (18) only recently realized the analytical potential of this tool in the 1950's. However, Delahay and Mamantov (9) are accredited for developing the method as an analytical technique.

The following simple schematic diagram serves to illustrate the basic features of the technique (36).



Power supply, P, maintains a constant current output regardless of the process occurring in the electrolysis cell where e_1 is the working cathode, e_2 is the reference electrode and e_3 is the working anode. The potential difference between e_1 and e_2 is followed by a potentiometer, V. The working range for this technique is from 10^{-6} to 10^{-2} molar with an accuracy of 1 to 2 percent.

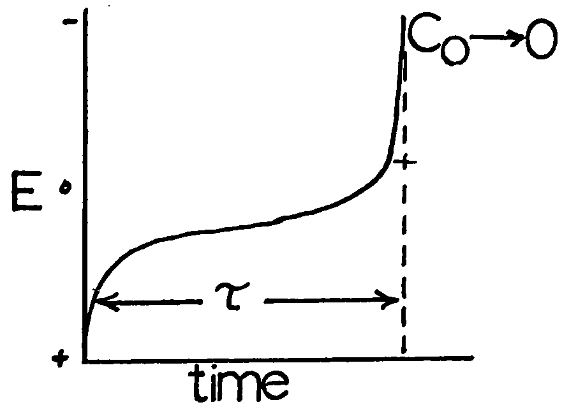
Consider the reaction:

$$O + ne^- \longrightarrow R \qquad (17)$$

As a chronopotentiometric electrolysis proceeds , the depletion of the electroactive species O at the surface of the working electrode causes the potential of e_1 to vary as predicted by the Nernst equation:

$$E = E^{\circ} + \frac{RT}{nF} \ln (C_O/C_R) \qquad (18)$$

Initially, the concentration of the reduced species, C_R, is equal to zero. Therefore, the potential of the working electrode is more positive than the standard potential, E°. Instantaneously, the potential rapidly proceeds to the decomposition potential of the electroactive species and levels off. During this time, the concentration of the oxidized species is decreasing at a constant rate while C_R is being generated at a constant rate. As a result, the potential of e_1 becomes more and more negative during the electrolysis until the concentration of the reducible species is essentially zero at the surface of the electrode. When this condition is attained, the potential of the working electrode rapidly becomes more negative until some new cathodic process occurs. If there are no other electroactive species present, the evolution of hydrogen gas or the decomposition of the supporting electrolyte occurs. The following diagram illustrates a typical chronopotentiogram.



The measureable quantity in chronopotentiometry is called the transition time, designated τ. The transition time is the span of time required for the depletion of the electroactive species at the surface of the working electrode. Transition times depend on the concentrations of the species undergoing reduction so that the measurement of this time has analytical utility. The accuracy of the results depend only on the measurement of times at which potential breaks occur in the graphical data rather than on accurate current and potential measurements.

The basic transition time relationship for reversible and irreversible processes occurring without kinetic complications is given by Equation 19 (39):

$$\tau^{1/2} = \pi^{1/2} n F C^{\circ} D^{1/2}/2i_{\circ} \qquad (19)$$

in which $i_{\circ}$ is the current density, C° is the bulk concentration of the species and all other terms have been used and identified previously. To determine if a given process is without kinetic complication, the $i_{\circ}\tau^{1/2}$ product at a given $i_{\circ}$ should be a constant. If a constant value is obtained, then one is able to relate $\tau^{1/2}$ to concentration by plotting the values versus concentration to yield a straight line with a slope which is dependent on the current density. Reinmuth (37) has also shown that the variation of τ with experimental parameters is of value in elucidating mechanisms and offers diagnostic criteria to aid in distinguishing between various reaction schemes.

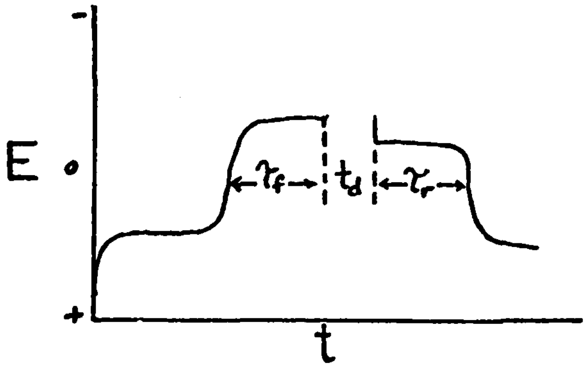
The basic equation for the potential of the working electrode for a reversible process with soluble reaction products at a mercury electrode is given be Equation 20 (23):

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \left[(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}} \right] \qquad (20)$$

in which t is any time during the electrolysis. Equation 20 has the same form as the equation for a reversible polarographic wave. Interestingly, Equations 19 and 20 were established for chronopotentiometry and buried in the literature some 20 to 30 years before the equivalent equations for polarography were derived by Heyrovsky and Ilkovic. Since the time of Sand and Karaoglanoff, theoretical relationships for processes other than reversible reactions have been considered by other workers (3,5).

Many improvements and variations have been introduced since the advent of chronopotentiometry. The earliest working electrodes were usually mercury pools. Later, a number of combinations of inert materials and modifications of the mercury pool were investigated as possible working electrodes. The hanging mercury drop electrode (HMDE) was developed by Gerischer (17) who also experimented with a gold plated platinum wire electrode. The mathematical treatment and theoretical equations for spherical diffusion at an HMDE have also been developed (5,16) while Ross and co-workers (38) studied the analytical applications of the HMDE. The application of platinum wire and mercury plated platinum disks as electrodes ushered in the era of thin layer electrochemistry (7,35). The advantage of this innovation is the elimination of diffusion of the electroactive species. Since the electrolysis is applied to extremely thin layers of solution (solution thicknesses on the order of 1 cm. to 10^{-3} cm.) diffusion to and from the electrode surface is no longer a factor.

Berzins and Delahay (4,8) developed chronopotentiometry with current reversal, a technique in which the polarity of the constant current is reversed at some time during the electrolysis to give chronopotentiograms of the following type:



The technique yields two transition times, forward (τ_f) and reverse (τ_r). The symbol t_d designates a time halt where no electrolysis is occurring and reaction products are allowed to take place. Experimentally, the current may be reversed either after the potential break when the theoretical concentration of C_O at the electrode surface is negligible or at some preselected time interval before the potential break. The length of time selected for the time-halt depends on the reaction to be investigated but can be as short as zero seconds (instantaneous current reversal) or as long as several seconds. The ratio, τ_r/τ_f, in conjunction with three other diagnostic criteria, also permits one to distinguish between several various reaction schemes (42). These schemes include reversible and irreversible processes, with or without kinetic complication; consecutive processes, stepwise reactions and processes involving chemical reactions preceding or following electron transfer. Chronopotentiometry with current reversal, then, is particularly useful for those electrochemical reductions involving kinetic or chemical complications.

The application of current reversal with a thin layer electrode is especially useful to kinetic studies. The study of the rates of chemical reactions that occur subsequent to the electrochemical generation of a species, which is then confined in a thin layer of solution in the vicinity of an electrode, is possible by this technique. Consider Reaction 17 for example, if no chemical reaction occurs during t_d, and since diffusion is virtually eliminated, the τ_r/τ_f ratio should be equal to unity if the reduction was reversible. However, the unique feature is that rate constants too small to be conveniently measured by diffusion chronopotentiometry with current reversal can be handled by this technique. Since chronopotentiometry at a thin layer electrode with current reversal appears to afford an excellent method for elucidating reaction mechanisms, application of this technique was attempted in this present investigation.

EXPERIMENTAL WORK

Reagents

Synthetic Preparations

Citraconic acid (methylmaleic acid) was prepared from citraconic anhydride (34, p.140). Recrystallization from water and washing with cold benzene gave a pure product with a melting point of 94° C.

Mesaconic acid (methylfumaric acid) was prepared from citraconic acid (34, p.382) by heating the latter in a dilute solution of nitric acid to bring about geometric interconversion. The solution was slowly evaporated down in volume to give a product which when recrystallized from water gave a pure material with a melting point of 208° C.

Bromocitraconic acid was prepared by a procedure based on that used by Vaughn and Milton (43). The synthetic route involves the bromination of mesaconic acid to give dl-erythro-α,β-dibromomethylsuccinic acid (M.P. 197°C). Dehydrohalogenation of this intermediate to give bromocitraconic anhydride is accomplished by heating with phosphorus pentaoxide. The anhydride was collected by sublimation to give a pure product with a melting point of 100-101°C. Additional product was salvaged from the tar in the reaction flask by rinsing with carbon disulfide. Evaporation and recrystallization from carbon disulfide gave a product with a melting point comparable to the sublimated product. Proof of structure, other than the satisfactory melting point, was confirmed by other means. Elemental analysis by Galbraith Laboratories, Inc. reported 31.28% carbon, 1.55% hydrogen and 41.93% bromine to give an empirical formula of $C_5H_3O_3Br$, calculating oxygen by difference, compared to theoretical values of 31.41%, 1.58% and 41.88% respectively. NMR analysis in deuterated chloroform gave one peak for the methyl group at 2.15 parts per million (ppm), the rest of the spectrum was void of peaks. An infrared spectrum of the compound exhibited the characteristic adsorptions for an unsaturated conjugated carboxylic acid. Gentle acid hydrolysis is required to produce the free acid from the anhydride.

Bromomesaconic acid was also prepared by a procedure based on that used by Vaughn and Milton (43). This synthetic route requires several steps initially involving a bromination of citraconic acid to give dl-threo-α,β-dibromomethylsuccinic acid (M.P. 153°C). The methyl ester (B.P. 94-96°C @ 1.8 mm) was then prepared by esterification with diazomethane to prevent the splitting out of water to form the anhydride in the succeeding steps. The methyl ester was then heated in the presence of pyridine to bring about dehydrohalogenation to give methylbromomesaconate (B.P. 118-121°C @ 2 mm). Acid hydrolysis of this material gives bromomesaconic acid which upon recrystallization from nitromethane gave a pure product with a melting point of 223-224°C. The NMR spectra in D_2O had one peak at 2.19 ppm for the methyl group, the acidic hydrogen adsorption was not present as a result of exchange with deuterium. The infrared spectra was consistent with the acid structure.

The synthesis of bromocitraconic acid and bromomesaconic acid were especially difficult primarily due to problems incurred in the bromination of citraconic acid and mesaconic acid. The double bond is very unreactive towards the addition of bromine because of the presence of the two carboxylic acid functional groups on the double bond. Consequently, very poor yields were obtained in the bromination step. To add to the problem, the reaction products were oils. The oils required anywhere from one to four weeks of setting before any crystals of the desired product appeared. Many modifications on the original Vaughan and Milton procedure were tried. As many as fifteen separate brominations were attempted on mesaconic acid varying such conditions as the solvent media and the catalyst. From considerations of Hammett acidity functions, Hanna and Siggia (19) suggested the use of a 50% methyl alcohol solution as the best solvent media for the bromination of unsaturated, conjugated carboxylic acids. An oil was also obtained from this media. The optimum conditions appeared to be a 50-50 chloroform-ethyl ether mixture with an iodine catalyst. The work-up of the thick oily product was tried several ways, other than patiently waiting for the product to slowly crystallize out on standing. The best yield of product from any of the oils was obtained by dissolving the oil in nitromethane and adding two parts of petroleum ether to give two immiscible layers. Overnight, a white flaky solid forms at the interface of the two layers and settles into the nitromethane layer. The solid material of fairly good purity is then easily filtered.

With each additional step in the synthesis of the two compounds, recovery was short of 100% of the theoretical. Also, with each step some of the precursor was wasted before perfection of the synthetic reaction was attained. Finally, unforeseen complications such as decarboxylation occurred during some of the synthetic work so that only one to two grams of bromocitraconic acid and bromomesaconic acid were available for this investigation.

Chemicals

Citraconic acid was obtained from the J.T. Baker Chemical Company, Phillipsburg, New York and used without further purification as a synthetic starting material.

Maleic acid was obtained from Eastman Organic Chemicals, Distillation Products Division, Rochester, New York and was recrystallized from water to give a material with a melting point of 131° C.

Fumaric acid was obtained from the Matheson Coleman and Bell, Norwood, Ohio and was recrystallized from water to give a material with a melting point of 294° C.

Triton X-100 was obtained from the Rohm and Haas

Chemical Company, Philadelphia, Pennsylvania.

Commercial pre-purified nitrogen was used to deaerate polarographic test solutions.

All other chemicals were reagent grade and were used without further purification.

Buffers

Buffer solutions of constant ionic strength were prepared from reagent grade chemicals for use in the polarographic, controlled potential coulometric and chronopotentiometric techniques. The following systems were used: pH 0.5 to 3.0, HCl-KCl; pH 3.0 to 8.0, $NaC_2H_3O_2$-$HC_2H_3O_2$; pH 8.0 to 10.0, NH_4OH-NH_4Cl; pH 10.0 to 12.0, Na_2HPO_4-NaOH and KCl-NaOH.

Apparatus and Procedures

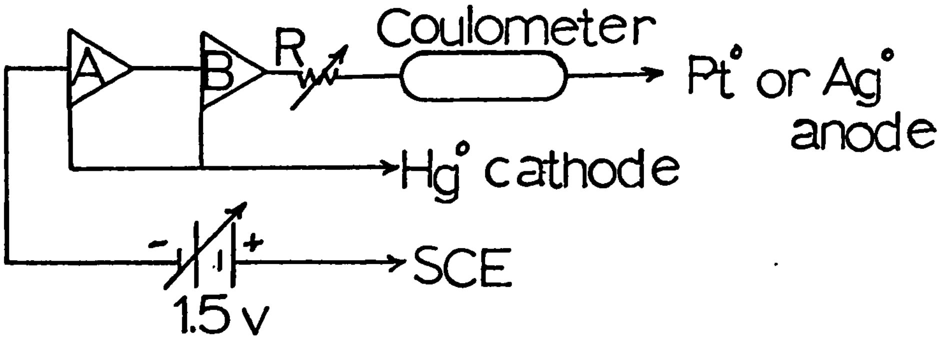
Polarography

The polarographic cell consisted of three compartments separated by Corning ultra-fine glass frits. The center compartment contained a saturated KCl solution to minimize the electrical resistance between the test solution compartment and the saturated calomel electrode (SCE) located in the third compartment. Cell resistances on the order of 200 to 300 ohms were obtained with the buffer solutions employed so that it was not necessary to make corrections for the iR drop through the cell. The dropping mercury electrode had a capillary constant, $m^{2/3} t^{1/6}$, of 1.68 $mg.^{2/3} \cdot sec.^{-1/2}$ at open circuit at 26°C. into distilled water with a mercury reservoir height of 34 cm., and was used with a Leeds and Northrup Type-E Electro-Chemograph. All polarograms were run in an air-conditioned room controlled to 26° ± 1°C.

Solutions for polarographic analysis were prepared with concentrations of 5.0 ± 0.5 millimolar in buffers of pH 0.5 to 12.0 Ten ml. aliquots were taken for analysis and were deaerated for five to ten minutes with pre-purified nitrogen. Where maxima occurred in the polarographic waves, 0.05 ml. of a 0.5% Triton X-100 solution was added as a maximum suppressor. Polarograms of the buffers alone were run to determine the decomposition potentials of the supporting electrolytes and to ensure polarographic purity.

Controlled potential coulometry

The electrolyses at a controlled potential were carried out using a potentiostat of the following design:



The components consist of a Heathkit Model EUW-19 operational amplifier containing a control amplifier (A) and a booster amplifier (B). The system has a rated capacity of 20 milliamperes at ± 50 volts. The variable resistor R, is used to limit the total current output to 20 milliamperes. A variable potential source is able to supply up to 1.5 volts to the mercury cathode relative to the SCE.

A hydrogen-nitrogen gas coulometer, described by Lingane (29), was used to integrate the total current passed during the electrolysis. It consists of two lengths of platinum wire (0.025" x 2") sealed into a 10 ml. buret just above the stopcock. The graduated portion of the buret was surrounded by a water jacket equipped with a thermometer for recording the temperature of the coulometer. A typical leveling bulb arrangement containing 0.1N hydrazine sulfate was connected to the stopcock end of the buret by a length of rubber tubing. A second stopcock was attached to the top of the buret above the water jacket so that the system could be sealed to trap the hydrogen and nitrogen gas generated during the electrolysis. This coulometer has the capacity for measuring the electrolysis of about 0.5 milliequivalents of material. The gas coulometer was checked by passing a known current from a Sargent Constant Current Source through the coulometer for a given time. The experimental volume of gas collected was about 2% low of the theoretical volume for five trials which was of sufficient accuracy.

The electrolysis cell used is illustrated in Figure 1. The H-type cell is separated into compartments of 200 ml. capacities by a Corning ultra-fine frit. A silver wire or platinum wire electrode in contact with a 0.1M KCl solution was used in the anode compartment. The cathode was a mercury

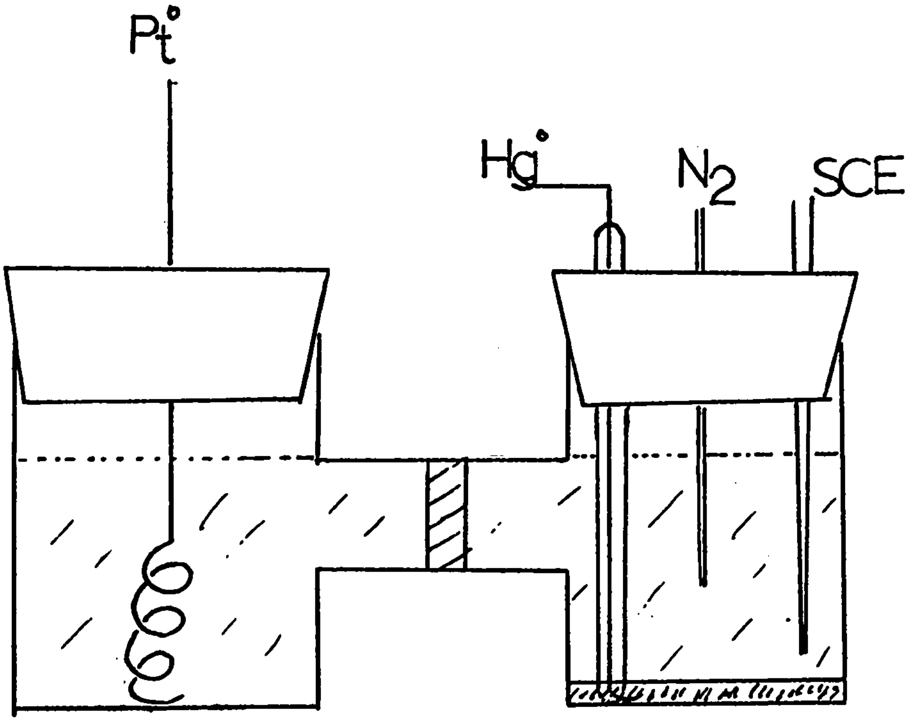


Figure 1. Controlled potential electrolysis cell

pool. Stirring of the test solution in the cathode cell was accomplished witha magnetic stirrer and a teflon-coated stirring bar lying on the surface of the mercury pool. The bottom of the cathode compartment was separted from the surface of the magnetic stirrer by insulation and a stream of compressed air to prevent heating of the test solution by the heat generated by the electric stirring motor.

A pre-electrolysis at the appropiate potential on the supporting electrolyte-buffer solutions was first run for two important reasons. First, any reducible impurities present in the supporting electrolyte-buffer chemicals are removed and a background current is established for the particular system under investigation. Secondly, the hydrogen-nitrogen coulometer solution is presaturated with gas to prevent the dissolution of gas that should be measured during the electrolysis of the unknown solution. In the latter stages of the pre-electrolysis, about 50 to 70 ml. of the solution is withdrawn. A portion of this solution is used to dissolve a weighed amount of compound (from 0.25 to 0.50 millimoles) to facilitate its introduction into the cathode compartment. Just before the test solution is added, the gas buret is sealed at the top, the time is recorded and the buret reading is taken at time zero. During the electrolysis the current decreases exponentially with time and asymptotically approaches the background current. Meanwhile, the leveling bulb is lowered as the liquid level in the gas buret drops to maintain atmospheric pressure on the contained gases. When the current has dropped to the background current, the electrolysis is stopped and the final buret reading is recorded. Also, the total time of electrolysis is recorded, as well as barometric pressure, room temperature and temperature of the water jacket. The total volume of gas collected is calculated from the reading at time zero and the final reading. This volume of gas is corrected for the volume of gas generated by the background current during the electrolysis time. The background current corrected volume is then corrected to standard temperature and pressure. The hydrogen-nitrogen coulometer produces 16.74 ml. of gas at STP for every milliequivalent of reducible species. Therefore, the volume of gas collected at STP divided by 16.74 ml./meq. gives the number of milliequivalents of material reduced. Finally, the number of milliequivalents divided by the total number of millimoles of material added yields the n-value or the number of electrons involved in the reaction. The n-value for a compound in a given supporting electrolyte-buffer was repeated several times. This was easily most accomplished by repetively adding more material to a previously reduced test solution. Thus, isolation and identification techniques were made possible on the accumulation of reduction products from several n-value determinations.

The isolation of the products proved to be an insurmountable problem as the consequence of the water soluble nature of the reduction products and by the rather small quantities of material with which to work. Only 50-150 milligrams of accumulated reduction products would be present after loss of a bromine which accounts for nearly 40% of the total mass of the starting compounds. Initially, solvent extractions of the aqueous test solutions were attempted. However, the affinity of the products for the aqueous layer afforded only a trace of extractables. Removal of the water by vacuum oven evaporation was next tried. The supporting electrolyte-buffer salts plus the reduction products were collected and placed in a soxhlet extraction apparatus and were repeatedly extracted with ether, a solvent in which the possible reduction products had some solubility. Again, a very disappointingly small amount of material was found in the ether and that which was recovered appeared to have undergone some decomposition.

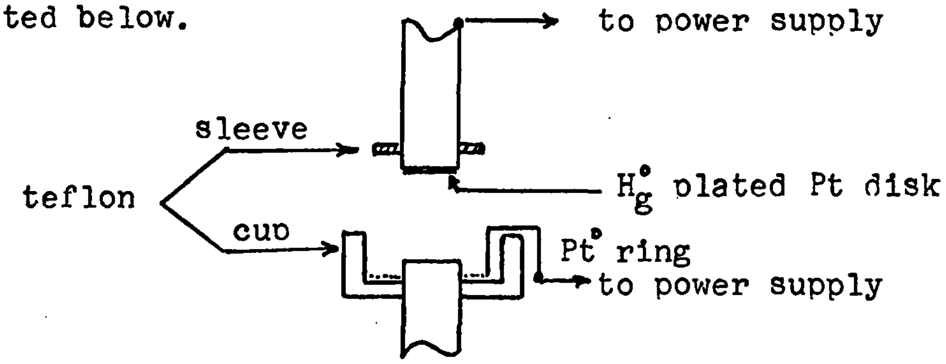
Preliminary investigations indicated that the reduction products such as citraconic acid, mesaconic acid and methylsuccinic acid could be separated and identified as the trimethylsilyl esters using gas chromatography. However, the silylating agent (available from Pierce Chemical Company, Rockford, Illinois) and its derivatives are sensitive to moisture and are subject to hydrolysis. Therefore, this technique was applied to a vacuum dried collection of salts from an n-value determination. Since approximately only 2 ml.

of silylating agent are required for the amount of products present, a slurry would result from the presence of the large amount of supporting electrolyte salts. Thus, various non-aqueous solvents that would not also react with the silylating agent were used as diluents. Unfortunately, solubility problems and the incompatibility of the non-aqueous solvents with the silylating agent solvent proved to be too troublesome for continuing any efforts in this area.

It was found that if citraconic acid and mesaconic acid were reduction products they could be identified and the mass ratios calculated from NMR data. The lone proton on the double bond in citraconic acid appears at 6.01 ppm while that for mesaconic acid shows up at 6.73 ppm. A synthetic mixture of 2.07 parts of citaconic acid to 1.00 parts of mesaconic acid was experimentally found to be a ratio of 2.05 to 1 from the integration of the NMR spectra of the mixture. The best solvent for the NMR technique was D_2O which, of course, cannot be used due to the water soluble inorganic salts present in the collected salts. The necessity of separating the organic acids from the inorganic salts so that the gas chromatographic or NMR technique could be applied was becoming readily apparent. A precipitation technique was tried whereby the KCl supporting electrolyte, for instance, was precipitated with $AgClO_4$ to give slightly insoluble $KClO_4$ and insoluble AgCl. Hopefully, the organic reduction products would remain behind in solution. However, the small quantity of material was apparently adsorbed by the large volume of precipitate. The small amounts of organic material made separation by other chromatographic means impractical so that hopes of identifying the reduction products were abandoned.

Chronopotentiometry

Chronopotentiometry with current reversal was attempted with a thin layer electrode described by Reilley (35) and built by the Chemistry Shop at Iowa State University is illustrated below.



The electrode and cell is constructed on the anvil and spindle of a precision micrometer. A mercury plated platinum disk is silver soldered onto the spindle to act as the cathode. The teflon cup and the anvil serve to contain the test solution. A small platinum wire ring anode of the proper diameter and an SCE probe (not shown in the above diagram) are inserted in the test solution. The thickness of the test solution is adjusted by rotating the spindle up or down so that the depth of the solution can be read from the barrel of the micrometer (correcting for the new micrometer "zero" resulting from the thickness of the silver-soldered platinum disk). An inlet for nitrogen gas is also available for deaeration of the test solutions.

The constant current source was designed and built by Dr. R.W. King of Iowa State University and consists of a Heathkit Model EUW-19 operational amplifier and a variable current source of up to one milliampere with means for current reversal. The chronopotentiograms are recorded on a Sanborn Direct Writing Oscillographic Recorder, Model 7701A. Transition times, forward or reverse, from two to nine seconds can be followed by this system with a variable timing mechanism.

Test solutions of the same concentrations and composition as those used in polarography were to be studied. An electrochemically reversible iron tartrate solution was employed to determine the zero setting of the micrometer and to check out the response of the thin layer electrode. While checking out this technique it was found that the thin layer electrode was limited to potentials somewhat lower than the dropping mercury electrode of polarography as shown by the data in Table 1. This difference in the potential of hydrogen evolution is accounted for by the fact that the mercury plated platinum disk does not respond like a mercury electrode but a combination of platinum and mercury electrodes due to the slight solubility or penetration of the mercury into the platinum surface. Despite this serious limitation of the thin layer electrode, the bromocitraconic acid and bromomesaconic acid solutions were analyzed by this technique even though the polarographic half-wave potentials of these compounds were more negative than the limiting hydrogen evolution potential at the various pH's. The test solutions were poured into the teflon cup and anvil assembly and deareated with pre-purified nitrogen. The chronopotentiograms were recorded several times with current reversal applied at various times during the electrolysis.

<u>Auxiliary equipment and instruments</u>

The infrared spectra were recorded with a Beckman Model IR 8 spectrophotometer using the KBr pellet technique.

NMR spectra were recorded with a Varian Associates Model A-60 instrument.

Table 1. Comparison of the potentials for the appearance of the hydrogen wave in supporting electrolyte-buffer systems by polarographic and thin layer electrochemical techniques

System	pH	Potential at appearance of hydrogen wave		
		Polarography	Thin layer	ΔE
KCl-HCl	1.0	-1.22	-0.60	0.62
KCl-HCl	3.0	-1.46	-0.90	0.56
$NaC_2H_3O_2$-$HC_2H_3O_2$	5.0	-1.52	-1.00	0.52
KCl-Na_3PO_4	7.0	-1.67	-1.05	0.62
NH_4Cl-NH_3	7.9	-1.77	-1.10	0.67
NH_4Cl-NH_3	9.9	-1.81	-1.15	0.66
KCl-NaOH	12.1	-1.89	-1.25	0.64

RESULTS AND DISCUSSION

Polarography

Table 2 summarizes the polarographic behavior of the eight compounds studied over the pH range 0.5 to 12.0. The data for monobromomaleic and monobromofumaric acids are taken from the work by Elving and co-workers (14). The polarographic data for the non-brominated dibasic acids are presented here for comparison purposes.

Bromocitraconic acid gives one cathodic wave except in the pH region where the wave-splitting phenomena are observed due to the presence of the carboxylic acid groups. Monobromomaleic acid gives two waves plus a third wave in the region of wave-splitting. Elving reports that the first wave represents C-Br bond fission and the second wave represents reduction of either or both maleic acid and fumaric acid. The C-Br bond fission and double bond reduction in bromocitraconic acid must then occur at roughly the same potential.

Comparison of the half-wave potentials for double bond reduction of the cis-acids, citraconic and maleic acids, provides information on the effect of a methyl substituent. Double bond reductions for citaconic acid occur at potentials from 0.06 to 0.16 volts more cathodic than for maleic acid; the difference in $E_{\frac{1}{2}}$'s increasing as the pH becomes more basic. This may indicate that the methyl group is increasing the electron density at the double bond by an inductive

Table 2. Effect of pH on the polarographic properties of cis-trans isomeric dibasic acids.

Compound	Wave/ pH	pH of supporting 0.5	1.0	1.5	2.0
Bromocitraconic acid	$-E_{\frac{1}{2}}$, volts	0.63	0.74^x	0.81^x	0.80
	I^c	14.7	8.42	14.8	10.2
		w^d	w	w	w
Citraconic acid	$-E_{\frac{1}{2}}$	0.62	0.66	0.70	0.74
	I	7.56	8.33	8.04	4.86
		w	w	w	w
Maleic acid	$-E_{\frac{1}{2}}$		0.60^x		0.68
	I		8.67		4.99
			w		w
Bromomesaconic acid	$-E_{\frac{1}{2}}$	0.66	0.78	0.86	0.95
	I	12.7	7.74	14.3	8.66
		w	w	w	w
Mesaconic acid	$-E_{\frac{1}{2}}$	0.65	0.71	0.78	0.84
	I	6.55	4.73	7.90	4.59
		w	w	w	w
Fumaric acid	$-E_{\frac{1}{2}}$		0.63^x		0.74
	I		8.31		7.78
			w		w
Monobromomaleic acid	$-E_{\frac{1}{2}}$ 1)	0.44	0.47		0.57
	2)	0.54	0.58		0.68
	I 1)	5.3	5.2		4.7
	2)	2.9	3.3		4.1
Monobromofumaric acid	$-E_{\frac{1}{2}}$ 1)	0.41	0.48		0.58
	2)	0.51	0.59		0.69
	I 1)	3.3	3.3		3.2
	2)	3.0	3.2		3.2

---

[a] NH_4Cl-NH_3 supporting electrolyte-buffer.
[b] Na_2HPO_4-NaOH supporting electrolyte-buffer.
[c] I, diffusion current constant, microamps/millimole.
[x] 0.05 ml. of 0.5% Triton X100 added.

electrolyte - buffer systems (± 0.1 pH units)								
3.0	4.0	5.0		6.0		8.0	10.0	12.0
		region of wave splitting						
		1	2	1	2			
0.94	1.06	1.11,	1.33	1.47[x]		1.51	NPWO[b,f]	1.65
7.16	5.72	1.30,	4.11	5.59		6.21		4.58
w	w/i[g]	w/i		i/w[h]		i		i
0.86	1.00[x]	1.11		1.20,	1.40	1.47[x]	1.56[a]	NPWO
7.80	3.12	7.00		2.14,	1.79	3.67	0.43	
w	w	w		w/i		w/i	i/w	
0.77	0.86	0.95		1.09,	1.24	1.31	1.48[b]	NPWO
8.25	3.44	7.50		3.25,	1.02	3.92	0.80	
w	w	w		w/i		w	i/w	
1.03	1.15	1.23		1.34		@1.50	1.59[a]	1.72
6.30	1.91	2.89		0.31		---	2.34	2.93
w/i	w/i	w		i/w		i	i/w	i/w
0.94	1.02	1.23		1.33		NPWO	NPWO[a]	NPWO
4.10	3.08	3.46		1.02				
w	w	w		w				
0.85	0.92	1.13[x]		1.21,	1.47	NPWO	1.58[a]	1.72
6.84	5.10	6.84		2.20,	3.93		7.23	---
w	w	w		w	i/w		i/w	i
0.61	0.80	0.97				1.38	1.41	
0.73	0.90	1.07,	1.17			1.56	1.60	
4.2	3.7	1.5				3.9	3.5	
3.8	3.2	0.4,	4.4			3.2	3.0	
0.74	0.95	1.05				1.55	1.56	
---	---	1.14,	1.40			---		
5.5	5.4	0.4				6.4	6.0	
---	---	0.4,	3.8			---		

---

[d] w, indicates a well-defined wave, i_d easily measured.

[e] i, indicates an ill-defined wave, i_d not measureable.

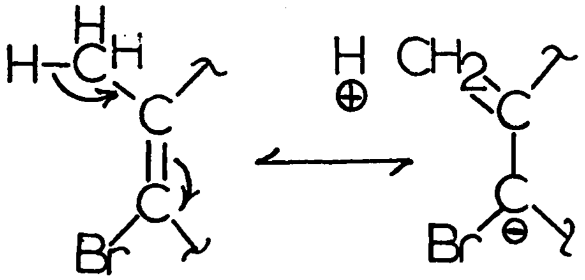
[f] NPWO, no polarographic wave observed.

[g] w/i, a fairly well-defined wave, i_d is measureable.

[h] i/w, a discernable wave but i_d is estimated.

effect thus requiring more negative potentials for reduction. This effect apparently becomes more important as the acidic protons are neutralized to form carboxylate anions. Further evidence of the effect of a methyl group in place of a hydrogen is found in the comparison of half-wave potentials for double bond reduction for bromocitraconic acid and monobromomaleic acid. In this case, the compound with the methyl group undergoes reduction at potentials some 0.09 to 0.21 volts more negative. This is good correlation for the effect of the methyl group on the double bond reduction but it does not help explain why C-Br bond fission and double bond reduction occur at the same potential in bromocitraconic acid. On the contrary, if C-Br bond fission occurs first in monobromomaleic acid as Elving suggests, then the effect of the addition of a methyl group for a hydrogen should have further separated the two half-wave reduction potentials in bromocitraconic acid rather than to cause them to coalesce. This leaves just three possibilities. The first is that the methyl group may affect the C-Br bond fission to a greater degree than double bond reduction. Secondly, the steric effects of the methyl group compared to hydrogen may alter the reduction mechanism. Finally, the C-Br bond fission may not be the first observed reduction in monobromomaleic acid.

Fission of the C-Br bond in bromocitraconic acid occurs at potentials some 0.19 to 0.36 volts more cathodic compared to monobromomaleic acid, again depending on the pH. Thus, the methyl group drives the C-Br bond fission potential more negative than it does the double bond reduction and thereby brings the two half-wave potentials closer together. It is not very easy to rationalize why a methyl group would have such an effect on the C-Br bond, particularly when the electron donating capabilities of a methyl group are not considered too important. However, if one employs the concept of hyperconjugation the C-Br bond is very much affected.



Using this theory, however, the argument can go either way. The negative charge on carbon could repell the uptake of electrons until more cathodic potentials are attained (an argument supported by the present data) or the splitting off of bromine as an anion may be facilitated to promote more anodic reductions. Consequently, this data may illustrate the effect of steric hinderance on electrode reductions since there is some doubt as to the extant of the inductive effect of a methyl group. The hyperconjugation theory has found little acceptance for explaining reaction mechanisms. The more cathodic potentials of C-Br fission in the methyl substituted compounds may then be better explained in terms of steric requirements rather than electronic effects.

One might expect the methyl group to have greater steric influence on the bromine atom than on the double bond due to their relative positions in the molecule.

Looking now to the behavior of the trans isomers, it is seen that bromomesaconic acid and mesaconic acid give only one cathodic wave even in the region of wave-splitting. The same is not true of monobromofumaric acid and fumaric acid, proof of the role of the methyl group as an influential factor in effecting the reduction of the carbon-bromine bond and the double bond. Reduction of the double bond in bromomesaconic acid occurs at potentials from 0.09 to 0.29 volts more negative than for monobromofumaric acid. These values compare with the data for the cis bromo-dibasic acids. Likewise, mesaconic acid double bond reduction occurs at potentials of 0.08 to 0.10 volts more cathodic than fumaric acid. Finally, fission of the C-Br bond in bromomesaconic acid occurs at potentials from 0.18 to 0.30 volts more cathodic than for monobromofumaric acid. Once again, the more pronounced effect of the methyl group on C-Br fission potentials compared to the effect on the double bond reduction must fortuitously level out the electrochemical difference between the double bond and the C-Br bond in monobromofumaric acid, to give a compound that contains two different reducible sites with reduction occurring at the same potential.

The trans isomers are reduced at potentials some 0.01

to 0.20 volts more cathodic than the corresponding cis isomers. The spread in $E_{\frac{1}{2}}$ values becomes larger as the pH becomes more basic. Such a dependence on pH should not be surprising since hydrogen bonding can occur in the cis isomer to modify the negative charge on the carboxylate anion. Hydrogen bonding in the trans isomers is not allowed by the rigid double bond. Consequently, the carboxylate anion in the trans acids interacts with the negative cathode to a greater extent, is repelled by the like charge, and requires more negative potentials for electron transfer.

For each of the polarographic waves, a plot of potential versus the log $\left[i/(i_d - i)\right]$ was made. In general, linear plots were obtained from the data. The slope of the line is equal to $0.059/\alpha n$ from which the value of αn can be calculated. If the value for n is known or can be determined, the value of α, the transfer coefficient can then be calculated. Table 3 summarizes the data obtained from the log plots.

The transfer coefficient is a characteristic of a given compound and represents the degree of reversibility for the reduction of that compound. Inspection of the data in Table 3 for the cis isomers illustrates the effect of bromine on the value of the transfer coefficient. Admittedly, there are two separate reductions occurring for the bromo-compound but if electron transfer for both reactions is taking place at the same time, the transfer coefficient reflects the nature of that transfer. Maleic acid and citraconic acid have similar values perhaps indicating that a methyl group has little effect on electron transfer when substituted on a double bond in place of hydrogen. The data for the trans isomers show a more logical sequence of decreasing value with increasing substitution on the double bond.

Table 3. Transfer coefficients[a] for cis-trans isomers as a function of pH from polarographic data.

Compound[b]	pH 0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
BCA	0.12	0.13	0.09	0.10	0.14	0.25	0.35[c] 0.50	0.12
CA	0.58	0.69	0.67	0.85	0.58	0.40	0.37	0.50 0.40
MaA		0.69		0.60	0.45	0.50	0.35	0.50 0.35
BMA	0.13	0.13	0.09	0.15	0.15	0.18	0.18	0.22
MeA	0.42	0.38	0.36	0.34	0.30	0.35	0.39	0.38
FA		0.50		0.40	0.42	0.43	0.40	0.45 0.37

[a] N-values of 4 were assumed for the bromo-compounds and a value of 2 electrons for the other compounds.

[b] BCA, bromocitraconic acid; CA, citraconic acid; MaA, maleic acid; BMA, bromomesaconic acid; MeA, mesaconic acid; FA, fumaric acid.

[c] Where more than one polarographic wave occurs, an equal number of transfer coefficients are so noted.

The value of the transfer coefficient can be simply thought of as being related to the distance of closest approach for the electroactive species to the electrode surface. Three different routes of approach for organic bromides have been discussed previously in this paper. The first route is with the carbon-halogen bond perpendicular to the electrode surface with the halogen atom directed away from the electrode (see diagram, page 10). Sease and co-workers (40) propose that the reverse is possible with the bromine atom foremost with the carbon following. The third, for unsaturated compounds, provides for a co-planar structure of the double bond with the electrode surface.

For geometric isomers of the type investigated in this present study, orientations corresponding to the first two proposals would require that bulky bromine atoms and/or carboxylic acid groups would have to approach the electrode straight on meaning that different steric hinderances would be presented by the cis and trans acids. If, indeed, the value of the transfer coefficient is indicative of the distance of closest approach, then one might expect that the cis isomers would have widely different values from the trans isomers. For example, bromocitraconic acid approaching the electrode with the bromine atom facing away would have two bulky carboxlyic acid groups projecting into the electrical double layer. The trans isomer, however, would have only one acid group and a methyl group facing towards the electrode. Surely the cis isomer is in a more unfavorable climate for the process of electron transfer. Similar arguments can be offered for a process where bromine is foremost when the compound diffuses towards the electrode. The data from

Table 3 for bromocitraconic acid and bromomesaconic acid show little differences in their transfer coefficients from pH 0.5 to 4.0 with some larger differences in the region of wave-splitting. Maleic and fumaric acid have corresponding values over the entire pH range. The citraconic and mesaconic acid data are not in good agreement, however. Excluding the latter values, these data favor a co-planar orientation of the geometric isomers with the electrode surface.

In a co-planar orientation it makes little difference if two carboxylic acid groups are cis or trans, either way they present the same degree of steric hinderance to the electrode surface. There is some affect in the pH region of wave-splitting, however, indicated by the α values for bromocitraconic and bromomesaconic acids at pH 5.0. Free rotation is allowed about the C-COOH bond, so that portions of the carboxylic acid group project above and below the plane of orientation. Consider now, the neutralization of the first proton in each of the cis and trans isomers (@ pH5). The acid groups of the cis isomer are more or less locked into position through intramolecular hydrogen bonding, disrupting the free rotation and projection of the atoms of the acid group above and below the plane. This could account for the increased transfer coefficient value at pH 5. The trans isomer cannot take part in intramolecular hydrogen bonding (intermolecular is possible) so that free rotation of at least one of the acid groups is still possible. Hence, very little difference in the value of the transfer coefficient is noted for bromomesaconic acid in the region of wave-splitting. After both acidic groups are neutralized in bromocitraconic acid, free rotation is again allowed and the transfer coefficient value drops as indicated at pH 6.0.

The reason for the anomalies in the citraconic and mesaconic acid data is not readily known. Reduction only of the double bond is involved but the same is true of maleic and fumaric acids whose values fall into line. The only other possibility (other than erroneous data) is that the steric requirements of a methyl group are of more importance in geometric isomers like citraconic acid and mesaconic acid compared to maleic and fumaric acid, but is over shadowed by the bulk of bromine in bromocitraconic and bromomesaconic acid. Additional data with similar compounds may be needed to clarify this point.

Figures 2 and 3 represent the dependence of the half-wave potentials on pH. If a reduction is independent of pH, a horizontal straight line should be obtained. If the reduction is pH dependent, it can be shown from the Nernst equation that the slope of the line is equal to $y(0.059)/\alpha n$; rearrangement of the slope equation gives:

$$y = \text{slope}(\alpha n/0.059) \tag{21}$$

in which y is equal to the hydrogen coefficient involved in the reduction according to the following reaction:

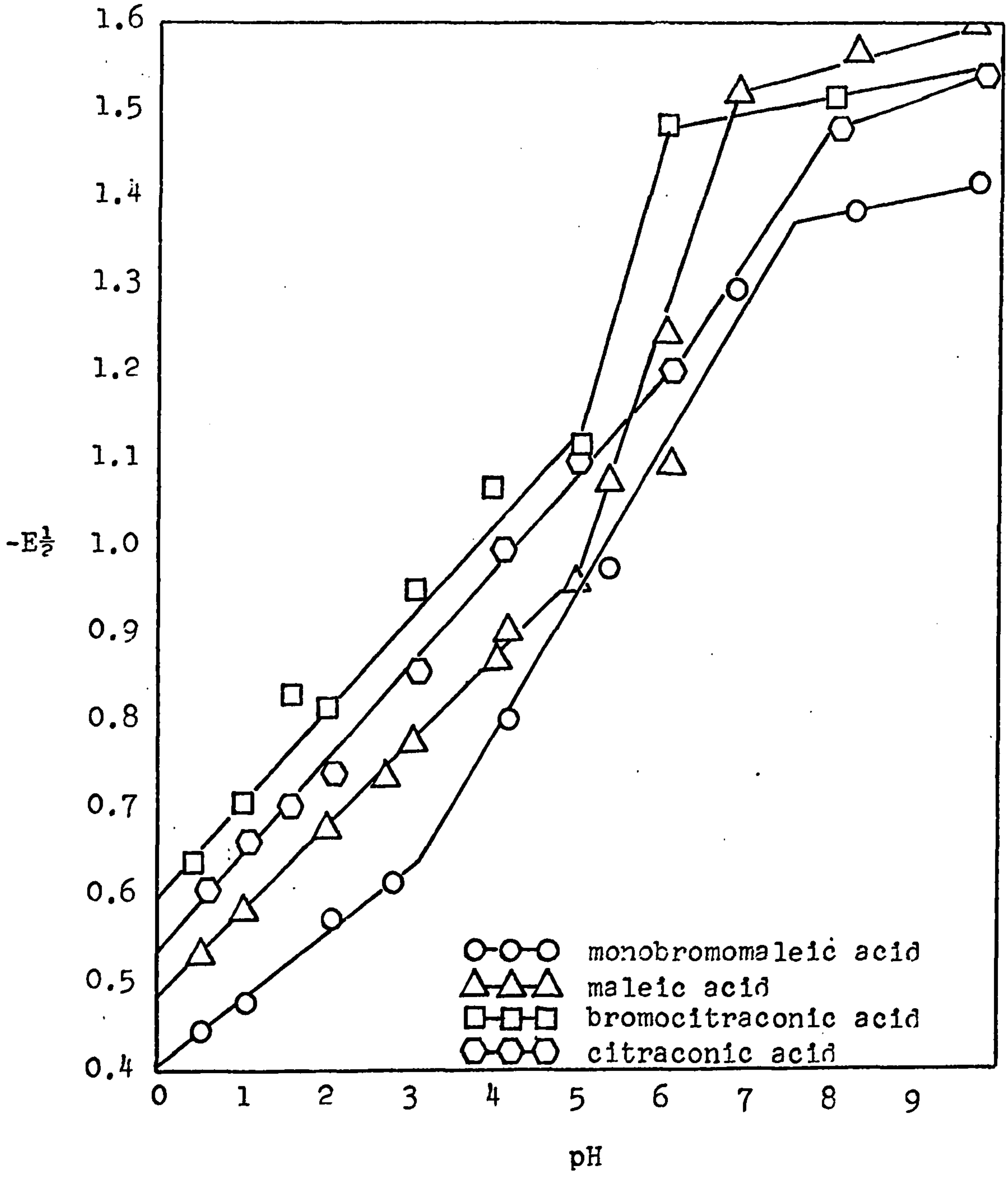


Figure 2. Half-wave potentials of cis geometric isomers as a function of pH

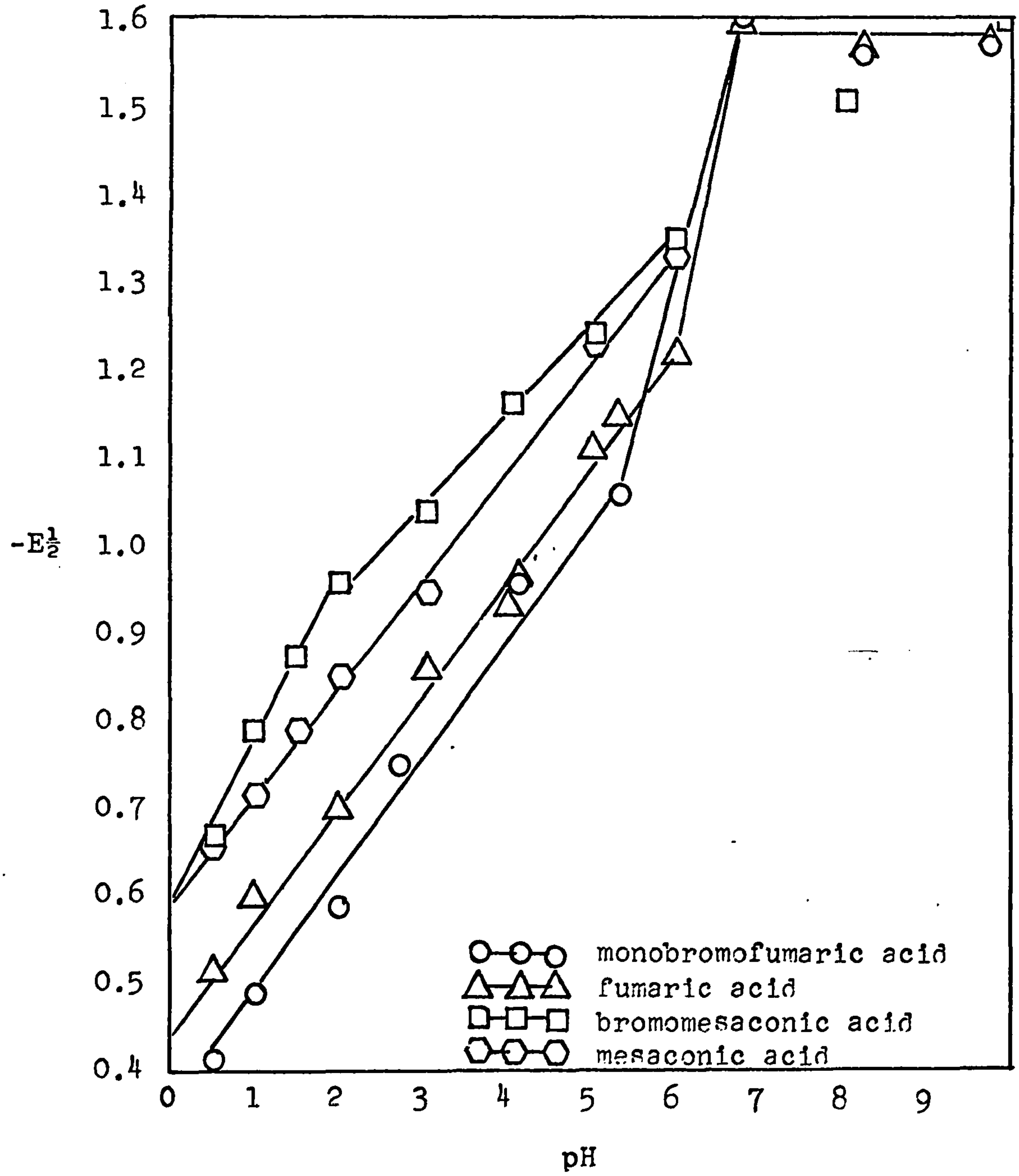


Figure 3. Half-wave potentials of trans geometric isomers as a function of pH

$$O + ne^{-} + yH^{+} \longrightarrow R \qquad (22)$$

The C-Br fission is reported to have a first order dependence on hydrogen ion while double bond reduction has a second order dependence (Reactions 1 and 2, page 4). In the case of bromocitraconic and bromomesaconic acid, where both reduction reactions are apparently proceeding at the same time. The polarographic data should yield an $E_{\frac{1}{2}}$ versus pH plot with a slope equal to $3(0.059)/\alpha 4$. The plots for monobromomaleic and monobromofumaric acids are also presented here. The α values for these two compounds are estimated from the values determined in this present work for similar compounds.

The half-wave potential versus pH plots show the same general trends for each series of isomer type. The slope of each linear portion of the curves for each compound was determined. The order of hydrogen dependence was calculated from Equation 21 using the value of the slope and the αn values determined from the data in Table 3. Table 4 summarizes the hydrogen dependence calculations for the reduction reactions.

Obtaining the correct or proposed hydrogen order dependence for maleic acid (pH 0-5), citraconic acid, fumaric acid and mesaconic acid was encouraging not only because the calculated values were within ± .2 units of being whole numbers but in addition, amounts to a confirmation of the transfer coefficient values used in the calculation.

Table 4. Evaluation of $E_{\frac{1}{2}}$ versus pH plots for order of hydrogen dependence in the reduction reactions.

Compound[a]	pH range	y[b]	Remarks
MBMA	0-3	1	calculated for fission of C-Br bond only
	4-7	2	
	7	I[c]	
MaA	0-5	2	
	5-7	3	
	7	I	
BCA	0-5	1	calculated for a 4e⁻ reduction
	5	I	
CA	0-6	2	
	6	I	
MBFA	0-2	1	calculated for fission of C-Br bond only
	2-5	3	
	5	I	
FA	0-6	2	
	6	I	
BMA	0-2	2	calculated for a 4e⁻ reduction
	2-6	1	
	6	I	
MeA	0-6	2	
	6	I	

---

[a] MBMA, monobromomaleic acid; MBFA, monobromofumaric acid; cf. Table 3 footnote for definition of other symbols.

[b] Y is the order of hydrogen dependence.

[c] I indicates that the reaction is independent of pH above the pH listed.

A first order dependence for monobromomaleic and monobromofumaric acids at low pH's also agrees with the proposed order of dependence for C-Br bond fission. The calculated value for the order of hydrogen dependence for bromocitraconic acid and bromomesaconic acid may mean one of two things. One, double bond reduction is not occurring polarographically for these two compounds, hence the reason for the observed value, or the transfer coefficient values for these two compounds are in error. Inspection of Table 3, however, shows that the values for these two compounds are in good agreement over the entire pH range. Later, we shall see from the coulometric data that the double bond in these two compounds are undergoing reduction. Hence, the reason for the anomally in the order of hydrogen dependence may be the result of the complex nature of having two completely different reductions occurring at the same potential.

All of the reductions appear to be independent of pH, at pH's where presumably, the second proton has been neutralized. The y values, at any rate, turn out to be some odd fraction less than one. Two of the trans isomers are not even polarographically reducible at basic pH's.

Controlled Potential Coulometry

The n-value determination data for bromocitraconic acid and bromomesaconic acid are summarized in Table 5. The values shown are the average of several determinations. The pH range above 6 was not investigated where the polarographic waves were not well defined.

In general, the coulometric data indicate that the two compounds undergo a four electron reduction at a mercury pool electrode with stirring. Values obtained that represent other than four electrons are probably due to difficulties in selecting the proper electrolysis potential due to poorly defined waves or the result of catalytic evolution of hydrogen from contamination of the mercury electrode.

Table 5. n-values from controlled potential electrolyses at a massive mercury pool cathode.

Compound[a] / pH		1.0	2.0	3.0	4.0	5.0	6.0
BCA	applied E, - volts	1.01	1.10	1.22	1.24	1.19[b] 1.42	1.55
	n	3.9	3.8	3.9	3.9	3.7 4.1	3.4
BMA	applied E, - volts	1.02	1.16	1.25	1.10[c] 1.25	1.33	1.45
	n	3.7	3.8	2.6	1.8	3.8	3.9

[a] cf. Table 3 footnote for definition of symbols.

[b] Electrolyses were run at plateaus of both waves for BCA at pH 5.

[c] Two different potentials tried as a check on n.

As mentioned previously, the reduction products were never successfully isolated and identified. Based on the n-values, one would speculate that the major product was methylsuccinic acid. If dimerization occurred, the end product would most likely be a tetracarboxlyic acid substituted hexane. It is doubtful that any citraconic or mesaconic acid were present in the reduction products so that the NMR technique for identification could not have been applied.

Elving and co-workers (14) were fortunate in their investigation of monobromomaleic acid and monobromofumaric acid. They were able to reduce the carbon-bromine bond without interferring with the double bond. Consequently, the products were maleic and fumaric acids which could be analyzed by the polarographic technique. Polarographic analysis of a few of the coulometrically reduced solutions in this work gave no evidence of containing either citraconic acid or mesaconic acid. The amount of mass that was unaccounted for by polarographic analysis in Elving's work was reported as dimeric product. They were successful in isolating and identifying a dimer from a large scale electrolysis supporting their conclusion.

Chronopotentiometry

Chronopotentiometry with current reversal at a thin layer electrode is an excellent method for investigating kinetic complications in electrode reactions. It was known that the C-Br bond fission and the reduction of the double bond were not reversible processes. It was hoped that if some sort of chemical reaction prior to electron transfer was occurring, that this technique would give evidence of any such complication. The chronopotentiograms for the bromo-compounds indicated that no complications were involved within the potential limitations of the thin layer electrode. Beyond this potential limit, however, there may be a complication occurring which cannot be recorded.

SUMMARY AND CONCLUSIONS

The mechanism of the electrochemical reduction of organic halides has been the topic of intensive investigation and discussion in the recent past. The most flagrant abuse by researchers in this field is to take the data for one series of compounds and attempt to make sweeping generalizations to cover the behavior of all organic halides.

This present work deals with the electrochemical reduction geometric isomers of organic bromides. The rigid nature of these compounds simplify the system by the presence of the double bond precluding any free rotation about single bonds and limiting the possibility of inversions resulting from S_N2-like displacements at the back side of carbon in the carbon-bromine bond. It was hoped that the information gained from this study would shed some light on the effect of steric requirements of certain groups on the reduction behavior of organic bromides.

The cis isomers, bromocitraconic acid and monobromomaleic acid, differ in structure by a methyl group where the latter compound contains a hydrogen atom. This also applies to the trans isomers, bromomesaconic acid and monobromofumaric acid. Evaluation of the polarographic data for these four compounds and comparison of similar data for citraconic, maleic, mesaconic and fumaric acids, clearly illustrates the effect of a subtle modification in structure on the reduction of these compounds.

Interpretation of the polarographic data indicates that the preferred orientation of a planar unsaturated geometric isomer is one where the atoms of the molecule are co-planar with the electrode surface. This type of orientation allows interaction of the pi-bonding with the mercury cathode as a possible mode of stabilization of the molecule and at the same time affords the electroactive sites the position of closest approach to the electrode for electron transfer.

A displacement on bromine as a possible reduction mechanism requiring the bromine atom to take part in electron transfer from the electrode is unlikely since the effect of bromine on the reduction of the double bond is small. If this mode of electron transfer were important, one would expect a more pronounced affect on the double bond reduction since its proximity to the electrode and the pi-bond interaction with the mercury cathode would be decreased to make more unfavorable the process of electron transfer. A modified S_N2-like reaction is not ruled out. Rather than an attack at the back side of carbon, 180° from the carbon-bromine bond, an attack at a right angle to the carbon-bromine bond may be possible. An S_N1-like reaction is not considered too likely. Ionization to give a bromide ion at the surface of the electrode is a poor model without somehow providing a driving force for such a process. The Lambert argument (28) concerning polarization of the C-Br bond by means of the increasing electrode potential to cause dissociation into a carbonium ion and a bromide anion should not apply to geometric isomers. Co-planar molecules of slight structural differences should benefit equally from polarization effects.

The steric effect of methyl, compared to hydrogen, on double bond reduction and C-Br bond fission appears to account for the shift in half-wave potentials for bromocitraconic acid and bromomesaconic acid. The increased steric hinderance of methyl causes the reduction potential of the double bond to occur about 0.1 volts more cathodic. The same steric effect causes the C-Br bond fission to occur about 0.2 volts more negative bringing about the overlap of reduction potentials in bromocitraconic acid and bromomesaconic acid. This constitutes a significant change considering that the smallest degree of modification possible was involved in going from hydrogen to a methyl group.

LITERATURE CITED

1. Annino, R., Erickson, R. E., Michalovic, J. and McKay, B., J. Amer. Chem. Soc., 88, 4424(1966).

2. Atkinson, E. R., Warren, H. H., Abell, P. I, and Wing, R. E., J. Amer. Chem. Soc., 72, 915(1950).

3. Bard, A. J., Anal. Chem., 33, 11(1961).

4. Berzins, T. and Delahay, P., J. Amer. Chem. Soc., 75, 4205(1953).

5. Berzins, T. and Delahay, P., J. Amer. Chem. Soc., 77, 6448(1955).

6. Butler, J. A. V. and Armstrong, G., Nature, 129, 613 (1932).

7. Christensen, C. R. and Anson, F. C., Anal. Chem., 36, 495(1964).

8. Delahay, P. and Berzins, T., J. Amer. Chem. Soc., 2486 (1953).

9. Delahay, P. and Mamantov, G., Anal. Chem., 27, 478(1955).

10. Diefenderfer, A. J., "Polarography of Benzyl Halides and Related Compounds", unpublished PhD. thesis, Library, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1961.

11. Elving, P. J. and Pullman, B., Advan. Chem. Phys., 3, 1(1961).

12. Elving, P. J., Martin, A. J. and Rosenthal, I., Anal. Chem., 25, 1082(1953).

13. Elving, P. J. and Rosenthal, I., Anal. Chem., 26, 1454 (1954).

14. Elving, P. J., Rosenthal, I., Hayes, J. R. and Martin, A. J., Anal. Chem., 33, 330(1961).

15. Elving, P. J., Rosenthal, I. and Martin, A. J., J. Amer. Chem. Soc., 77, 5218(1955).

16. Frankelthal, R. P. and Shain, I., J. Amer. Chem. Soc., 78, 2696(1956).

17. Gerischer, H., Z. Physik. Chem.(Leipzig), 202, 302(1953).

18. Gierst, L. and Juliard, A., J. Phys. Chem., 57, 701(1953).

19. Hanna, J. G. and Siggia, S., Anal. Chem., 37, 690(1965).

20. Heyrovsky, J., Chem. Listy, 16, 256(1922).

21. Heyrovsky, J. and Kuta, J., Principles of Polarography, Academic Press, New York, 1966.

22. Hickling, A., Trans. Faraday Soc., 38, 27(1942).

23. Karaoglanoff, Z., Z. Elektrochem., 12, 5(1906).

24. Kirrmann, A. and Kleine-Peter, M., Bull. Soc. Chim. France, 894(1957).

25. Klopman, G., Helv. Chim. Acta, 44, 1908(1961).

26. Laitinen, H. A., Chemical Analysis, Mcgraw-Hill Book Company, Inc., New York, 1960.

27. Lambert, F. L. Albert, A. H. and Hardy, J. P., J. Amer. Chem. Soc., 86, 3155(1964).

28. Lambert, F. L. and Kobayashi, K., J. Amer. Chem. Soc., 82, 5324(1960).

29. Lingane, J. J., Electroanalytical Chemistry, 2nd edition, Interscience Publishers, Inc., New York, 1958.

30. Lingane, J. J., J. Amer. Chem. Soc. 67, 1916(1945).

31. Lothe, J. J. and Rogers, L. B., J. Electrochem. Soc., 101, 258(1954).

32. Marple, L. W., Hummelstedt, L. E. I. and Rogers, L. B., J. Electrochem. Soc., 107, 437(1960).

33. Meites, L. and Meites, T., Anal. Chem. 28, 103(1956).

34. Organic Syntheses, Collective Volume 2, John Wiley and Sons, Inc., New York, 1944.

35. Reilley, C. N., Anal. Chem., 37, 1312(1965).

36. Reilley, C. N., Everett, G. W. and Jones, R. H., Anal. Chem., 27, 483(1955).

37. Reinmuth, W. H., Anal. Chem., 33, 322(1961).

38. Ross, J. W., Demars, R. D. and Shain, I., Anal. Chem., 28, 1768(1956).

39. Sand, H. J. S., Phil. Mag., 1, 45(1901).

40. Sease, J., Chang, P. and Groth, J., J. Amer. Chem. Soc., 86, 3154(1964).

41. Streitwieser, A. and Perrin, C., J. Amer. Chem. Soc., 86, 4938(1964).

42. Testa, A. C. and Reinmuth, W. H., Anal. Chem., 32, 1512 (1960).

43. Vaughn, W. R. and Milton, K. M., J. Amer. Chem. Soc., 73, 5497(1951).

44. Von Stackelberg, M. and Stracke, W., Z. Electrochem., 53, 118(1949).

45. Warshowsky, B., Elving, P. J. and Mandel, J., Anal. Chem., 19, 161(1947).

46. Wawzonek, S., Science, 155, 39(1967).

47. Wawzonek, S., Duty, R. C. and Wagenknecht, J. H., J. Electrochem. Soc., 14, 74(1964).

48. Weber, H. F., Wied Ann., 7, 536(1879).

49. Zavada, J., Krupicka, J. and Sicher, J., Collection Czech. Chem. Commun., 28, 1664(1963).

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