Electrochemical reduction of chlorinated nitro and nitrosobenzenes in dimethylsulfoxide [pt.I] Power series representation in the high temperature phase equilibria of several metal oxide systems [pt. II]
by Harlan Jay Byker

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:
This dissertation encompasses two separate and unrelated research topics.

I. Electrochemical Reduction of Chlorinated Nitro and Nitrosobenzenes in Dimethylsulfoxide The reduction potentials of nitrobenzene and all possible isomers of its chlorine derivatives have been obtained by cyclic voltammetry in dimethylsulfoxide. The first reduction wave in each case, except pentachloronitrobenzene, appears to be a one electron reversible wave. Subsequent reduction waves are irreversible and have been interpreted in terms of either loss of chloride from the benzene ring or reduction of the nitro group to nitroso. The loss of chloride is the dominant reduction process for the higher chlorinated isomers while concomitant reaction of the nitro group and chlorine is observed for the monochloronitrobenzenes. The proposed reduction processes are indicated by the observation of new electrochemical processes when a second cycle of the voltammogram is recorded. Nitrosobenzene and all possible isomers of its chlorine derivatives, except pentachloronitrosobenzene, were synthesized and cyclic voltammograms were recorded for each. The reduction potentials of nitrosobenzene and the monochloronitrosobenzenes correspond to some of the reduction potentials for the second cycle voltammograms for the polychloronitrobenzenes.

II. Power Series Representation in the High Temperature Phase Equilibria of Several Metal Oxide Systems The use of Redlich Kister power series representations of thermodynamic quantities in the study of high temperature phase equilibria is described. Literature data was used to obtain power series equations for the activity and enthalpy of the rutile phase of titanium dioxide treated as a solution of titanium metal in titanium dioxide. Mass spectrometric data for the vaporization of potassium oxides was obtained from another researcher. This data was interpreted to give new values for the heats of formation of $K_2O(s)$ and $K_2O_2(g)$. These new values and literature data were used to determine power series equations and calculate a potassium oxide phase diagram. The phase equilibria of lithium oxide and aluminum oxide was treated by power series representations and a revised phase diagram is proposed. Power series representations in the potassium oxide, calcium oxide, and silicon dioxide ternary system are presented.

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I. ELECTROCHEMICAL REDUCTION OF CHLORINATED NITRO AND NITROSOBENZENES IN DIMETHYLSULFOXIDE II. POWER SERIES REPRESENTATION IN THE HIGH TEMPERATURE PHASE EQUILIBRIA OF SEVERAL METAL OXIDE SYSTEMS

by

HARLAN JAY BYKER

A thesis submitted in partial fulfillment
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in

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His invisible attributes, that is to say his everlasting power and deity, have been visible, ever since the world began, to the eye of reason, in the things he has made.

Romans 1:20 (The New English Bible)

Vita

Harlan Jay Byker was born on August 31, 1954 in Grand Rapids, Michigan to Gary and Henrietta Byker. He graduated from Unity Christian High School in Hudsonville, Michigan in 1972 and attended Calvin College in Grand Rapids, Michigan for two years. Harlan attended Montana State University in Bozeman, Montana for two more years and received a B. Sc. degree in chemistry with departmental honors in 1976. In 1973, Harlan married Terri Lynn Northouse and they presently have two daughters, Erin Nichole and Cori Darleen.

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Abstract

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The reduction potentials of nitrobenzene and all possible isomers of its chlorine derivatives have been obtained by cyclic voltammetry in dimethylsulfoxide. The first reduction wave in each case, except pentachloronitrobenzene, appears to be a one electron reversible wave. Subsequent reduction waves are irreversible and have been interpreted in terms of either loss of chloride from the benzene ring or reduction of the nitro group to nitroso. The loss of chloride is the dominant reduction process for the higher chlorinated isomers while concomitant reaction of the nitro group and chlorine is observed for the monochloronitrobenzenes. The proposed reduction processes are indicated by the observation of new electrochemical processes when a second cycle of the voltammogram is recorded. Nitrosobenzene and all possible isomers of its chlorine derivatives, except pentachloronitrosobenzene, were synthesized and cyclic voltammograms were recorded for each. The reduction potentials of nitrosobenzene and the monochloronitrosobenzenes correspond to some of the reduction potentials for the second cycle voltammograms for the polychloronitrobenzenes.

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The use of Redlich Kister power series representations of thermodynamic quantities in the study of high temperature phase equilibria is described. Literature data was used to obtain power series equations for the activity and enthalpy of the rutile phase of titanium dioxide treated as a solution of titanium metal in titanium dioxide. Mass spectrometric data for the vaporization of potassium oxides was obtained from another researcher. This data was interpreted to give new values for the heats of formation of $K_2O(s)$ and $K_2O_2(g)$. These new values and literature data were used to determine power series equations and calculate a potassium oxide phase diagram. The phase equilibria of lithium oxide and aluminum oxide was treated by power series representations and a revised phase diagram is proposed. Power series representations in the potassium oxide, calcium oxide, and silicon dioxide ternary system are presented.

SECTION I.

INTRODUCTION

The electrochemical reduction of nitrobenzene is one of the classical reactions of organic polarography. However nitrobenzene is rather prolific in its reduction products, and complex reduction pathways are possible. Under the proper solvent and electrode conditions one can reduce nitrobenzene to nitrosobenzene, phenylhydroxylamine, aniline, azoxybenzene, azobenzene, or hydrazobenzene. Most of these compounds can be electroactive, as well as many of their possible anions and dianions. There are indeed then, many possible intermediates and products observable electrochemically even for the reduction of unsubstituted nitrobenzene.

The focus of this present work is on the electrochemical reduction mechanisms of polychlorinated nitrobenzenes in the solvent dimethylsulphoxide, (DMSO). Therefore the reduction of nitrobenzene in aqueous systems will be considered only briefly and the remainder of this introductory discussion will be limited to the reactions of nitrobenzene, the halonitrobenzenes, and their decomposition products in aprotic solvent systems.

Electrochemistry of Nitrobenzene

Nitrobenzene can be reduced in acidic aqueous media, pH less than 4.7, and the following mechanism has been proposed:[1]

$$C_6H_5NO_2H_2^{2+} + 2e^- + H^+ \longrightarrow C_6H_5NOH^+ + H_2O \qquad \text{(slow)}$$

$$C_6H_5NOH^+ + 2e^- + 2H^+ \longrightarrow C_6H_5NH_2OH^+ \qquad \text{(fast).}$$

The rate determining step is the reduction of nitrobenzene to the protonated form of nitrosobenzene. Nitrosobenzene is more easily reduced than nitrobenzene and the second step leading to protonated phenylhydroxylamine is rapid. Following this four electron wave, at a more cathodic potential, a two electron reduction to the protonated form of aniline is observed:

$$C_6H_5NH_2OH^+ + 2e^- + 2H^+ \longrightarrow C_6H_5NH_3^+ + H_2O$$

In neutral and alkaline solution, pH greater than 4.7, the proposed mechanism is:

$$C_6H_5NO_2 + 2e^- + H_2O \longrightarrow C_6H_5NO_2H^- + OH^- \qquad \text{(slow)}$$

$$C_6H_5NO_2H^- + 2e^- + 2H_2O \longrightarrow C_6H_5NHOH + 3OH^- \qquad \text{(fast).}$$

The second reduction wave of phenylhydroxylamine to aniline, as in the acid case, is not observed.

In the nonaqueous solvents N,N-dimethylformamide[2], (DMF), and acetonitrile[3], (ACN), nitrobenzene is first reduced in a reversible one electron transfer to its stable anion radical. At a more cathodic potential an irreversible three electron transfer with protonation occurs to form the major product, phenylhydroxylamine. With an added proton donor, such as phenol, the first reduction wave grows and the second decreases. At a mole ratio of acid to nitrobenzene of four to one only one irreversible four electron wave is observed as in the alkaline aqueous systems.

Reduction of nitrobenzene in the presence of a suspension of activated neutral alumina to remove every trace of electrophilic impurity, can result in the formation of the nitrobenzene dianion which is stable on the time scale of cyclic voltammetry.[4] This observation of reversible behaviour for the dianion is successful in DMF, hexamethylphosphoramide, and pyridine, but in ACN where the solvent itself can donate protons more easily the dianion decomposes more rapidly.

In anhydrous liquid ammonia the dianion of nitrobenzene is stable with respect to protonation on the time scale of cyclic voltammtry and does not protonate even on an electrolysis time scale, although it does precipitate as the potassium salt.[5]

Electrochemistry of Halonitrobenzenes

Haloaromatics can generally be divided into two classes with respect to the mechanism of halogen loss.[6] The first class contains aromatic compounds with only halogen substituents or if other substituents are present they are electrochemically inactive. These compounds, such as the halogenated benzenes, biphenyls, benzonitriles, and naphthalenes, lose halide in a two electron reduction with the addition of a proton to quantitatively form the dehalogenated aromatic.

The second class of compounds, examples of which are some halogenated benzophenones, quinolines, phenzaines, and nitrobenzenes, can lose halide after less than two electrons transferred and the reductions usually result in substantially less than 100% conversion to the dehalogenated aromatic. The unhalogenated parent compounds in this class are electrochemically reducible at potentials similar to those of their halogenated derivatives and after electron transfer halide loss from these derivatives may have to compete with, or be replaced by chemical reactions of the non-halogen functional groups.

In 1962 Holleck and Becher[7] reported the polarographic halfwave potentials for the first reduction waves of several of the isomers of iodo, bromo, and chloronitrobenzene in DMF and ACN. They observed anomalous reduction waves following the initial ones for p-bromo and p-iodonitrobenzene. Maki and Geske[8], previous to this had not been able to observe an electron spin resonance, (ESR), signal for electrochemically generated p-iodonitrobenzene anion radical.

Adams and coworkers[9] set about to resolve this problem. They observed two reduction waves at a hanging mercury-drop electrode, (HMDE), for each of the six isomers of bromo and chloronitrobenzene and three reduction waves for each of the three isomers of iodonitrobenzene in DMF. By observation of its ESR spectrum during electrolysis at a potential between the second and third waves, they determined that the result of the second reduction of each of the iodonitrobenzenes was the formation of the nitrobenzene anion radical. Although they were able to show that iodide is lost by electrolysis on the first wave, no ESR signal was observed at this potential. Electrolysis of o-bromonitrobenzene in the presence of tetraethylammonium perchlorate as supporting electrolyte and of p-bromonitrobenzene in the presence of tetraethylammonium iodide at a potential more cathodic than their first reduction waves also resulted in the generation of the nitrobenzene anion radical. Loss of chloride was not observed during the time for which they electrolyzed solutions of the chloronitrobenzenes.

From these observations, Adams and coworkers postulated for the iodonitrobenzenes that the first wave was a two electron transfer resulting in the elimination of iodide and that the second wave was the formation of the nitrobenzene anion radical. Lawless and Hawley[10] interpreted them as postulating the following mechanism:

$$C_6H_4NO_2I + 2e^- + H^+ \longrightarrow C_6H_5NO_2 + I^- \qquad \text{(first wave)}$$

$$C_6H_5NO_2 + e^- \rightleftharpoons C_6H_5NO_2^{\overline{\cdot}} \qquad \text{(second wave).}$$

This mechanism is not consistent with the original data in that the halfwave potentials for the second waves of the iodonitrobenzenes are isomer dependent and fifty to eighty millivolts more cathodic than the first reduction of nitrobenzene.

Fujinaga and coworkers[11] electrolyzed the three chloronitrobenzene isomers on the first wave in ACN in an ESR cavity and did not observe chloride loss. Electrolysis of the meta and para isomers in DMF at the potential of the second wave resulted in the respective anion radical ESR spectra although at reduced intensity to that observed when the electrolysis potential was held between the two waves. In DMF electrolysis of o-chloronitrobenzene at the potential of the first wave resulted in the slow disappearance of the o-chloronitrobenzene anion radical ESR spectrum and the slow appearance of that of the nitrobenzene anion radical. When three moles of phenol were added for each mole of o-chloronitrobenzene dehalogenation was not observed at any potential. The following mechanism was proposed for o-chloronitrobenzene:

$$C_6H_4NO_2Cl + e^- \longrightarrow C_6H_4NO_2Cl^{\overline{\cdot}} \qquad \text{(first wave)}$$

$$C_6H_4NO_2Cl^{\overline{\cdot}} + 2e^- + H^+ \longrightarrow C_6H_5NO_2^{\overline{\cdot}} + Cl^- \qquad \text{(second wave).}$$

The behaviour of p-bromonitrobenzene was similar to o-chloronitrobenzene, o-bromonitrobenzene rapidly dehalogenated even when electrolyzed in ACN and dehalogenation was not observed for m-bromonitrobenzene. All of the iodo isomers showed rapid dehalogenation with formation of the nitrobenzene anion radical and the following order was deduced for the ease of dehalogenation:

p,m-Cl, m-Br $<$ o-Cl $<$ p-Br $<$ o-Br, p,m,o-I.

Chronoamperometric techniques were used by Lawless and Hawley[10] to determine that the first two reduction waves for p-iodonitrobenzene are the result of approximately two electrons being transferred. They proposed the following mechanism, where SH represents the solvent:

$$C_6H_4NO_2I + e^- \rightleftharpoons C_6H_4NO_2I^{\dot{-}}$$

$$C_6H_4NO_2I^{\dot{-}} \rightleftharpoons C_6H_4NO_2\cdot + I^- \qquad \text{(fast)}$$

$$C_6H_4NO_2\cdot + SH \longrightarrow C_6H_5NO_2 + S\cdot$$

$$C_6H_5NO_2 + e^- \rightleftharpoons C_6H_5NO_2^{\dot{-}}$$

This mechanism, in contrast to the one they assumed to be proposed by Adams and coworkers[9], has a total of two electrons transferred instead of three to end up with the formation of the nitrobenzene anion radical.

Lawless and Hawley also used their chronoamperometric data and a current-reversal chronopotentiometric technique to measure pseudo first order rate constants for hydrogen abstraction by nitrophenyl radicals. The half life of the p-nitrophenyl radical, from their measurements, ranges from approximately one second in DMF to approximately nine seconds in DMSO with tetraethylammonium iodide present as supporting electrolyte. From their survey of decomposition rates these workers conclude that the stability of anion radicals in the different solvents used increases in the order DMF < ACN < DMSO.

In two subsequent publications Lawless, Hawley, and coworkers have described investigations into the mechanism of decomposition of dihalonitrobenzenes[12] and steric effects on reduction potential and rate of halide elimination.[13]

Electrolysis of 2,6-dichloro, 2,3-dichloro, and 2,4 dichloronitrobenzene at potentials just past the first reduction waves in DMF and/or ACN resulted in the formation of o-chloro, m-chloro, and p-chloronitrobenzene anion radicals respectively. Three reduction waves were observed for o-chloronitrobenzene in DMF as compared to two waves observed by Adams and coworkers[9] under supposedly the same conditions. The second wave was attributed to the further reduction of the o-chloronitrobenzene anion radical to form the nitrobenzene.

anion radical and the third wave was considered to be the further reduction of the nitrobenzene anion radical. Controlled potential electrolysis of 2,6-dibromonitrobenzene to the point where two electrons had been transferred per mole of substrate resulted in 98% disappearance of starting material and the only product analysis they could determine was 24% conversion to nitrobenzene and 8% conversion to o-bromonitrobenzene.

Investigation of steric effects on halonitrobenzene electrochemistry led Hawley and coworkers to conclude that the twisting of the nitro group out of the plane of the ring by ortho substituents causes more loss of resonance energy for the nitro anion radical than for the neutral molecule. The higher energy product requires a more cathodic potential for anion radical formation, while the possibility for relaxation of the twisted nitro group enhances the rate of elimination of the ortho substituent. They also postulate that the cathodic reduction potential shift does not reflect the entire loss of resonance energy since part of this loss should be made up by increased solvation of the twisted nitro anion radical. Methyl substitutions on the halonitrobenzenes were observed to increase the rate of halide loss even when steric effects were not involved.

Nelson, Carpenter, and Seo[14] have used cyclic voltammetry, chronoamperometry, and chronopotentiometry to investigate the reduction mechanisms of all the monohalonitrobenzenes. They have demonstrated that the first reduction wave is a one electron transfer for all of the compounds investigated except o-bromo and o-iodonitrobenzene. They concur with Lawless and Hawley[10] on the one electron transfer followed by loss of halide and hydrogen atom extraction followed again by one electron transfer for the decomposition of p-iodonitrobenzene to the nitrobenzene anion radical. They observed the ESR spectrum for the nitrobenzene anion radical during electrolysis of all the monohalonitrobenzenes in ACN, although for the fluoro and chloronitrobenzenes up to several hours of electrolysis time were required. The inference is made that the p-iodonitrobenzene decomposition mechanism is general for the halonitrobenzenes. However excessive electrolysis time for generation of the nitrobenzene anion radical demonstrates that this is a very slow pathway for the fluoro and chloronitrobenzenes.

The first order rate constants measured for halonitrobenzene decomposition from chronoamperometric data show the following trends:

$$k_{meta} < k_{para} < k_{ortho} \text{ and } k_F < k_{Cl} < k_{Br} < k_I.$$

In experiments with deuterium oxide and deuterated ACN they were able to persuasively show that the solvent and not residual water is the source of hydrogen for halide replacement.

During electrochemical synthesis investigations, at high substrate concentration, 4-nitrobiphenyl was formed by electrolysis of p-iodonitrobenzene in a 50/50 mixture of ACN/benzene, also 50 - 60% yields of 4,4'-dibromoazoxybenzene were obtained by electrolysis of p-bromonitrobenzene at the potential of its second reduction wave. Notably, no dinitrobiphenyls or solvent addition products could be isolated or characterized although several unidentified products were produced.

Sosonkin and coworkers[15,16] have used both electrochemical and chemical reduction of halonitrobenzenes to determine the mechanism of halide substitution by hydrogen. They support the mechanisms proposed for o-chloro, p-bromo, and the iodonitrobenzenes by Fujinaga and coworkers[11]. They elaborated on these mechanisms as follows:

$$C_6H_4NO_2X + e^- \rightleftharpoons C_6H_4NO_2X^{-\cdot} \qquad \text{(first wave; X=Cl,Br)}$$

$$\left.\begin{aligned}
&C_6H_4NO_2X^{-\cdot} + e^- \longrightarrow C_6H_4NO_2X^{=} \longrightarrow C_6H_4NO_2^- + X^-\\
&C_6H_4NO_2^- + H^+ \longrightarrow C_6H_5NO_2\\
&C_6H_5NO_2 + e^- \longrightarrow C_6H_5NO_2^{-\cdot}
\end{aligned}\right\}\text{(second wave)}$$

and

$$\left.\begin{array}{l} C_6H_4NO_2I + e^- \rightleftharpoons C_6H_4NO_2I^{\cdot -} \longrightarrow C_6H_4NO_2^{\cdot} + I^- \\ C_6H_4NO_2^{\cdot} + e^- \longrightarrow C_6H_4NO_2^- \\ C_6H_4NO_2^- + H^+ \longrightarrow C_6H_5NO_2 \end{array}\right\} \text{(first wave)}$$

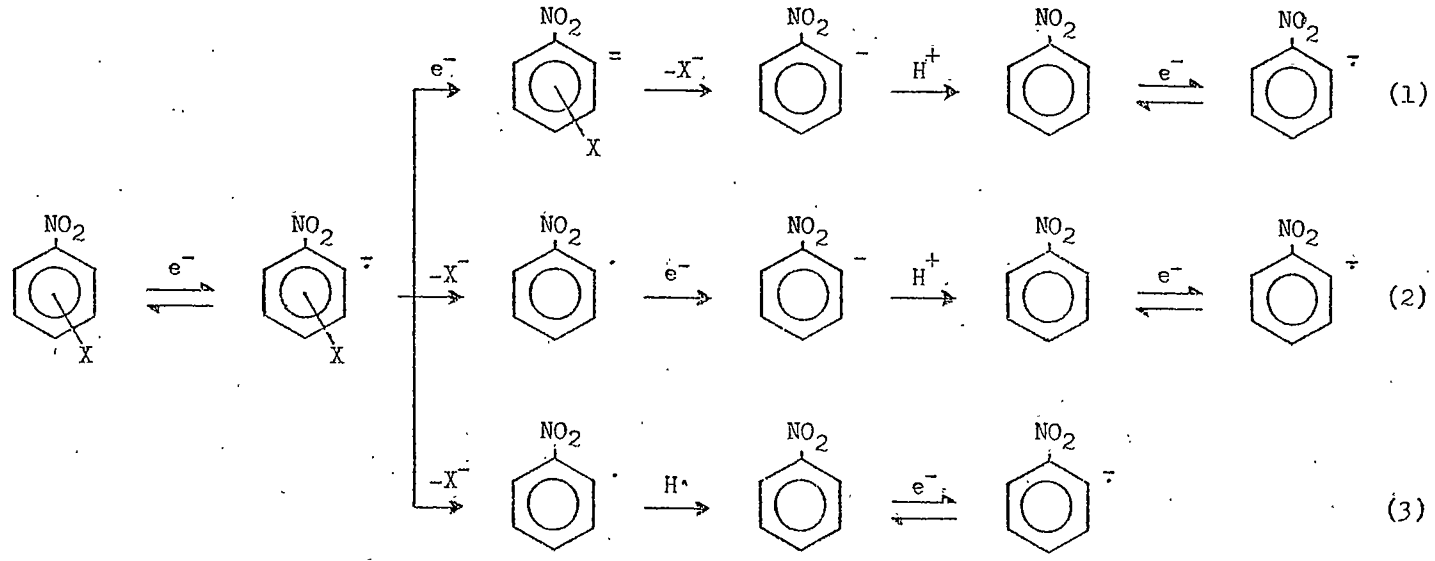
$$C_6H_5NO_2 + e^- \rightleftharpoons C_6H_5NO_2^{\cdot -} \qquad \text{(second wave)}$$

Thus far in this section, pertinent results of the electrochemical investigations of halonitrobenzenes have been presented with a minimum of personal comments. These results will now be summarized and critically analyzed.

The several proposed mechanisms are illustrated in figure 1. Pathway (1) encompasses an initial one electron reversible wave to form the stable halonitrobenzene anion radical. At a more cathodic potential, (c.a. one volt), a second electron is added, rapid dehalogenation occurs, and the resulting carbanion extracts a proton from the solvent to form nitrobenzene. Nitrobenzene is reduced more easily than the halonitrobenzene anion radical so it is rapidly reduced in a one electron transfer to make the second wave a two electron reduction. This pathway is the one originally suggested by Fujinaga and coworkers[11] and also supported by Sosonkin and coworkers.[15,16]

The pathway represented by (2) begins with a two electron wave which can be broken down into an initial one electron transfer to

FIGURE 1. Halonitrobenzene Reduction Pathways



Note: Carbanions and neutral radicals will be localized on the ring position from which halide was lost.

yield an unstable halonitrobenzene anion radical. It loses halide and is rapidly reduced by a second electron to a carbanion. Protonation results in the formation of neutral nitrobenzene which is reduced at a slightly more cathodic potential, (c.a. 0.2 volts), resulting in the second wave. This pathway was inferred by the data of Adams and coworkers[9] for the decomposition of the iodonitrobenzenes. It was also supported by the observations in references 11, 15, and 16.

Pathway (3) again begins with an initial one electron transfer to yield an unstable halonitrobenzene anion radical which loses halide. The neutral radical which results is reasonably stable and decomposes by hydrogen atom extraction from the solvent. Nitrobenzene is then reduced at the same or a slightly more cathodic potential and a total of two one electron waves are supposedly observed. The work of Hawley and coworkers[10,11] and that of Nelson and coworkers[14] support this pathway.

The following observations are made:

1. It appears obvious that any supposed conflict between the mechanisms of pathways (1) and (3) can be explained by allowing both to be valid. If an electrode is held at the potential of the first reversible wave the halonitrobenzene anion radical can lose halide at a rate characteristic of the particular halogen

and isomer involved. If as in the case of iodine, halide loss is rapid and if hydrogen atom extraction is valid, the nitrobenzene anion radical can be generated with only two electrons transferred.

When the halonitrobenzene anion radical is quite stable as for chlorine, reaction by pathway (3) will be slow. Application of an electrode potential as cathodic as the second wave can then produce the nitrobenzene anion radical with a transfer of three electrons.

2. Neither pathway (2) or (3) explain the iodonitrobenzene electrochemistry of Adams and coworkers[9]. The first reduction wave of these compounds is at least twice as large, (twice as much current), as the second wave. The halfwave potentials of the second and third waves do not correspond to those of nitrobenzene, the supposed product of the first wave. A reduction mechanism involving a solvent addition product may be able to explain these results.

3. Product analyses after controlled potential electrolysis have not resulted in the identification of the nitrobenzene radical coupling product, dinitrobiphenyl, even though the postulated lifetime of the radicals is quite long. Also the fate of the solvent radicals

remains a mystery. A number of its addition products are possible, (figure 2), and they should be identifiable.

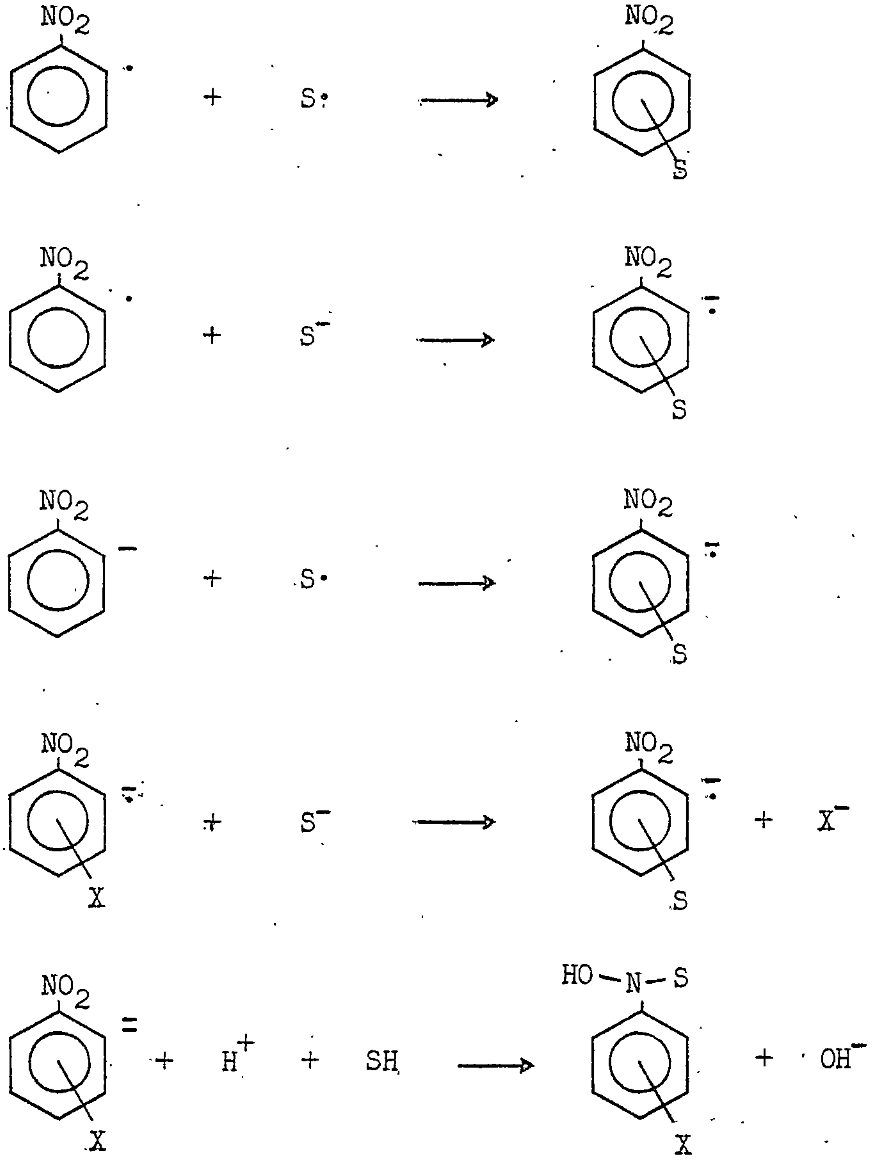
4. Failure to minimize residual water can have a substantial effect on the potentials and possibly the mechanisms of decomposition at the more cathodic irreversible reductions. As mentioned earlier, Adams and coworkers[9] observed one reversible and one irreversible wave for the reduction of o-chloronitrobenzene. Lawless and Hawley[12] observed one reversible and two irreversible waves for this compound under nearly identical conditions. This author has observed that addition of traces of water to dry DMSO can cause a change from a total of three waves to a total of two for the reduction of this compound and that changes in the voltammograms of polychloronitrobenzenes by traces of water is a general feature.

5. No reactions of the nitro group concomitant to halide loss have been described previous to this investigation.

Electrochemistry of Nitrosobenzene and Azoxybenzene

Kemula and Sioda[17] have investigated the electrochemical reduction of nitrosobenzene in DMF with sodium nitrate as supporting electrolyte. They observed two polarographic waves for this reduction, and the first was attributed to the formation of the nitroso-

FIGURE 2. Secondary Reactions With Solvent



$$2S\cdot \longrightarrow S\text{-}S$$

$$S\cdot + e^- \longrightarrow S^- \xrightarrow{H_2O} SH + OH^-$$

benzene anion radical. The second wave was postulated to be a combination of the further reduction of the nitrosobenzene anion radical and the reduction of azoxybenzene formed by the reaction of two anion radicals from the first wave or anion radicals reacting with neutral nitrosobenzene molecules. Electrolysis of nitrosobenzene on the first wave resulted in the current decaying to zero before the passage of one electron per molecule of substrate. Polarography of an electrolyzed solution indicated only the formation of azoxybenzene.

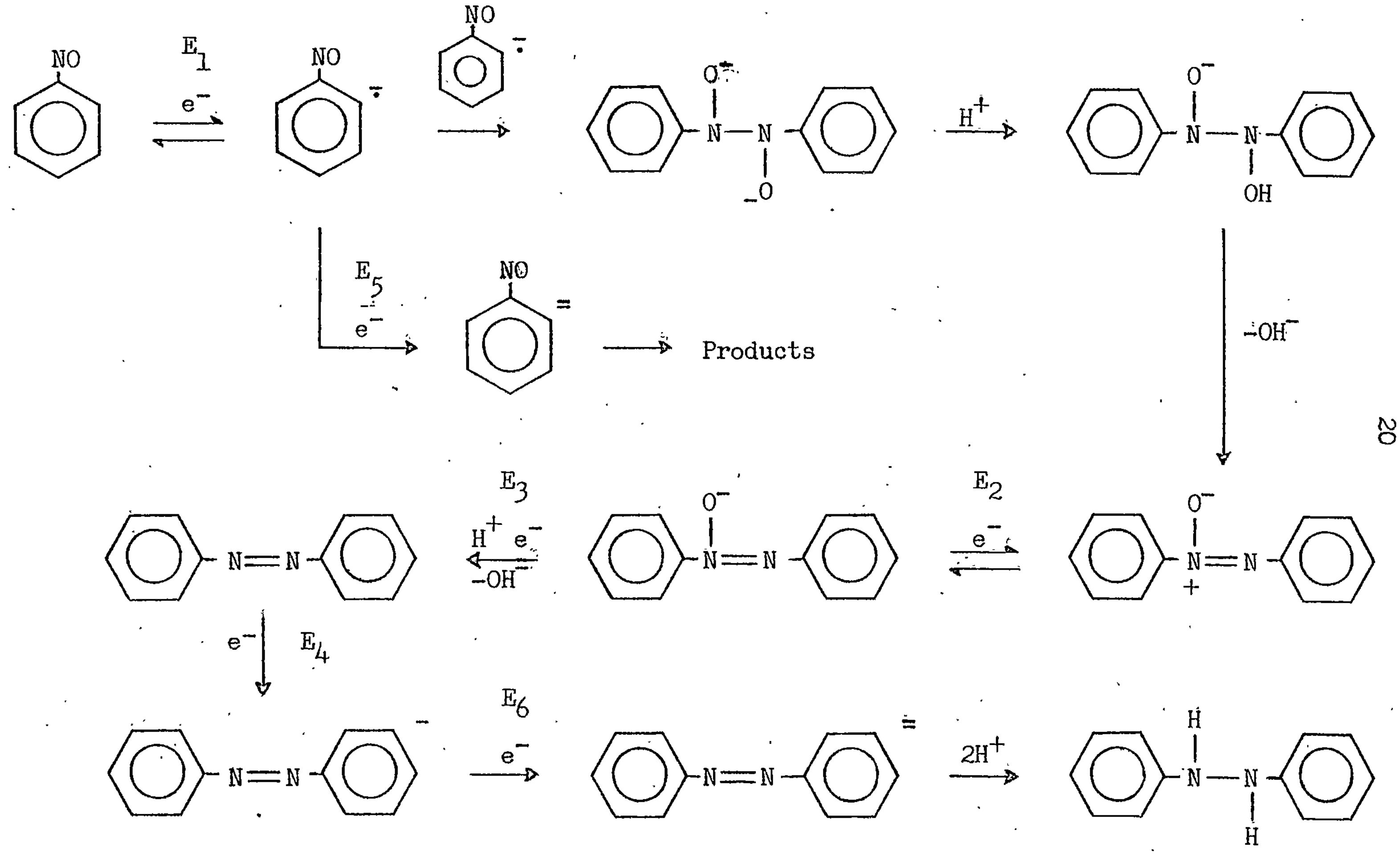
Asirvathan and Hawley[18] have studied the controlled potential electrolysis of nitrosobenzene in ACN and DMF. In ACN they observed unusually rapid decomposition which was complete after the passage of 0.3 moles of electrons per mole of substrate. They proposed that hydroxide ions produced during the formation of azoxybenzene also caused the decomposition of nitrosobenzene to azoxybenzene. This was supported by the fact that each 0.3 of a mole of tetraethylammonium hydroxide added to a solution of nitrosobenzene caused the disappearance of one mole of nitrosobenzene, with the formation of azoxybenzene at a 70% yield. At least nine other minor products were isolated but not identified. Similar yields of azoxybenzene were obtained from exhaustive electrolysis and again it was the only product that could be identified.

Although the nitrosobenzene anion radical was somewhat more stable in DMF, similar results were obtained for both electrochemical and chemical decomposition in this solvent.

Lipsztajn and coworkers[19] observed three polarographic waves for the reduction of nitrosobenzene in DMF with tetraethylammonium perchlorate as supporting electrolyte. However under the same conditions, four reduction waves were observed on a chrono-voltammogram taken at a hanging mercury drop electrode. They interpreted their results as shown in figure 3. Nitrosobenzene is reduced in a partially reversible one electron wave to the nitrosobenzene anion radical which can dimerize and lose hydroxide to form azoxybenzene. From the electrochemistry of authentic azoxybenzene[20], they were able to interpret the second wave as the reversible one electron reduction of azoxybenzene. The third wave was believed to be a combination of further reduction of nitrosobenzene anion radicals that had survived dimerization and the irreversible reduction of azoxybenzene anions to give azobenzene. The azobenzene formed is more easily reduced than the azoxybenzene anions so a second electron is instantly transferred to give azobenzene anions, whose reduction to hydrazobenzene constitute the fourth wave.

They found that changing the concentration or the cation of the supporting electrolyte could cause substantial changes in the electrochemistry of nitrosobenzene and in the presence of sodium perchlorate

FIGURE 3. Electrochemical Reduction Pathways for Nitrosobenzene


NO
E1
e−
NO
NO
O−
N
N
O−
H+
O−
N
N
OH
E5
e−
NO
=
Products
−OH−
E3
H+ e−
−OH−
N═N
O−
N═N
E2
e−
O−
N═N
+
e−
E4
N═N
−
E6
e−
N═N
=
2H+
H
N
N
H

$E_1 < E_2 < E_3 \approx E_5 < E_6$ $\qquad E_3 > E_4$

their results were similar to those of Kemula and Sioda.[17]

In anhydrous liquid ammonia nitrosobenzene can be reduced in two reversible one electron steps to its stable dianion.[5] Nitrosobenzene is also observed as a stable reduction product of nitrobenzene in liquid ammonia with isopropyl alcohol added as a proton donor. The proposed mechanism is as follows:

$$C_6H_5NO_2 \overset{e^-}{\rightleftharpoons} C_6H_5NO_2^{-\cdot} \overset{e^-}{\rightleftharpoons} C_6H_5NO_2^{=}$$

$$C_6H_5NO_2^{=} + ROH \longrightarrow C_6H_5NO_2H^- + RO^-$$

$$C_6H_5NO_2H^- \longrightarrow C_6H_5NO + OH^-$$

$$C_6H_5NO \overset{e^-}{\rightleftharpoons} C_6H_5NO^{-\cdot} \overset{e^-}{\rightleftharpoons} C_6H_5NO^{=}$$

$$C_6H_5NO^{=} + ROH \longrightarrow C_6H_5NOH^- + RO^-.$$

The cathodic cycle of a cyclic voltammogram shows two waves. The nitrobenzene anion radical is formed on the first wave and the protonated nitrosobenzene dianion is formed on the second wave. On the anodic scan two new waves are seen. The first is from the oxidation of the protonated nitrosobenzene dianion which after loss of an electron, rapidly deprotonated to give the nitrosobenzene anion radical. The oxidation of the nitrosobenzene anion radical makes up the second new wave. A second cathodic sweep shows the reduction of nitrosobenzene at a potential anodic of nitrobenzene reduction.

No reports of electrochemical investigations of halogenated nitrosobenzenes in aprotic media were discovered during an extensive literature search.

STATEMENT OF PROBLEM

This work has grown out of that of S. O. Farwell[21] and F. A. Beland.[22] They investigated the electrochemical reduction of several chlorinated homologs such as the polychlorobenzenes and polychlorobiphenyls. The only electroactive functions in these compounds were the chlorine substituents and they concluded that each electrochemical reduction wave was the result of an irreversible two electron transfer with the loss of chloride and proton abstraction. They applied controlled potential electrolysis and CNDO molecular orbital calculations to the problem of determining electrochemical reduction mechanisms and product distributions for these compounds.

The electrochemical behaviour of molecules with more than one electroactive functional group, specifically the chlorinated nitro and nitrosobenzenes, are the subject of this investigation. Furthermore, both reversible and irreversible electrochemical processes are involved in the reduction of these compounds and cyclic voltammetry is needed to distinguish between the two processes. The elucidation of the mechanism of reduction in the presence of competing electrochemical and chemical reactions and the cataloging of the reduction potentials in the solvent dimethylsulfoxide for the polychloronitro and polychloronitrosobenzenes is the problem addressed in this portion of this dissertation.

EXPERIMENTAL

Electrochemical Cell and Electrodes

A small volume H-cell was constructed with a glass wool plug to divide the two compartments. A total sample volume of 8 to 10 milliliters for the two compartments was found to be convenient. Between analysis of samples the cell was rinsed repeatedly with distilled water and the cell was then dried by rinsing three or four times with acetone followed by forcing a current of air through the glass wool plug.

The working electrode was a platinum flag with a total area of approximately 60 mm^2, coated with mercury by the procedure of Enke and coworkers.[23] An auxiliary or counter electrode was formed by a coil of 20 gauge platinum wire. The reference electrode was a silver wire which had been anodized in the presence of chloride to form a silver chloride coating. This coated wire was placed in a glass tube with a fine capillary tip and the tube was filled with a saturated aqueous solution of potassium chloride and silver chloride.

Although aqueous reference electrodes have large, unknown junction potentials when used in nonaqueous systems, these junction potentials can be made reproducible with a properly constructed reference electrode.[24] This Ag/AgCl reference has an equilibrium potential 0.197 volts positive of the standard hydrogen electrode. This is 0.045

volts negative of the potential of the more commonly used saturated calomel electrode and approximate comparison to potentials reported versus the saturated calomel can be obtained by subtracting 0.045 volts from the potentials reported herein.

The reference electrode was placed in contact with the solution in one compartment of the H-cell and the working and counter electrodes were placed in the other compartment. The working compartment solution was flushed with nitrogen for several minutes to remove oxygen prior to recording of a voltammogram.

Cyclic Voltammetry Instrumentation

A conventional cyclic voltammeter with a standard three electrode, operational amplifier potentiostat was constructed as shown schematically in figures 4 and 5. This design allowed for the initial potential and the cathodic and anodic limits to be independently and arbitrarily set. The anodic and cathodic sweep rates were also independently variable, but for all the work reported herein they were set equal to each other at 75 mv/sec. The uncompensated IR drop in the system was deemed negligible and was not corrected for electronically. All voltammograms were recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder and peak potentials were determined graphically.

Figure 4. Cyclic Voltammeter Block Diagram.

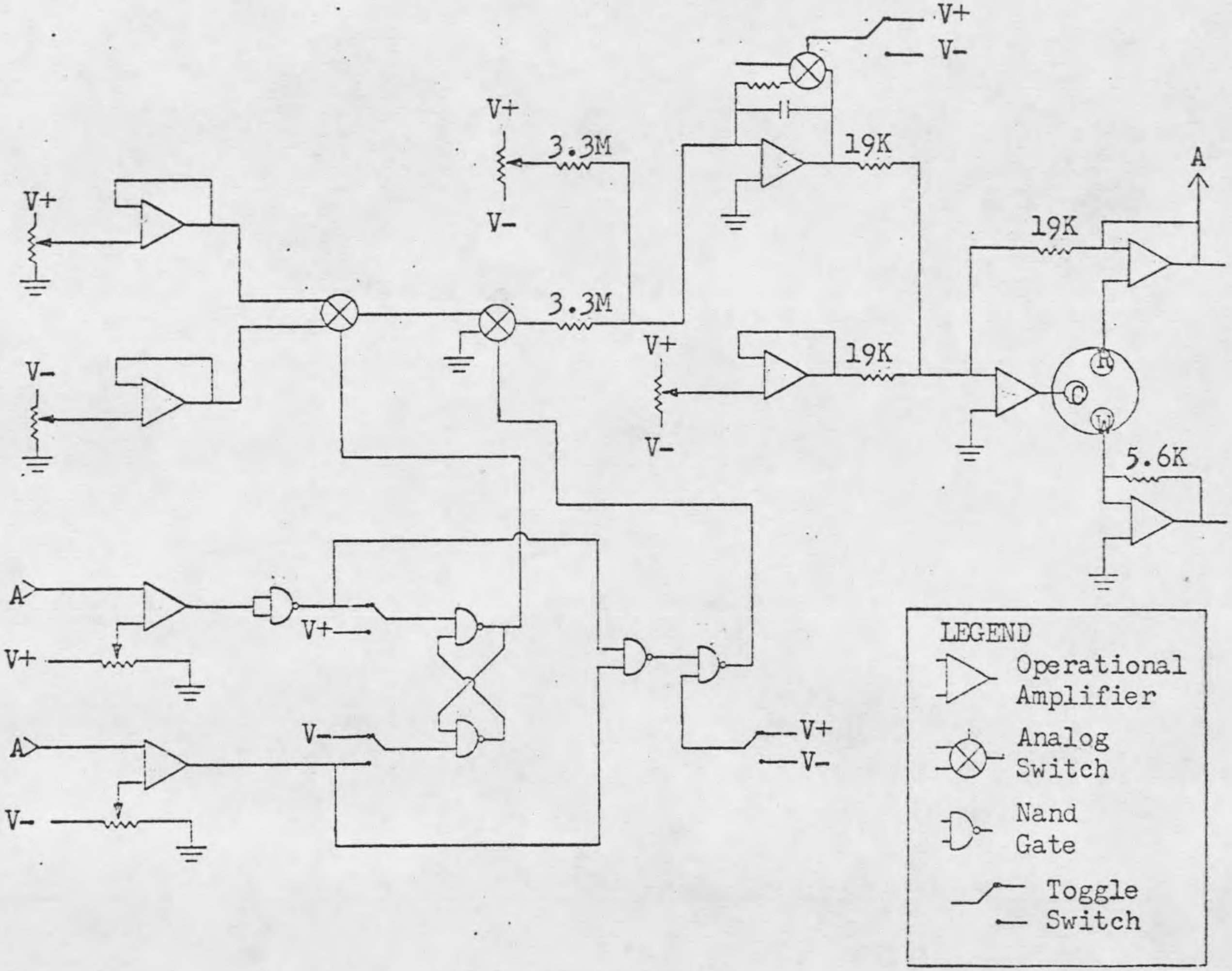
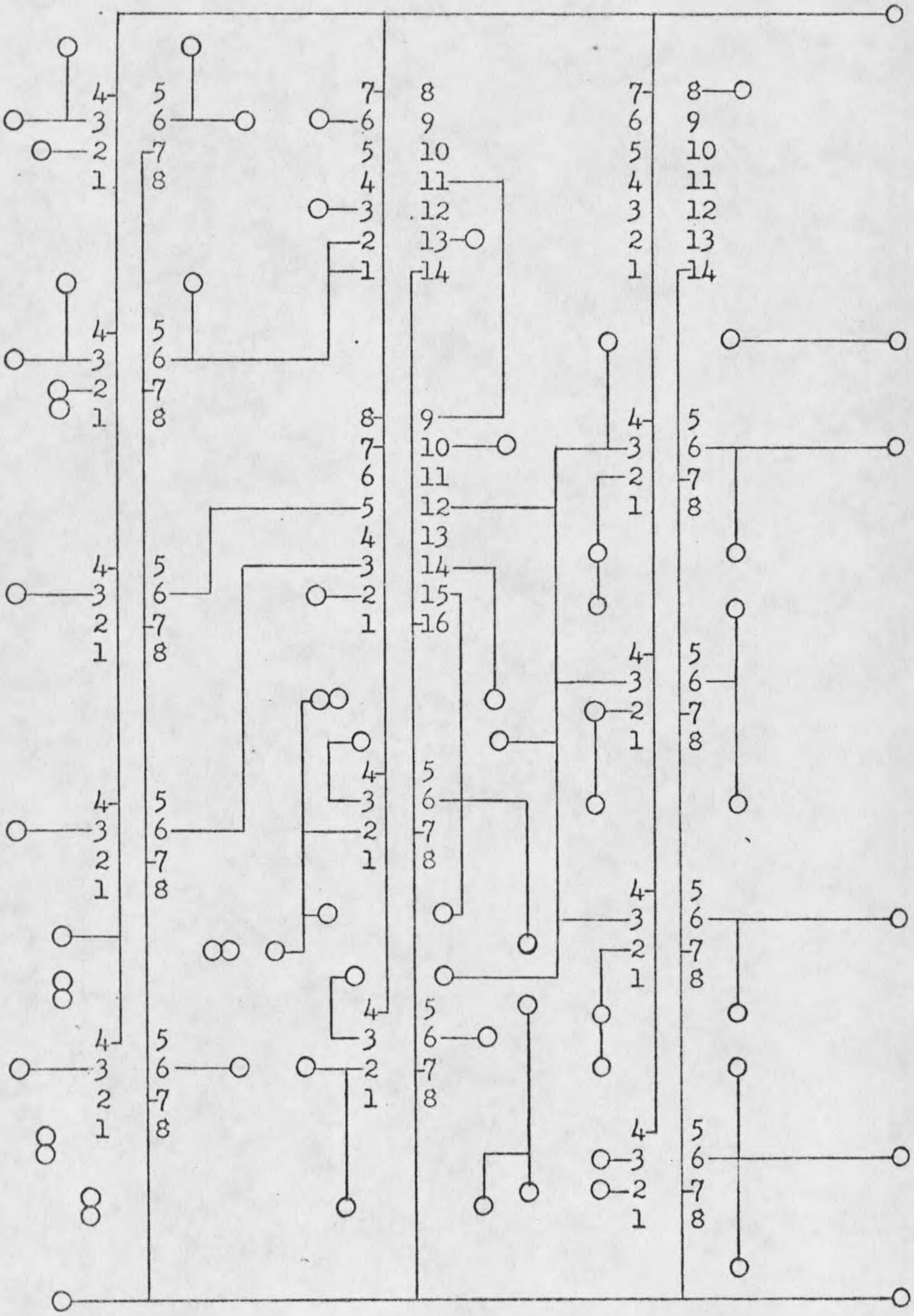

V+
V-
V+
V-
3.3M
3.3M
V+
V-
19K
19K
19K
V+
V-
A
R
C
W
5.6K
A
V+
A
V-
V+
V-
V+
V-
V+
V-
LEGEND
Operational Amplifier
Analog Switch
Nand Gate
Toggle Switch

Figure 5. Cyclic Voltammeter Circuit Diagram.


4 5 7 8 7 8
3 6 6 9 6 9
2 7 5 10 5 10
1 8 4 11 4 11
3 12 3 12
2 13 2 13
1 14 1 14
4 5
3 6
2 7
1 8
8 9 4 5
7 10 3 6
6 11 2 7
5 12 1 8
4 5 4 13
3 6 3 14
2 7 2 15
1 8 1 16
4 5
3 6
2 7
1 8
4 5
4 5 3 6
3 6 2 7
2 7 1 8
1 8
4 5
3 6
2 7
1 8
4 5
4 5 3 6
3 6 2 7
2 7 1 8
1 8
4 5
3 6
2 7
1 8

Solvent Purification

Reagent grade dimethyl-sulfoxide, (DMSO), was obtained from J. T. Baker Co. and was found to contain at least one electroactive impurity which interferred with the recording of voltammograms of substrates at $5 \times 10^{-4}\underline{M}$ concentrations.

The solvent was purified by refluxing 300-400 ml per batch over ten grams of sodium hydroxide at approximately 75°C for two and a half hours. The refluxing mixture was continuously stirred and maintained under an atmosphere of nitrogen at reduced pressure. The solvent was then decanted into a flask containing five grams of pulverized calcium hydride, to remove water, and the mixture was stirred for three to four hours while a nitrogen atmosphere was maintained above the liquid. The DMSO was then distilled under vacuum, with the first and last 20-30 ml being discarded. The collection flask was cooled in an ice bath and the middle fraction was obtained as a solid. All solutions for electrochemical analysis were prepared and analyzed within 48 hours after this purification and drying procedure.

Electrolyte and Organic Substrates

The supporting electrolyte used throughout this study was tetraethylammonium perchlorate from Eastman Organic Chemicals, halogens as bromide 100 ppm or less.