



The effects of a proton source on the electrochemical reduction of the chlorinated nitrobenzenes in dimethylsulfoxide, dimethylformamide and acetonitrile
by Kathleen Elizabeth Brunke

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:

Cyclic voltammograms of the chlorinated nitrobenzenes and nitrobenzene itself were obtained in DMSO, DMF and AN with and without the addition of a proton source. Reduction potentials for all primary processes were obtained from the voltammograms. The first reduction wave corresponds to the one-electron reversible transfer to form the radical anion. The second reduction wave represents the addition of more electrons to form the dianion followed by loss of chlorine with subsequent reduction or protonation. The protonated species can either deprotonate or lose hydroxide to yield nitroso compounds. With proton addition, the competition between processes is altered and protonation increases. The potentials of the "irreversible" waves shift anodically and some waves are no longer seen as the corresponding process is no longer as competitive with increased protonation. Changes in reduction pathways are noted, sigma rho calculations for the radical anion are obtained and these factors are compared in different solvents.

Adjacent chlorine interactions are determined to cause pathway changes and these interactions were also found to be in need of correction in the sigma rho calculations. An interpretation of the effects of proton addition on the dianion is made using sigma rho radical anion data and cyclic voltammograms.

i

To my parents

But I will bring you forth out of the midst of it

Ezekiel 11:7

THE EFFECTS OF A PROTON SOURCE ON THE ELECTROCHEMICAL REDUCTION
OF THE CHLORINATED NITROBENZENES IN DIMETHYLSULFOXIDE,
DIMETHYLFORMAMIDE AND ACETONITRILE

by

KATHLEEN ELIZABETH BRUNKE

A thesis submitted in partial fulfillment
of the requirements for the degree

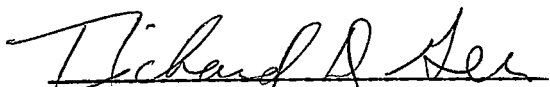
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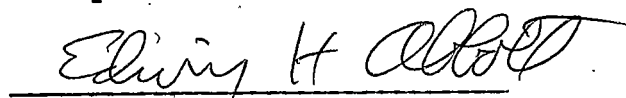
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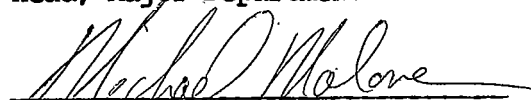
in

Chemistry

Approved:


Chairperson, Graduate Committee


Head, Major Department


Graduate Dean

Montana State University
Bozeman, Montana

May, 1982

ACKNOWLEDGMENT

I wish to extend my sincere gratitude to a number of individuals who have helped me attain this goal.

My advisor, Dr. Richard Geer, put up with me throughout my graduate career as I went through many trying periods. His patience, guidance and willingness to "come to the rescue" were appreciated.

I would like to thank Dr. Bradford Mundy who gave me unending encouragement, helped me build my self-confidence and showed me, by example, the finer arts of teaching.

My sister, Susan, gave me spiritual support as well as her friendship and kept me enthusiastic about life.

I could never have reached this goal without the love and support of my husband, Bruce. He inspired me and helped me through many difficult times. This has been a growing experience for both of us.

Finally, I would like to thank my parents who forever reassured me and gave me their love, support and understanding.

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ABSTRACT

Cyclic voltammograms of the chlorinated nitrobenzenes and nitrobenzene itself were obtained in DMSO, DMF and AN with and without the addition of a proton source. Reduction potentials for all primary processes were obtained from the voltammograms. The first reduction wave corresponds to the one-electron reversible transfer to form the radical anion. The second reduction wave represents the addition of more electrons to form the dianion followed by loss of chlorine with subsequent reduction or protonation. The protonated species can either deprotonate or lose hydroxide to yield nitroso compounds. With proton addition, the competition between processes is altered and protonation increases. The potentials of the "irreversible" waves shift anodically and some waves are no longer seen as the corresponding process is no longer as competitive with increased protonation. Changes in reduction pathways are noted, sigma rho calculations for the radical anion are obtained and these factors are compared in different solvents. Adjacent chlorine interactions are determined to cause pathway changes and these interactions were also found to be in need of correction in the sigma rho calculations. An interpretation of the effects of proton addition on the dianion is made using sigma rho radical anion data and cyclic voltammograms.

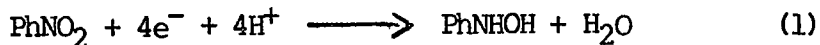
INTRODUCTION

Electrochemistry in Amphotropic Solutions

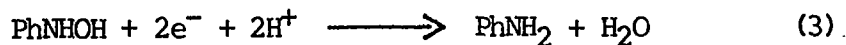
I. Nitrobenzene

Nitrobenzene was one of the first organic compounds to be studied by polarography. It is known to undergo electrochemical reduction in both protic and aprotic solvents. The aprotic solvents are important in the formation of a stable anion radical while protic solvents have proven to be valuable for analytical methods.

In aqueous solutions, the pH has a great effect on the cyclic voltammograms of nitrobenzene, nitrophenols, dinitrophenols and dinitrobenzenes.¹⁻⁴ At pH values below 5, there are two reductive waves while at higher pH values, only one reduction is observed.⁵ The first wave corresponds to a four electron process with the formation of phenylhydroxylamine as the product in solutions with pH's higher than 5.⁶

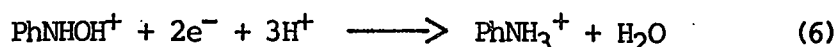
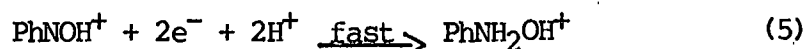


At pH<5, the occurrence of two waves indicate a four electron process (Equation 2) followed by a two electron process (Equation 3).

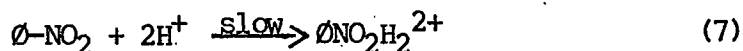


Though both waves are dependent on pH, the second wave is effected to a greater extent than the first wave.⁷ The anion radical which is formed when one electron is transferred, has been found to be stable in nonaqueous solutions but unstable in aqueous solutions.⁸

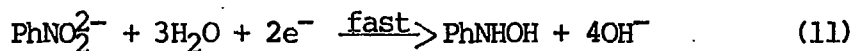
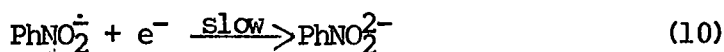
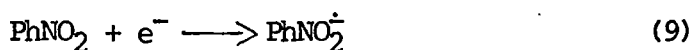
In acidic solutions, preprotonation is assumed to occur at the electrode surface yielding the $\text{PhNO}_2\text{H}_2^{2+}$ ion that is reduced according to the following mechanism:⁹



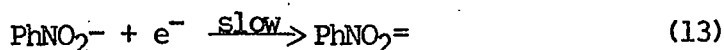
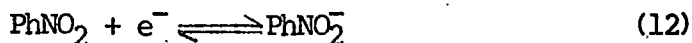
Equations 4 and 5 represent the four electron process of wave 1 while Equation 6 is the second wave and a two electron process. The rate determining step occurs during the formation of PhNOH^+ . This cation has been found in the reduction of nitrobenzene appearing as a prewave at a less negative potential than the nitrobenzene radical anion. The pre-wave corresponding to preprotonation has been determined by Sadek and Aba-El-Nabey¹⁰ to be the result of an interaction between adsorbed nitrobenzene molecules and hydrogen ion at the electrode surface. The four electron process in an acidic solution with preprotonation can then be written as:



In neutral and alkaline aqueous media, there is not a preceding surface reaction between adsorbed nitrobenzene molecules and protons.⁹ The rate determining step (Equation 10) is irreversible. The half-wave potentials are not pH dependent indicating hydrogen ions are not involved in the reduction process.



In solutions of low proton donor concentration¹¹ and in alcohol-water solutions (concentration alcohol > 10 wt%)⁹ there are two consecutive single electron transfer processes (Equations 12-13)



In liquid ammonia, the first wave is a one-electron irreversible process. The second wave is a one-electron transfer yielding a dianion that is stable on a long coulometric time scale.¹² The formation of a dianion precipitate, characterized by a bright red color, causes a sharpening of the reduction wave.

II. Nitrosobenzene

Less detailed studies of nitrosobenzene have been undertaken in the same manner as nitrobenzene.¹³ It has been found that

nitrosobenzene reduces at a less negative potential than nitrobenzene, accounting for the direct reduction of nitrobenzene to phenylhydroxylamine.¹⁴

In 10% ethanol water solutions, buffers were added to vary the pH. As the pH increased, the first reductive wave moved more negative. The second wave was identical to the wave representing the formation of phenylhydroxylamine and shifted more negative as the solution became more basic. The general scheme of reduction is shown in Equations (15-17).¹⁵



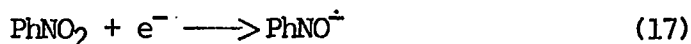
In a 50% ethanol buffered solution, nitrosobenzene yielded one reduction wave below pH 12.5. Above pH 12.5, two reduction waves appeared. The second wave corresponded to the reduction of azoxybenzene. above pH 12.5.¹³ It was found that the half-wave potential of the first wave varied linearly with pH. Ethanol, dioxane and acetone with acid solutions yielded a positive movement of the first wave on increasing the concentration of the acid.¹⁶

Using liquid ammonia as the solvent, nitrosobenzene was reduced in two successive reversible steps, each being a one-electron transfer with the dianion being more stable than the nitrobenzene dianion on

the coulometric time scale.¹²

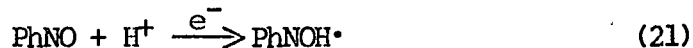
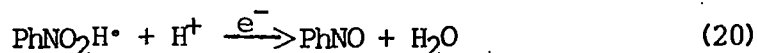
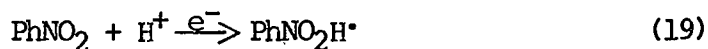
Nitrobenzene in Aprotic Solvent

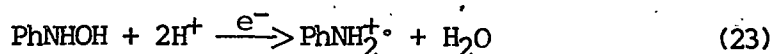
In aprotic solvents, the lack of proton availability causes a change in the reduction mechanism of nitrobenzene. Nitrobenzene is reduced by a one-electron reduction to a stable radical anion. This is followed by a three electron reduction at a more negative potential with proton donation from the solvent to yield phenylhydroxylamine.



Maki and Geske used acetonitrile (AN) and a mercury pool electrode to study the nitrobenzene anion radical.¹⁷ They repeated the early polarography done by Runner and Balog¹⁸ and found two reduction waves. The first wave corresponded to a one-electron reduction to yield the radical anion followed by a wave representing a one electron reduction at a more negative potential to yield the dianion.

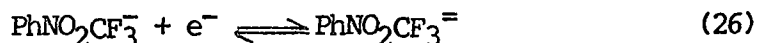
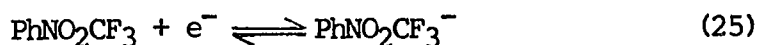
In an acidic dimethylformamide (DMF) solution,¹⁹ the reduction of nitrobenzene has been described by a series of steps with protonation following each step.





The transfers that occur in Equations 21 and 23 are rapid at the reduction potential of Equation 20. The phenylhydroxylamine formed in Equation 23 is relatively stable in acid solution but in alkaline solution, it reacts with nitrosobenzene to yield azoxybenzene.¹⁶

Substitution of a trifluoromethyl group in the para position of nitrobenzene results in a one electron reduction for the first wave and a two electron reduction for the second wave.²⁰ A new couple appears anodic of wave 1 that is thought to be a radical product of the ECE process. The reductive mechanism appears to be:



(26)

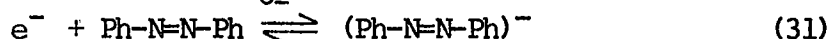
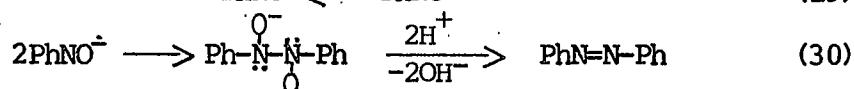


Electrolysis of this solution produces a cathodic shoulder on the radical anion reduction and oxidation wave that is thought to correspond to azo or azoxy formation.

Nitrosobenzene in Aprotic Solvent

In DMF, nitrosobenzene can be reduced by a two step mechanism.²¹ The first wave represents the formation of the unstable radical anion

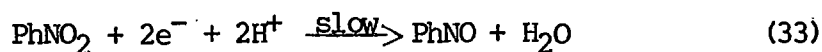
and reacts with another molecule of nitrosobenzene to form azoxybenzene. Cyclic voltammetry and electrolysis studies in DMF revealed a three step mechanism in which dimerization of the nitrosobenzene radical anion is more plausible and corresponds to the following mechanism:^{1,27,23,15}



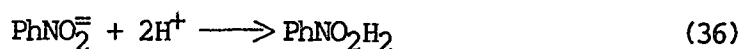
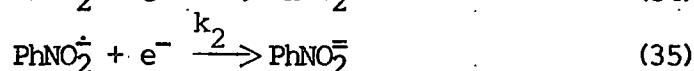
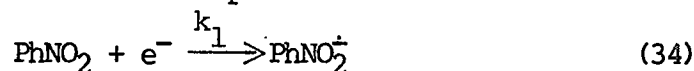
Dimerization resulted in formation of a dianion intermediate that abstracts a proton from the solvent and then releases hydroxide ion to yield azoxybenzene. If the mole ratio of hydroxide ion to nitrosobenzene was .3, the nitrosobenzene would be completely consumed in acetonitrile (AN) but the consumption would not be complete in dimethylformamide.¹⁵ This mechanism also fitted the data for a 80:20 dimethylsulfoxide (DMSO)/t-butyl alcohol solution.²⁴

Effects of Proton Addition

Nitrobenzene. At low alcohol concentrations (3.2 wt% (.55M) ethanol in water) the reduction of nitrobenzene proceeds through one rate-determining step that may consume two electrons as the system does in pure aqueous solution.⁹



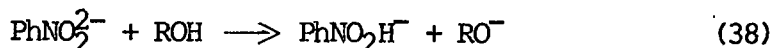
At higher alcohol concentrations (>10 wt% (1.72M) ethanol in water), the process involves two consecutive rate-determining electrochemical reactions followed by two chemical steps.



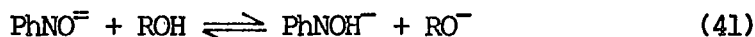
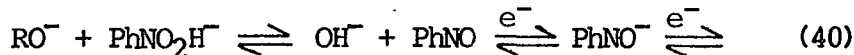
The half-wave potential of the second wave shifted negatively at low alcohol concentrations but at concentrations greater than 3.5 wt%, it shifted positively. This is due to enhanced ion association between the nitro anion and the cation of the electrolyte. Isopropyl alcohol has a greater effect than ethanol for producing this two way shift.

In solutions of .1M hydrochloric acid and ethanol, changes in the potential of the first wave were noted with increasing alcohol concentration.²³ The half-wave potential shifted negatively as the alcohol concentration increased.

The addition of alcohol to a solution of liquid ammonia, nitrobenzene and an electrolyte resulted in the appearance of an anodic shoulder on the wave that represents the formation of the dianion.¹² Smith and Bard determined the shoulder was caused by the following reaction:



However, an electrochemical process for the protonation of a dianion would cause the entire wave to shift and protonation of the radical anion would appear as a shoulder. Two oxidative waves appeared that corresponded to nitrosobenzene oxidation waves in the presence of alcohol. This indicated both reactions give the same final product, PhNOH^- , by the following mechanism:



The addition of *o*-phthalic acid to aprotic solvents caused the formation of a new wave positive of the first wave.²⁴ The height of the first wave decreased with increasing acid concentration while the new wave continued to increase. The new wave represents the preprotonation of nitrobenzene at the electrode surface prior to the rate-determining step. The reduction potential of the preprotonation wave can be correlated with pK_a values. When phenol was added to acetonitrile, the second reduction wave shifted positive so that the sequential reduction no longer occurred.

According to Greig and Rogers, addition of hydroquinone to a DMF solution containing an electrolyte and *o*-trifluoromethylnitrobenzene does not affect the first wave but the second wave shifts

anodically.²⁰ The relationship of current between waves 1 and 2 does not change, indicating no affect on the number of electrons transferred. The shift of wave 2 is caused by protonation of the radical anion. The protonated radical anion is reduced at a more positive potential than the unprotonated radical anion. The nitroso couple which appeared cathodic of wave 1, also protonates and is reduced more anodically. The proton donor should increase the rate of formation of the nitroso intermediate and therefore, increase the intensity of the oxidation-wave.

Holleck and Becher observed a positive shift in the half-wave potential of the second wave of p-chloronitrobenzene with increasing water concentration.²⁵ The addition of phenol was shown to cause rapid protonation of nitrobenzene¹¹ that would cause a positive shift in the reduction potential. This was observed by noting a decrease in the rate of radical anion formation at a high phenol concentration indicating a lower radical lifetime.

Carre and Belin²⁶ studied the effects of a proton source added to a DMF/nitrobenzene solution. Using phenol and benzoic acid, they found that at pH >12.5 two waves appeared corresponding to a one-electron reduction and a three-electron reduction, respectively. The first wave corresponded to the formation of the radical anion while the second wave appeared to represent the formation of

phenylhydroxylamine and azoxybenzene. At pH < 12.5, a four electron reduction wave appeared corresponding to the reduction of nitrobenzene to phenylhydroxylamine (Equation 42).



Nitrosobenzene. When a proton donor was added to nitrosobenzene in liquid ammonia, the second reduction wave decreased and a new wave appeared 120mV more positive than the second wave while the first wave was unaffected.¹² When the alcohol concentration was increased, the new wave shifted positively and increased in height. The new wave can be represented by:



The nitroso radical anion can protonate rapidly producing the neutral nitroso radical that is oxidized at potential more anodic than the unprotonated anion radical oxidation.²⁰

Substituents on Nitrobenzene

The stability of the substituted nitrobenzene radical anion depends on the nature of the substituent and its position on the ring.^{27,28} Stability increases when an electron withdrawing group is present and by increased delocalization of the negative charge over the ring. The degree of localization depends on the amount of twist of the nitro group out of the plane which depends on the

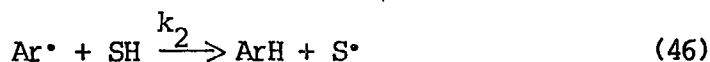
substituent.²⁹ It is well known that the nature of the substituent affects the half-wave potential. It has been observed that p-nitrophenol is not as easily reduced as nitrobenzene.⁶ The electron density on the nitro group increases because of the electron-donating effect of the hydroxyl group in the para position. At low pH values, the o- and m-nitrophenol are reduced slightly more readily than nitrobenzene. In the case of the ortho substituent, the hydrogen bonding cancels the increased electron density due to an substituent ortho to the nitro group. The meta substituent of any nature is more stable than the corresponding o- and p- derivatives.²⁷

The reduction potential of o-methylnitrobenzene is more negative than the reduction potential of nitrobenzene itself.³⁰ When the substituent is a t-butyl group, the compound will be reduced at a more cathodic potential due to an inductive effect. When the substituents are electron donators, the half-wave potentials are found more negative than when the substituents are electron acceptors.²⁵ This is thought to be due to ion-pair formation occurring prior to the first reductive wave. It is apparent that electron donor substituents hinder electron addition, making the compound harder to reduce.³¹ It will reduce at a more negative potential than compounds that have electron acceptor substituents.

EPR studies show the nitrogen coupling constant decreases as the

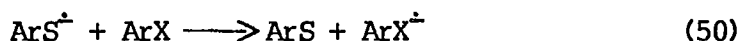
ease of reduction increases.³² When the substituent is a chlorine, the electron attracting (withdrawing, accepting) effect of the substituent causes the reduction to occur more easily than in nitrobenzene and the nitrogen coupling constant to decrease. The nitrogen coupling constant of o-chloronitrobenzene is greater than for the corresponding meta and para isomers indicating a steric effect.¹¹

Halonitrobenzenes. The halonitrobenzenes are reduced by two different mechanisms. One mechanism involved the solvent and can be shown as follows:



This scheme has been seen when the ArX reduction wave corresponds to less than a two electron transfer and less than 100% yield of ArH.³³ The proton donor in aprotic solvents is thought to be residual water which is a much stronger acid than the solvent itself. However, a deuterium study examining whether residual water or the solvent is responsible for the proton used has shown that if the Ph⁻ anion is fairly basic and the PhH/Ph⁻ pKa's are much more negative than the pKa's of the organic solvents, the protonation rates by water and the solvent may reach the diffusion limit and the solvent may yield the

proton.^{33,34} It was determined that less than 100% yield was achieved because of further reaction of the solvent radical to yield substituted products as is shown in Equations 47-50.²⁷



Compounds which have been found to undergo this type of reduction include halogenated acetophenones, iodonitrobenzenes, 2-bromonitrobenzene, 3- and 4-bromobenzophenone, 2-iodophenazine, 6-chloroquinoline, 6-bromoquinoxaline and 6-iodoquinoxaline.

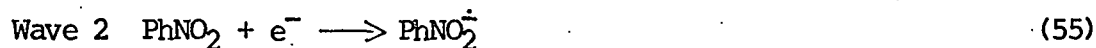
The other mechanism of halonitrobenzene reduction may be associated with systems which are less delocalized so that reduction of $Ar^{\bullet}$ at the electrode will occur more readily than proton transfer. This will yield 100% ArH and a two electron transfer.



Included in the compounds undergoing this reaction are bromobenzene, chlorobenzene, halobenzonitriles, chlorobiphenyl, and the halonaphthalenes.

Maki and Geske observed electron spin resonance (ESR) for the p-

chloro, p-bromo and p-fluoronitrobenzene radical anions but not for the p-iodonitrobenzene radical anion.³¹ Other studies revealed that the three iodonitrobenzenes lose their iodine, yielding the nitrobenzene radical anion.^{11,35} An intermediate wave is observed that corresponds to the formation of the radical anion with preceeding iodine loss. The proposed mechanism of reduction is:³⁵

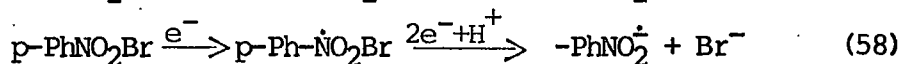
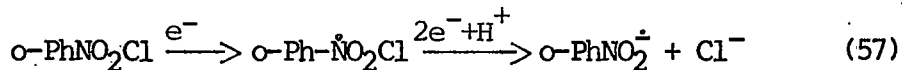


There are some inconsistencies in the data, namely, the potentials for the reductions that occur at wave 2 and 3 should correspond with the reduction potentials for nitrobenzene under the same conditions. The second wave is (-) 70mV more negative than the potential of the radical anion of nitrobenzene given in the paper while wave 3 is (-) 200mV more negative than the dianion of nitrobenzene. The intermediate has also been observed for p-bromonitrobenzene.²⁵ However, the p-bromonitrobenzene ESR spectra yielded a mixture of the nitrobenzene radical anion and the p-bromonitrobenzene radical anion.³⁵ Only the o-bromo isomer loses bromine readily. Further studies revealed that the ortho isomer yields an ESR spectrum identical to the nitrobenzene anion radical indicating loss of bromine prior to radical anion formation. The spectra of the other two

isomers were identical to the chloro isomers where no halogen loss is observed.¹¹ These results are not surprising since the order of carbon-halogen bond strengths is $F > Cl > Br > I$.³⁶ Therefore, iodide should be lost readily while the bromide isomers may yield a mixture. Chlorine isomers are much more stable and won't lose the halogen as readily.

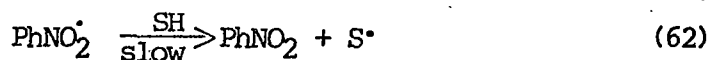
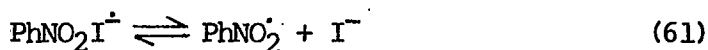
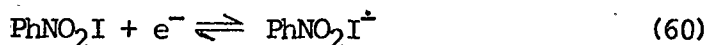
Electrolysis of the chloro and bromonitrobenzenes yielded no halogen loss in acetonitrile after the first wave for all isomers except the o-bromonitrobenzene.¹¹ In DMF, o-chloronitrobenzene yielded the nitrobenzene radical anion when the potential was held between the first and second waves during electrolysis. Addition of phenol inhibited halogen loss. The para isomer of bromonitrobenzene behaved the same as the ortho-chloro isomer, yielding the radical anion of nitrobenzene when the potential was held between the first and second waves.

Iodonitrobenzene isomers all showed nitrobenzene radical anion formation in DMF and AN. The proposed mechanism of reduction for the o-chloro, p-bromo and iodo isomers is:



Lawless and Hawley interpreted the iodo reduction mechanism more

precisely.³⁷



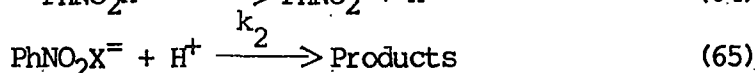
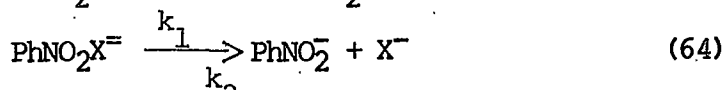
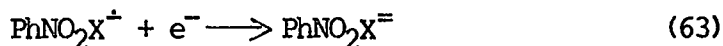
The slow step was determined by noting that the addition of iodide slowed the rate of formation of nitrobenzene indicating that the chemically slow step follows the loss of the halogen. Rates of decomposition of the radical anion of nitrobenzene as determined by current reversal chronopotentiometry can be ordered as o-iodo > o-bromo >> p-iodo > m-iodo. These were determined by current reversal chronopotentiometry. The ease of dehalogenation of the possible halogen and isomers are ordered p, m-Cl, m-Br < o-Cl << p-Br < o-Br, p-, m-, o-I.¹¹ It is obvious that the ease of dehalogenation is dependent on the steric conditions. In terms of general rate constants, the sequence above yields $k_{\text{F}} < k_{\text{Cl}} < k_{\text{Br}} < k_{\text{I}}$.³⁴

The ortho isomers have a slightly greater rate due to steric effects which are noted by looking at the rate constant for the isomers: $k_{\text{m}} < k_{\text{p}} < k_{\text{o}}$. These orders were further demonstrated by Hawley et al. by studying the stability of the nitrobenzene radical anion.³⁸ When a methyl group was placed in the 6-position in 3-iodonitrobenzene, loss of the iodide increased 30-fold in the anion radical. When methyl groups were placed in both ortho positions in 4-

iodonitrobenzene, a 280-fold increase in the rate of iodide loss resulted. It was determined that steric interaction increases with size of the ortho-halogen, thus causing an increase in the rate of halide loss. An anodic shift in the reduction potential results because of increasing loss of halide ion. This shift compensates for the cathodic shift that occurs as steric interaction increases.³⁹

Lawless and Hawley looked more closely at the effects of steric strain by observing the reduction of 2,6-dichloronitrobenzene³⁸ in DMF using tetraethylammonium perchlorate (TEAP) as the electrolyte. They noted that the steric effect may be observed by predicting the half-wave potential for the first wave. This is accomplished by using a rho (ρ) value for the reduction of a series of nitrobenzenes in DMF obtained previously, a half-wave potential for nitrobenzene and a Hammett substituent constant (σ) for an ortho- or para-substituted chlorines. The value they predicted was -180mV from the observed value, indicating that steric interaction occurs between the nitro group and the two ortho chlorines. The predicted value for o-chloronitrobenzene is -60mV from the observed value. The addition of a chlorine to o-chloronitrobenzene causes the nitro group to twist from 30° to 65° out of plane. It is obvious that the elimination of a chlorine relieves strain, thus o-chloronitrobenzene can be reduced to nitrobenzene. Observations of the reduction of 2,4-

dichloronitrobenzene showed the p-chloronitrobenzene radical anion is formed, also relieving steric strain. Cyclic voltammetry of p-bromonitrobenzene demonstrates first a one-electron reduction to the radical anion then a one-electron reduction to the p-bromo dianion. This is followed by loss of bromide and subsequently, a one-electron reduction of the nitrobenzene radical anion. When the potential is reversed before the third wave, a new couple appears as a cathodic shoulder on wave 1. This wave corresponds to the nitrobenzene radical anion and proves that wave 3 results from the formation of the nitrobenzene dianion. The anion radical of p-chloronitrobenzene does not lose its chloride. This is due to competitive pathways.



The above reaction by the k_2 process depends upon proton availability. The reduction of 2,3-dichloronitrobenzene yielded the m-chloronitrobenzene radical anion by ESR spectroscopy but it was not apparent in cyclic voltammetry. The steric interaction was found to be greater in the 2,3-dichloro compound than in the o-chloro compound by 50mV. Lawless and Hawley believed that neighboring chlorines effect the steric interaction.

It has been observed that more resonance energy is lost between

the nitro group and the ring due to the nitro group being decoupled as it twists out of the plane of the ring.²⁸

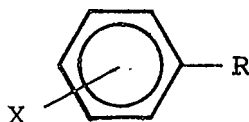
The decoupling of the nitro group results in a charge transfer from the ring to the nitro group that indicates a decrease in the strength of the π -system interaction between the ring and the nitro group.⁴⁰

ESR studies of nitrobenzene radical anions in aqueous solution proved that the transfer of the electron occurs via the nitro group, but that the efficiency of transfer is determined by the ability of the radical anion to delocalize the additional electron over the rest of the molecule.⁴¹ The one electron reduction potential is more negative when $a_{\text{NO}_2}^{\text{N}}$, the nitrogen hyperfine splitting constant, increases due to the twist of the nitro group when other substituents are present. The activation energy for the anion formation increases due to the loss of delocalization for the twisted radical anion.

The meta proton splitting constant $a_{\text{meta}}^{\text{H}}$, is not affected the same as the ortho and para constants which decrease when $a_{\text{NO}_2}^{\text{N}}$ becomes large. This indicates the shift of spin density is towards the nitro group. The effect of the twist of the nitro group is greater on $a_{\text{ortho}}^{\text{H}}$ and $a_{\text{para}}^{\text{H}}$ than $a_{\text{meta}}^{\text{H}}$. In DMF, the para splitting constant, $a_{\text{para}}^{\text{H}}$, decreases from 3.95 to 3.55 Gauss when water is added while the ortho and meta constants are stable.⁴² The change occurs rapidly at

first and then begins to level off. There is a 1:1 correlation between $a_{\text{NO}_2}^{\text{N}}$ and $a_{\text{para}}^{\text{H}}$ with and without water added. When the nitrogen is twisted out of the plane of the ring, it is more open to solvation and hydrogen bonding.⁴¹

Sigma Rho. Sigma rho calculations are used to correlate the nature of



the substituent X, with the reactivity of the side chain R.

The Hammett equation expresses this relationship as

$$\log (k/k^{\circ}) = \sigma \rho \quad (66)$$

The terms k and k° are equilibrium or rate constants for substituted benzene derivatives, sigma (σ) is the substituent constant that only depends on the nature of the substituent and its position and rho (ρ) is the reaction constant that is independent of the substituents but dependent on the reaction, the nature of the side chain and the reaction conditions.⁴³

When a reaction site on a substituent is insulated from the benzene ring (more than a carbon away), the energy of activation is affected by the change of electron density at the site of the reaction but there will not be a change in resonance energy from the ground

state to the transition state.⁴⁴ When the reaction site is directly attached to the ring, the resonance energy will be affected.

For electrochemical systems, the effect of substituents is also determined by use of the Hammett equation. The half-wave potentials for reversible processes are given by the difference between the standard free energies of the oxidized and reduced forms:

$$E_{1/2} = E^\circ - \frac{RT}{nF} \ln \left(\frac{D_{\text{ox}}}{D_{\text{red}}} \right)^{1/2} - \frac{RT}{nF} \ln \frac{f_{\text{red}}}{f_{\text{ox}}} \quad (67)$$

where R is the gas constant, T is the absolute temperature, n is the number of electrons transferred, F is the Faraday charge, D_{ox} and D_{red} are the diffusion coefficient of the oxidized and reduced forms, respectively and f_{ox} and f_{red} are the activity coefficients.⁴⁵ At a given unit strength at which the activity coefficients are constant and $D_{\text{ox}} \approx D_{\text{red}}$,

$$E_{1/2} = E^\circ \quad (68)$$

$$E_{1/2} = \Delta G^\circ / nF \quad (69)$$

The shift in the half-wave potential $(\Delta E_{1/2})_X$ caused by adding a substituent X onto a reference compound can be represented by

$$(\Delta E_{1/2})_X = \frac{2.3RT}{nF} (\Delta \log k)_X \quad (70)$$

where K is the equilibrium constant of an oxidation reduction reaction and $\Delta \log K = \log K_X - \log K_0$ where K_0 is the value for the reference

system.⁴⁶ Because the Hammett equation can be expressed as $(\Delta \log K)_X = \sigma \rho$, it is possible to use the Hammett expression in terms of half-wave potential

$$\Delta E_{1/2} = \sigma \rho \quad (71)$$

for meta and para substituent. This relates polar and inductive effects. When mesomeric (resonance) interactions between the group R and a para substituent on a benzene ring occur, the equation is written as⁴⁷

$$\Delta E_{1/2} = \rho \sigma_X^- \quad (72)$$

Occasionally, the reaction constant is negative due to an electrophilic mechanism and the equation is written as

$$\Delta E_{1/2} = \rho \sigma_X^+ \quad (73)$$

For ortho substituents, X, the equation takes on the form

$$\Delta E_{1/2} = \sigma \rho + \delta E_S \quad (74)$$

where δE_S is the term for steric interactions. Other attempts have been made to find an equation for the ortho sigma constant but have not proved successful.⁴⁸ The constant, σ° , was found to yield better precision than $\sigma_{m,p}$.⁴⁹ The values are based on the ionization of phenyl acetic acid derivatives instead of benzoic acid. Many systems have been used to find σ_{ortho} values with poor agreement between values.⁵⁰⁻⁵⁴ When several substituents are on the ring, the substituent constants are additive.

$$\Delta E_{1/2} = \rho \sum \sigma_X \quad (75)$$

Hammett's value for the 3,4-dimethyl substituent agrees with the sum of the para and meta methyl substituents constants.⁵⁵ Additive effects have been observed for systems such as β -naphthyl and phenyl-3,4-methylenedioxy derivatives in which two benzene rings are fused. When rings are symmetrically located with respect to the reaction site, additivity is still found.⁵⁶ Shorter and Stubbs proved additive effects for a number of polysubstituted benzoic acids but substituents in the 2,3- and 2,6- positions did not conform to the $\rho \sum \sigma$ theory.⁵⁷

Many attempts have been made to explain the effects of ortho substituents on the benzene ring. Some treatments have assumed the reactant constants were equal for each position⁵⁸ ($\rho_o = \rho_m = \rho_p$) and have used the same values for the para and meta positions ($\sigma_p = \sigma_m$)⁵⁹ and for para and ortho constants.⁶⁰ Ortho substituent constants have been thought to depend on electrical effects but not steric effects.⁶¹ Further investigations have determined that resonance effects are extremely important.^{62,63} It has been suggested that each substituent and reaction series yields a unique constant.⁶⁴ More recently, it has been determined that ortho effects are a result of both polar and steric effects.^{46,65} Classification of reactivity into resonance or inductive divisions depends on the reference site.⁶⁶

Electrochemical studies have been used to determine steric

effects of substituents.^{13,19,67-69} The first wave of nitrobenzene (radical anion formation) has been used to study reactivity.^{26,46} The results are very limited. Recent results show that corrections can be made for polar interactions of adjacent chlorines for chlorinated nitrobenzenes in DMSO that make the sigma constants additive.⁷⁰ It was determined that σ° constants were more appropriate than constants for this type of compound.

Rodante studied the effect of solvent on the linear free energy relationship.⁷¹ In a water-DMSO solution, o-nitrophenol was found to have internal hydrogen bonding due to strong electrostatic attractions between the positively charged hydroxyl hydrogen and the negative charge on a oxygen of the nitro group. The reaction constant was larger than that found in pure water. With increasing DMSO concentration, ρ increased to a maximum near .7% mole fraction then decreased. The increase is due to a reduced number of intermolecular hydrogen bonds between the anions and the water molecules. The solvent is causing a slight perturbation with the interactions between the substituent and the reaction site.

Solvents and Their Effects

The effect of adsorbed ions and proton addition are dependent on the properties of individual solvents. It has been shown that the stability of the nitrobenzene radical anion for the decomposition of

iodonitrobenzene to the nitrophenyl radical anion and iodide decreases in the order DMSO>AN>DMF.³⁶ The rate of decomposition of the anion radical is ten times faster in DMF than in AN and fifteen times faster in DMF than in DMSO for the para and meta iodo compounds.

Anion radicals of benzophenone have been shown to be more stable in liquid ammonia than in AN or DMF.⁷² It appears that the anion solvating ability is most influential on the stability of the anion radical in various solvents. The negative charge will become more delocalized by solvation of the radical anion, decreasing the amount of charge at the carbon attached to a halogen. This will increase the stability of that bond.

Dimethylsulfoxide (DMSO) contains two acceptor sites: the oxygen and the sulfur.⁷³ The oxygen has the greater amount of electron density associated with it. Anions are much less strongly solvated due to the lack of hydrogen bonding. There is a strong dipole-dipole interaction between DMSO and water which is stronger than the molecular association of water. Results of various studies have not agreed on the mole ratio of water:DMSO bonds. Two studies revealed that one molecule of water is bonded to two molecules of DMSO^{74,75} or DMF⁷⁵ while another study showed one molecule of DMSO associated with two molecules of water.⁷⁶ Alcohols have been shown to be weaker proton donors toward DMSO than water and form only hydrogen bonded

complexes.⁷³ It has been found that anions can be specifically adsorbed by DMSO solutions in the order $I^- > Br^- > Cl^- > NO_3^- > ClO_4^-$ but that cations are not readily adsorbed.⁷⁷ Mixed DMSO-water solutions enhance specific adsorption of anions.

DMSO is strongly adsorbed at a mercury or platinum electrode. The adsorbed DMSO is reduced and oxidized because the sulfur atom is an electron pair donor.⁷⁸ The DMSO capacity hump due to adsorption onto the electrode appears at $E = 0V$ (volts) on a platinum electrode while in pure aqueous solutions this hump occurs at $-0.35 V$. DMSO is more active than water towards a platinum electrode, so that the DMSO layer is between the electrode and the water layer.⁷⁹ DMSO can adsorb onto the surface of a platinum electrode with one molecule of DMSO occupying four adsorption sites on platinum.⁸⁰ DMSO can be reduced to dimethylsulfide while it is adsorbed.

It is possible that reduction products can also adsorb to the electrode. In solutions of sulfuric acid and also in phosphate buffers, nitrobenzene derivatives are found to adsorb strongly to a platinized platinum electrode with hydroxylamines adsorbing to a much lesser degree.⁸¹ Amines are found to adsorb less than hydroxylamines.

DMSO yields two waves for oxygen in .1M tetraethylammonium perchlorate which were found at $-0.85V$ and $-2.20V$ vs SEC while carbon dioxide reduces at $-2.24V$ vs a mercury pool electrode.⁸² The position

of these waves depends on the supporting electrolyte. The first step in the reduction of oxygen in DMSO is the formation of the superoxide ion which is a reversible reaction.⁸³ The superoxide ion can undergo its own complete series of reactions.

DMSO has a viscosity of 1.98 centipoises (CP) at 25°C while DMF has a viscosity of .796 CP and in AN, .345 CP. This makes the diffusion coefficient larger in AN than in DMSO and consequently, the current in AN solutions will be higher due to increased rate of diffusion. DMSO has a dielectric constant of 47 compared to 37 for DMF and AN.⁸⁴ It is somewhat polar and its association with water helps to make radical anions more stable in it. It is odorless except for traces of dimethylsulfide. It rapidly penetrates the skin and may carry with it toxic substances.

In DMF, tetra-alkylammonium salts are strongly adsorbed at the mercury solution interface. There is depletion of water from this interface relative to the bulk solution which changes the composition of the double layer at the electrode surface.³⁶ Quarternary ammonium salts as a group are essentially free ions in DMF and are much less surface active in DMF than in water.²⁹

DMF is susceptible to hydrolysis yielding dimethylamine which is easily oxidized and formic acid, a reducing agent. The limiting cathodic range of DMF is either reduction of the solvent or the cation

of the electrolyte while the anodic range is limited by the oxidation of DMF at a platinum electrode where an electron is removed from the amide nitrogen.⁸³

Acetonitrile is used as an electrochemical solvent because it is a weaker base and a much weaker acid than water.⁸⁴ The high dielectric constant³⁷ decreases the amount of solvent clustering.⁸⁵ The limiting range is the reaction of the electrolyte at the electrode in both the anodic and cathodic directions.⁸⁶ Holleck and Becker noted the influence of water is greater in AN than in DMF because of the lack of hydrogen bonding in acetonitrile (hence, less solvation).²⁵ Jezorek and Mark agreed that the influence of water is greater in AN but they found that this was due to rapid protonation in AN.⁸⁷ Radical anions usually have a shorter half-life in AN than in DMSO or DMF because they react with traces of water rapidly.⁸⁴

STATEMENT OF PROBLEM

We started this work with the goal of determining the mechanistic effect water had on the electrochemical reduction of chlorinated nitrobenzenes in DMSO. The work grew out of a study initiated by H. Byker.⁸⁸ He observed the electrochemical reduction of the chlorinated nitro and nitrosobenzenes in DMSO and catalogued the reduction potentials. He paid particular attention to the first reduction wave which is important for sigma rho calculations. The pathways of reduction were observed. Prior to his work, S. O. Farwell⁸⁹ and F. A. Beland⁹⁰ investigated the electrochemical reductions of polychlorobiphenyls and polychlorobenzenes which are homologous to the chlorinated nitrobenzenes. They observed irreversible two-electron transfers for each reduction wave, corresponding to loss of chloride and proton abstraction.

As the data for this thesis were collected, it became apparent that other solvents might yield different mechanistic pathways of reduction. Ethanol was used along with water to determine whether ethanol gave a clearer picture of the mechanism than water. Then the subject of adjacent chlorine interaction was included to deal with the competing processes. Adjacent chlorine interactions are handled by using sigma rho calculations. The problem to be addressed in this paper is to determine the mechanisms of reduction of the chlorinated

nitrobenzene upon addition of a proton source in DMSO, AN and DMF and to determine and compare the effect of a proton source on sigma rho calculations in DMSO, DMF and AN.

EXPERIMENTAL

Instrumentation, Electrochemical Cell and Electrodes

Voltammograms were obtained using a standard cyclic voltammeter which consisted of an attenuator module (Figure 1), a logic module (Figure 2), a voltage module (Figure 3) and a potentiostat module (Figure 4). The system, built by R. Geer, allowed the cathodic, anodic and initial potentials to be set independent of one another. The sweep rates used were 37mV/sec, 64mV/sec, 124mV/sec, 253mV/sec, 504mV/sec and 1004mV/sec. All of the voltammograms presented in the discussion section were recorded at a sweep rate of 127 mV/sec except for the acetonitrile work which occurred at a sweep rate of 64 mV/sec. The instrument allowed for anodic and cathodic limit holds with very little drift. Intermediate potentials could also be held at any desired limit. Uncompensated resistance was used to correct for the IR drop. The voltammograms were recorded on a Houston Instruments Omnigraphic 2000-X-Y recorder. Peak potentials were determined graphically.

The cell was constructed from a four-dram glass bottle with a teflon lined lid (Figure 5). The total volume used was 15 milliliters (ml) of solvent plus the addition of 100 to 200 microliters (μ l) of proton source. The cell contained three electrodes. The reference electrode consisted of a silver wire inside a fritted glass tube

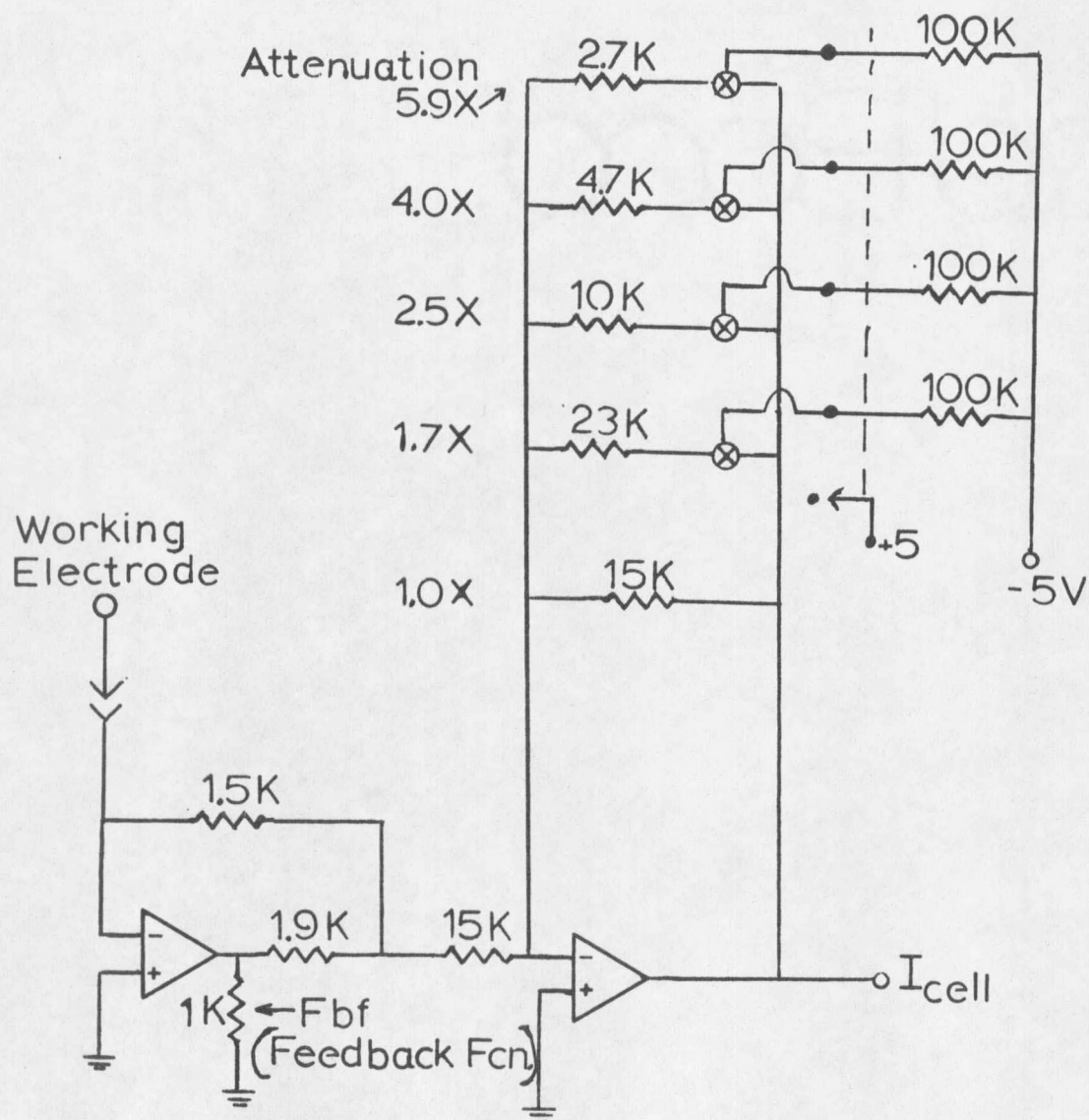


Figure 1. Cyclic voltammeter: circuit diagram for attenuator module.

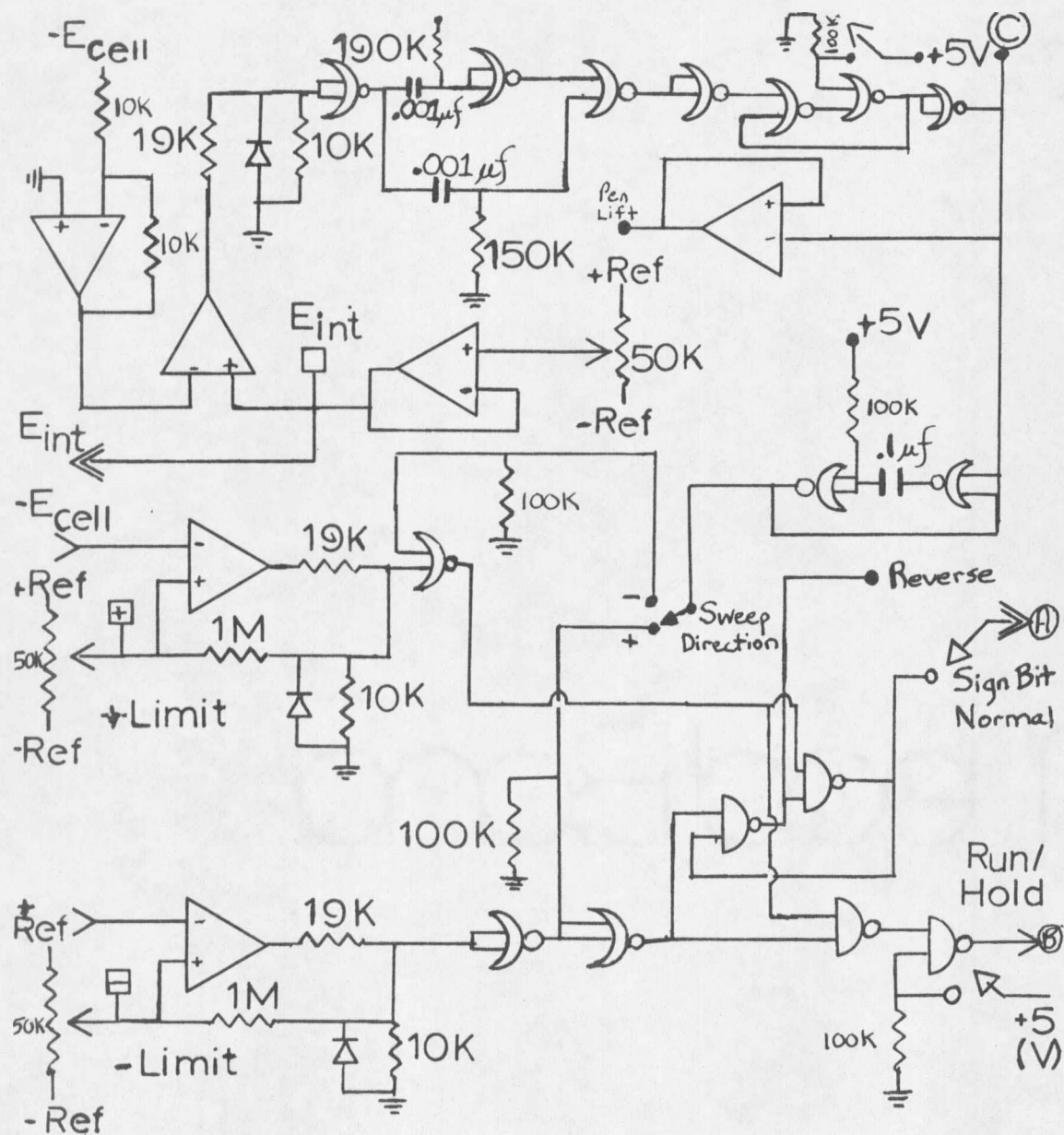


Figure 2. Cyclic voltammeter: circuit diagram for logic module.

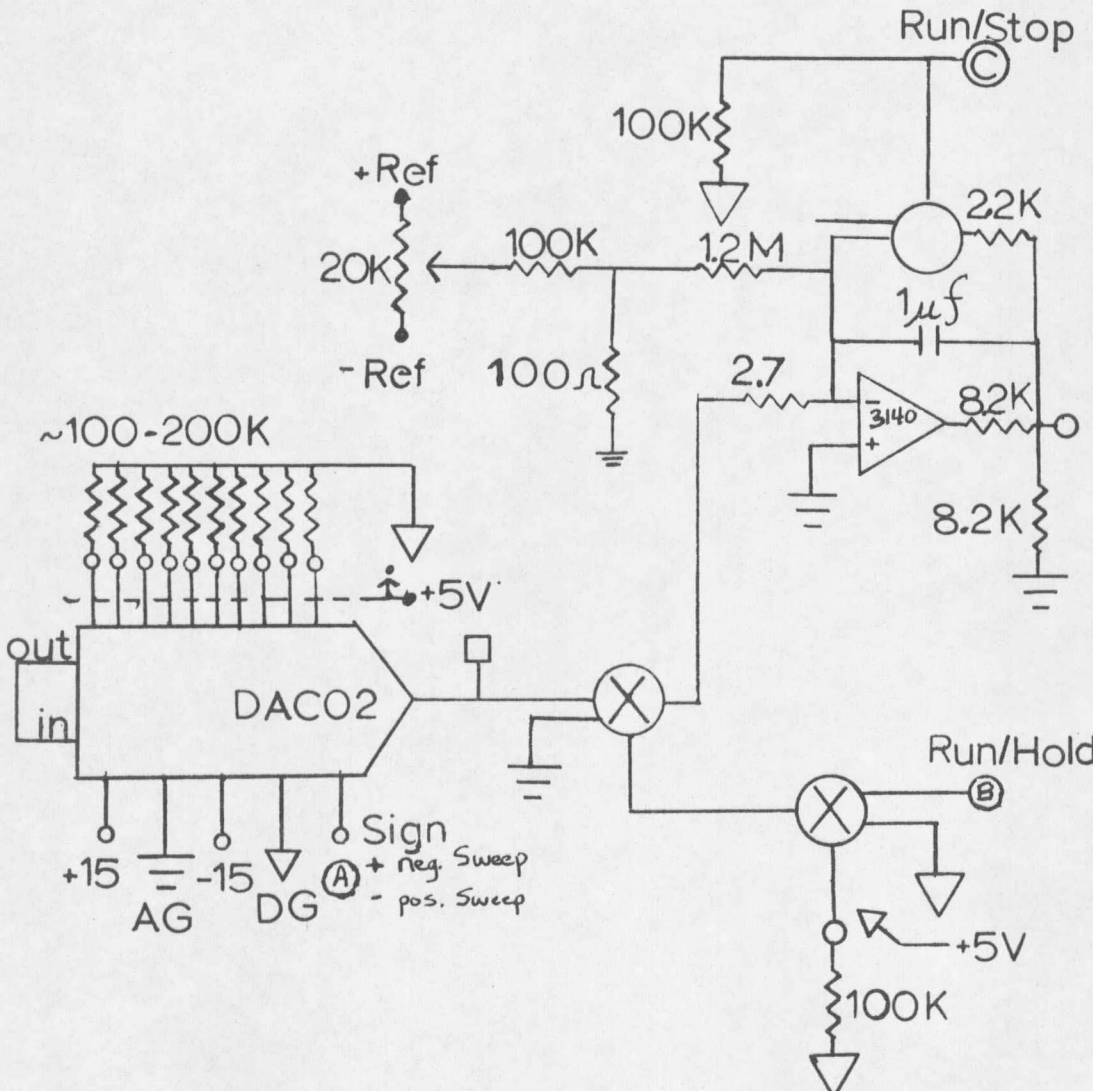


Figure 3. Cyclic voltammeter: circuit diagram for voltage module.

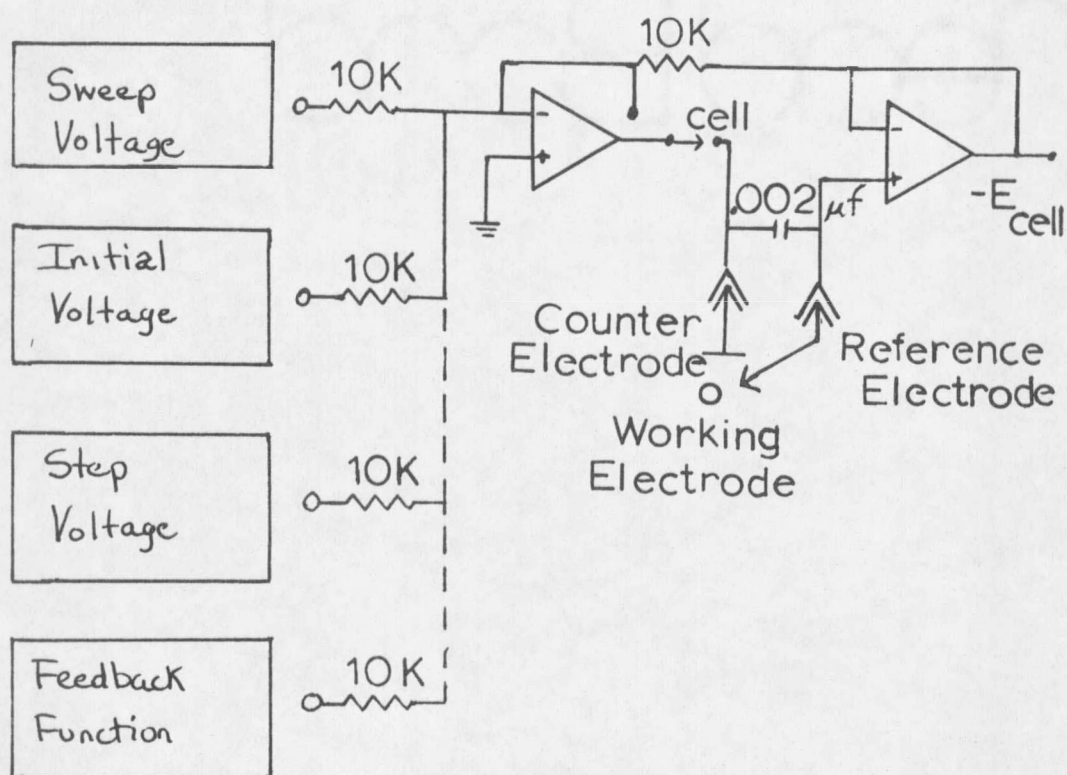


Figure 4. Cyclic voltammeter: circuit diagram for potentiostat module.

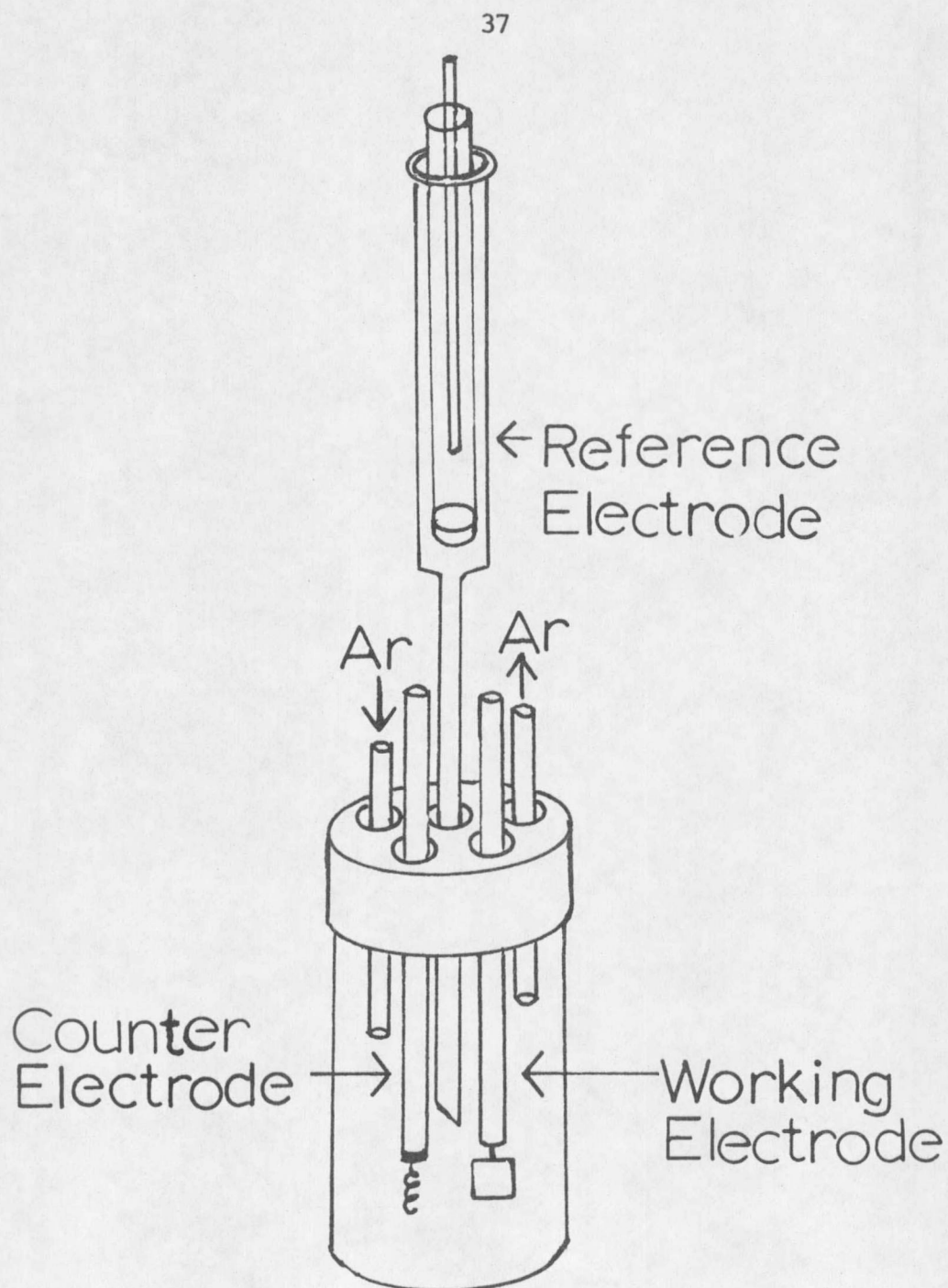


Figure 5. Cell diagram for cyclic voltammetry.

Containing .1M tetraethylammonium chloride (TEACl). The glass tube fit into a syringe body that was filled with the electrolyte (.1M tetraethylammonium perchlorate (TEAP)), in dimethylsulfoxide (DMSO). The reference electrode was connected to the sample by a 1.7 millimeter (mm) O.D. teflon tube with capillary flow tip. The working electrode was a mercury coated platinum flag electrode with a total area of approximately .25 cm². The platinum was coated with mercury by the procedure of Enke and coworkers.⁹¹ The platinum flag was attached to a platinum wire which was sealed into the bottom of a 3.4 mm glass tube. Mercury was placed in the tube and surrounded the platinum wire while a copper wire attached to a 20 gauge insulated wire was placed into the mercury from the top of the tube. The counter electrode was a coiled platinum wire protruding from a 3.4 mm glass tube and connected to the instrument via a insulated wire attached to the platinum.

The electrode and teflon lined lid were rinsed with the appropriate solvent between samples. A clean four-dram bottle was used for each sample. The bottles were cleaned with Microlab cleaner and a Branson ultrasonic cleaner, rinsed with distilled water and were allowed to air dry.

The cell was filled with 15 ml of .1M TEAP in DMSO, AN or DMF. The electrodes were rinsed with the solvent and placed into the system

along with a stirring bar. The system was sealed and deaerated with Argon while stirring for fifteen minutes. While stirring and deaerating continued, the voltammeter was allowed to cycle between limits for five minutes at 120 mv/sec. The background was run at 120 mv/sec. Backgrounds for all three solvents are shown in Figure 6. The sample was added so that the concentration of the sample in solution was $5 \times 10^{-4}M$. Argon continued to deaerate the system by blowing across the top of the solution without disturbing it. The solution was stirred thirty seconds between voltammograms.

Solvents

Gold label dimethylsulfoxide (DMSO) was obtained from Aldrich Chemical Co. This was found to be suitable for electrochemical use if stored in a dessicator. DMSO purified by the method of Byker⁸⁸ was found to have more electroactive impurities than the gold label DMSO. However, it probably contained less water. NMR studies done by E. Abbott revealed the gold label DMSO contained .04% water.⁹² Use of neutral alumina to keep solvents free of proton donors⁹³ was tried but no noticeable difference was observed in the voltammograms.

Acetonitrile (distilled in glass) was obtained from MCB (Omnisolv). Dimethylformamide (DMF) was obtained from Burdick and Jackson and was also distilled in glass. Both of these solvents picked up water in two to three days so experiments with them were done quickly. NMR

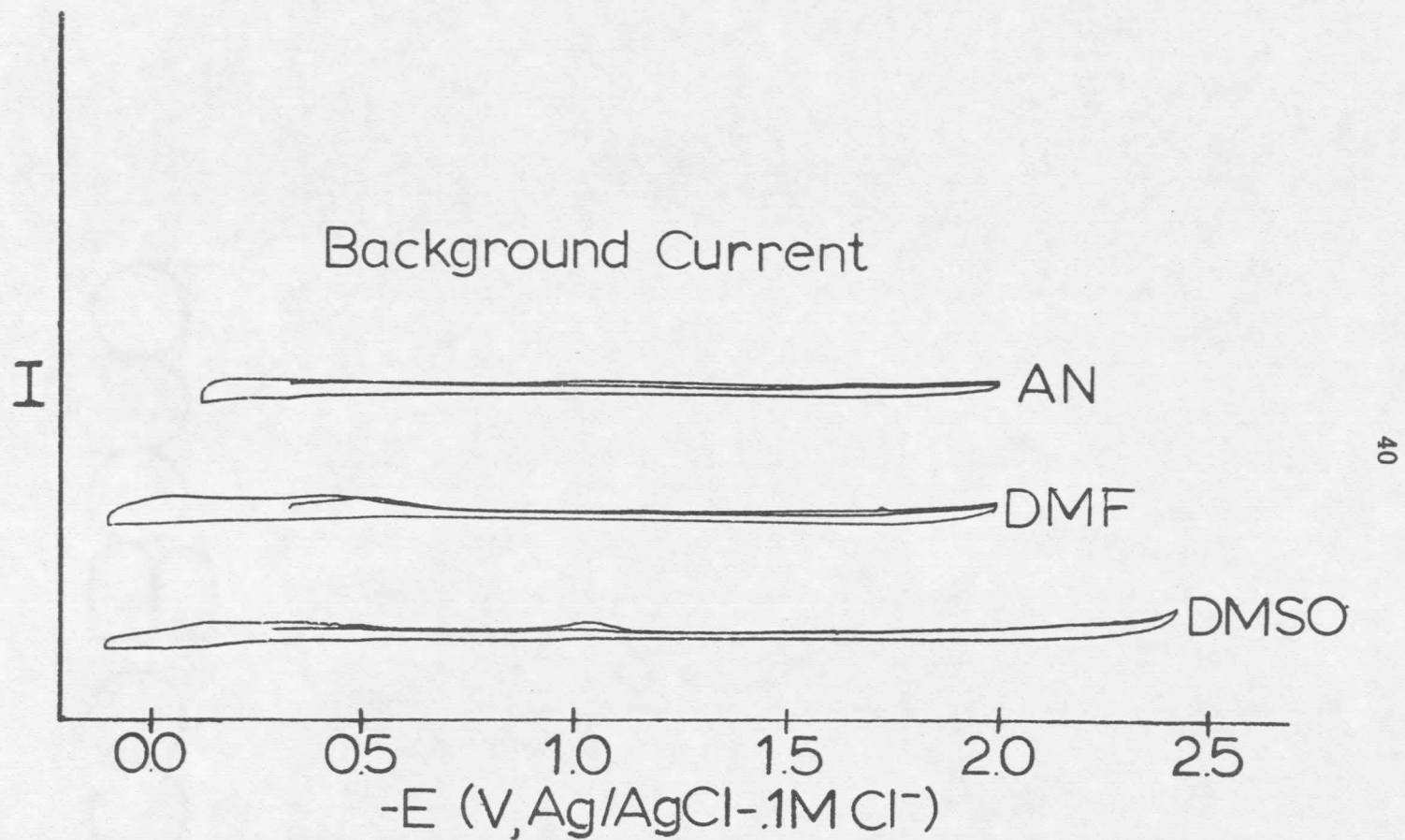


Figure 6. Background current for solvents (DMSO, DMF, AN).

studies by E. Abbott showed the DMF contained .04% water but AN data could not be obtained because the peak due to water protons was obscured by the methyl group protons and could not be separated.⁹²

Electrolyte

The supporting electrolyte used in this study was tetraethylammonium perchlorate (TEAP). It was synthesized by a modification of the method of Sawyer⁸⁴. Tetraethylammonium bromide (Et_4NBr) (31.8 gr) from Sigma Chemical Co. was placed in a 125 ml erlenmeyer flask containing 48 ml of distilled water. After heating slightly, warmed perchloric acid (Allied Chemical, 70% solution, 12.8 ml) was added to the warm Et_4NBr solution with stirring. A white precipitate formed immediately. The solution was cooled for fifteen minutes in an ice bath. The precipitate was suction filtered using a very small amount of ice water for rinsing. The undried precipitate was recrystallized with a small amount (5 ml) of hot water. The solution was filtered and cooled in a ice bath. After suction filtration and air drying, the precipitate was placed in a Aberhalter drying apparatus and vacuum dried.

Polychloronitrobenzenes

Nitrobenzene was obtained from Fisher Scientific Co. Samples of 2,4-dichloro, 3,4-dichloro, 2,4,5-trichloro, and pentachloronitro-

benzene were purchased from Aldrich Chemical Co, Inc. and used without further purification. Samples of 2-chloro, 4-chloro, 2,3,4-trichloro, 2,3,4,5-tetrachloro and 2,5-dichloronitrobenzene were purchased from J. T. Baker Chemical Co. The 2,6-dichloro, 3,5-dichloro, 2,3,5-trichloro, 2,3,6-trichloro, 2,4,6-trichloro, 3,4,5-trichloro and 2,3,4,6-tetrachloro compounds were synthesized by L. Davis, R. Geer and/or the author by procedures given in reference No. 91.

RESULTS AND DISCUSSION

The cyclic voltammograms for each compound, with and without water added, will be discussed in this section. Each solvent is discussed individually for each compound since the mechanisms do change in most cases when the solvent is changed.

Peak Resolution and Reproducibility

Cyclic voltammograms were repeated consecutively for a variety of compounds and a ± 3 mV error was found in the potentials for the sharp peaks. For those waves that are rounded, such as most waves from nitroso compounds or waves that appear on the shoulder of another peak, the error in measurement is ± 1 mm, equivalent to ± 12 mV. Combining this with the instrumental error, the total error becomes ± 15 mV. In most cases, measurements are obtained with greater resolution than the X-Y recorder is capable of producing. When cyclic voltammograms of compounds were repeated with a new solution, and at time intervals ranging from a few days to a few months, there were differences between the voltammograms due to changes in experimental conditions. The chief factor in these changes was the variation in water content of the solvents. This seemed to be dependent on humidity, storage time, exposure to air and lot number of the solvent. Other factors affecting the voltammograms are instrumental noise,

changes in uncompensated resistance, the high impedance of the reference electrode, electrolyte purity, electrode surface changes and contamination from the reference electrode (chloride leakage) or from previous compounds remaining on the electrodes. Most of the effects were immediately noticeable and could be corrected. In all cases, the best data are used to deduce mechanisms. Peak potentials (half-wave potentials) for the reduction and oxidative waves, with and without an added proton source, are listed in Tables 1-6. The general mechanism is reported in Figure 7.

Interpreting Voltammograms

Each voltammogram will be discussed with some detail in order to propose possible mechanisms. It may be helpful for the reader to interpret a voltammogram in much greater detail so the less detailed explanations will be easier to understand. Using Figure 8, which is the cyclic voltammogram of 3-chloronitrobenzene, the vertical axis represents current while the horizontal axis corresponds to potential, linearly varied linearly with time. When there is an electron flow from the working electrode to the electroactive species in solution, the current is considered positive (a reduction current) and when the electrons move to the working electrode, the current is considered negative (a oxidation current). Starting from point a, the initial potential, a positive current flows. This is composed of a

Table 1. Peak potentials (-V) of chlorinated nitrobenzenes in DMSO.

Compound	Rev	ORev	ONitroso	Irr 1	Irr 2	Irr 3	Irr 4
NB	1.126	1.029	.810	2.032	-	-	-
2	1.102	1.019	.830/.653	1.891	2.037	-	-
3	.972	.888	.650	1.879	-	-	-
4	1.046	.954	.758	1.934	-	-	-
23	.987	.905	.822/.661	1.635	1.878	2.029	-
24	1.004	.931	.724	1.733	1.949	2.023	-
25	.877	.798	.572	1.652	1.841	-	-
26	1.109	.979	.769	1.696	1.888	2.020	-
34	.938	.869	.691	1.763	1.913	-	-
35*	.742	.668	.449	1.640	1.794	-	-
234	.862	.781	.599	1.473	1.685	1.849	-
235	.812	.716	.594	1.435	1.697	1.806	-
236	1.005	.911	.828/.619	1.428	1.668	1.853	1.976
245	.813	.756	.593	1.532	1.672	1.822	-
246	1.088	.930	.777	1.545	1.743	1.946	-
345	.813	.763	.535	1.493	1.740	1.819	-
2345	.759	.589	-	1.342	1.480	1.704	1.847
2346	.948	-	.674	1.209	1.517	1.655	1.797
2356	.924	.751	.589	1.178	1.442	1.738	1.885
23456	.899	-	-	1.300	1.457	1.677	1.808
Nitroso	.905	.822	-	1.305	1.283	1.743	1.957

*3,5 DCNB was recrystallized to get rid of impurity peaks, potentials prior to recrystallization were .856, .783, .540, 1.742, 1.850(-V).

Table 2. Peak Potentials (-V) of chlorinated nitrobenzenes in DMF.

Compound	Rev	ORev	ONitroso	Irr 1	Irr 2	Irr 3	Irr 4
NB	1.004	.922	.720	1.949	-	-	-
2	.959	.889	.720	1.741	1.920	-	-
3	.846	.779	.544	1.769	-	-	-
4	.901	.830	.618	1.824	1.875	-	-
23	.872	.796	.550	1.469	1.788	1.928	-
24	.868	.798	.630	1.551	1.832	1.895	-
25	.838	.746	.544	1.614	1.820	1.820	-
26	1.023	.925	.728	1.497	1.747	1.915	-
34	.781	.721	.542	1.625	1.779	-	-
35	.719	.647	.558	1.655	1.789	-	-
234	.801	.731	.545	1.298	1.619	1.785	-
235	.743	.661	.538	1.312	1.676	1.814	-
236	.937	.874	.771	1.258	1.596	1.778	-
245	.748	.695	.522	1.451	1.634	1.800	-
246	.936	.842	.548	1.301	1.557	1.826	-
345	.676	.587	.544	1.342	1.495	1.666	1.791
2345	.692	.619	.539	1.150	1.364	1.553	1.780
2346	.885	.815	.536	1.056	1.435	1.614	1.769
2356	.874	.775	.534	1.012	1.305	1.670	1.798
23456	.808	-	.533	1.142	1.362	1.571	-
Nitroso	.887	.826	-	1.342	1.258	1.709	1.907

Table 3. Peak potentials (-V) of chlorinated nitrobenzenes in AN.

Compound	Rev	ORev	ONitroso	Irr 1	Irr 2	Irr 3
NB	1.053	.980	.791	1.865	-	-
2	1.010	.936	.587	1.741	-	-
3	.919	.838	.633	1.669	-	-
4	.966	.899	.683	1.742	-	-
23	.929	.875	-	1.463	1.665	-
24	.928	.868	.521	1.600	1.737	-
25	.885	.822	.444	1.546	-	-
26	1.054	.951	.586	1.524	1.657	-
34	.861	.791	.560	1.654	1.675	-
35	.809	.742	.518	1.571	-	-
234	.876	.817	-	1.349	1.650	1.675
235	.819	.758	.515	1.361	1.569	-
236	.996	.920	.466	1.387	1.618	-
245	.829	.776	.435	1.488	1.582	1.758
246	.988	.910	.557	1.449	1.628	1.750
345	.764	.709	.539	1.420	1.557	-
2345	.776	.713	-	1.213	1.435	1.573
2346	.944	.875	.476	1.178	1.516	1.638
2356	.935	.865	.756	1.079	1.371	1.572
23456	.895	.727	-	1.261	1.451	1.580

Table 4. Peak potentials (-V) of chlorinated nitrobenzenes in DMSO with a proton source added (either water or ethanol). Value in brackets is generally at twice the concentration of the first value. See figures for specific values.

Cmpd	Rev Waves	ORev	Irr 1	Irr 2	Irr 3
NB	1.110(1.089)	1.024(1.003)	1.909(1.854)	-----	-----
2	1.095(1.077)	1.008(.987)	1.797(1.749)	-----	-----
3	.945(.937)	.864(.864)	1.748(1.697)	-----	-----
4	1.041(1.035)	.939(.967)	1.815(1.765)	-----	-----
23	.989(.966)	.917(.913)	1.635(1.606)	1.790(1.715)	-----
24	.994(.990)	- (.915)	1.682(1.643)	1.791(1.737)	-----
25	.869(.864)	.780(.771)	1.551(1.528)	-----	-----
26	1.131(1.128)	1.040(1.036)	1.815(1.772)	-----	-----
34	.925(.926)	.876(.865)	1.655(1.624)	-----	-----
*35	.776(.775)	.681(.659)	1.536(1.480)	-----	-----
234	.858(.850)	.776(.796)	1.435(1.388)	1.615(1.545)	-----
235	.809(.805)	.720(.696)	1.399(1.388)	1.563(1.507)	-----
236	1.001(.995)	.904(.880)	1.440(1.416)	1.621(1.566)	-----
245	.829(.825)	.755(.737)	1.525(1.502)	1.598 -----	-----
246	1.016(1.017)	.878(.857)	1.506(1.508)	1.651(1.638)	1.757(1.706)
345	.796(.794)	.755(.748)	1.450 -----	1.548(1.516)	-----
2345	.764(.753)	.689 -----	1.306(1.280)	1.539(1.491)	-----
2346	.958(.945)	-----	1.241(1.231)	1.553(1.517)	1.672(1.598)
2356	.924(.924)	-----	1.229(1.229)	1.473(1.473)	1.592(1.565)
23456	.899(.886)	-----	1.284(1.284)	1.531(1.470)	-----

*Potentials (-V) prior to recrystallization were .844(.842), ---(.802), 1.526(1.550).

Table 5. Peak potentials (-V) of chlorinated nitrobenzenes in DMF with water added. Values in brackets are at twice the concentration of the first value.

Cmpd	Rev Waves	ORev	Irr 1	Irr 2	Irr 3
NB	.991(.974)	.912(.907)	1.674(1.591)	-----	-----
2	.953(.938)	.875(.845)	1.546(1.481)	-----	-----
3	.839(.830)	.771(.765)	1.516(1.440)	-----	-----
4	.888(.876)	.819(.812)	1.557(1.489)	-----	-----
23	.864(.857)	.788(.776)	1.443(1.373)	-----	-----
24	.861(.852)	.784(.774)	1.471(1.413)	1.558(1.508)	-----
25	.829(.826)	.732(.731)	1.493(1.423)	-----	-----
26	1.014(1.003)	.924(.918)	1.561(1.492)	-----	-----
34	.773(.765)	.704(.695)	1.500(1.420)	-----	-----
35	.710(.705)	.640(.636)	1.430(1.356)	-----	-----
234	.793(.792)	.720(.700)	1.278(1.271)	-----	-----
235	.740(.732)	.651(.657)	1.312(1.273)	1.477(1.364)	-----
236	.930(.919)	.863(.841)	1.264 -	1.435(1.361)	-----
245	.745(.738)	.681(.668)	1.432(1.347)	- (1.427)	-----
246	.932(.918)	.854(.840)	1.303 -	1.457(1.392)	-----
345	.665(.657)	.605(.584)	1.446(1.375)	-----	-----
2345	.687(.682)	.617(.606)	1.142(1.131)	1.353(1.353)	1.427(1.360)
2346	.876(.877)	-----	1.060(1.058)	1.365(1.304)	1.563(1.511)
2356	.869(.862)	-----	1.023(1.002)	1.304(1.274)	1.453(1.363)
penta	.816(.810)	-----	1.149(1.142)	1.389(1.348)	1.455(1.415)

Table 6. Peak potentials (-V) of chlorinated nitrobenzenes in AN with water added. Values in brackets are at twice the concentration of the first value.

Cmpd	Rev Waves	ORev	Irr 1	Irr 2	Irr 3
NB	1.006(.982)	.911(.779)	1.443(1.302)	-----	-----
2	.978(.961)	.904(.876)	1.370(1.261)	-----	-----
3	.882(.859)	.831(.788)	1.356(1.188)	-----	-----
4	.925(.899)	.856(.787)	1.376(1.258)	-----	-----
23	.897(.886)	.828(.718)	1.206(1.074)	-----	-----
24	.894(.878)	.816(.797)	1.301(1.193)	-----	-----
25	.860(.844)	.798(.744)	1.226(1.083)	-----	-----
26	1.002(.971)	.938(.916)	1.355(1.260)	-----	-----
34	.829(.808)	.761(.747)	1.296(1.174)	-----	-----
35	.779(.762)	.706(.704)	1.249(1.144)	-----	-----
234	.846(.827)	.787(.732)	1.193(1.087)	1.141(1.318)	-----
235	.798(.786)	.736(.719)	1.163(1.048)	-----	-----
236	.955(.926)	.884(.867)	1.295(1.212)	-----	-----
245	.804(.786)	.742(.724)	1.237(1.128)	-----	-----
246	.951(.925)	.881(.857)	1.354(1.282)	-----	-----
345	.738(.719)	.671(.656)	1.229(1.121)	-----	-----
2345	.761(.739)	.691(.691)	1.152(1.038)	1.239 -	-----
2346	.910(.885)	.839(.749)	1.231(1.134)	-----	-----
2356	.898(.872)	.828(.755)	1.149(1.062)	-----	-----
23456	.884(.865)	.704(.704)	1.160(1.049)	1.219 -	1.334 -

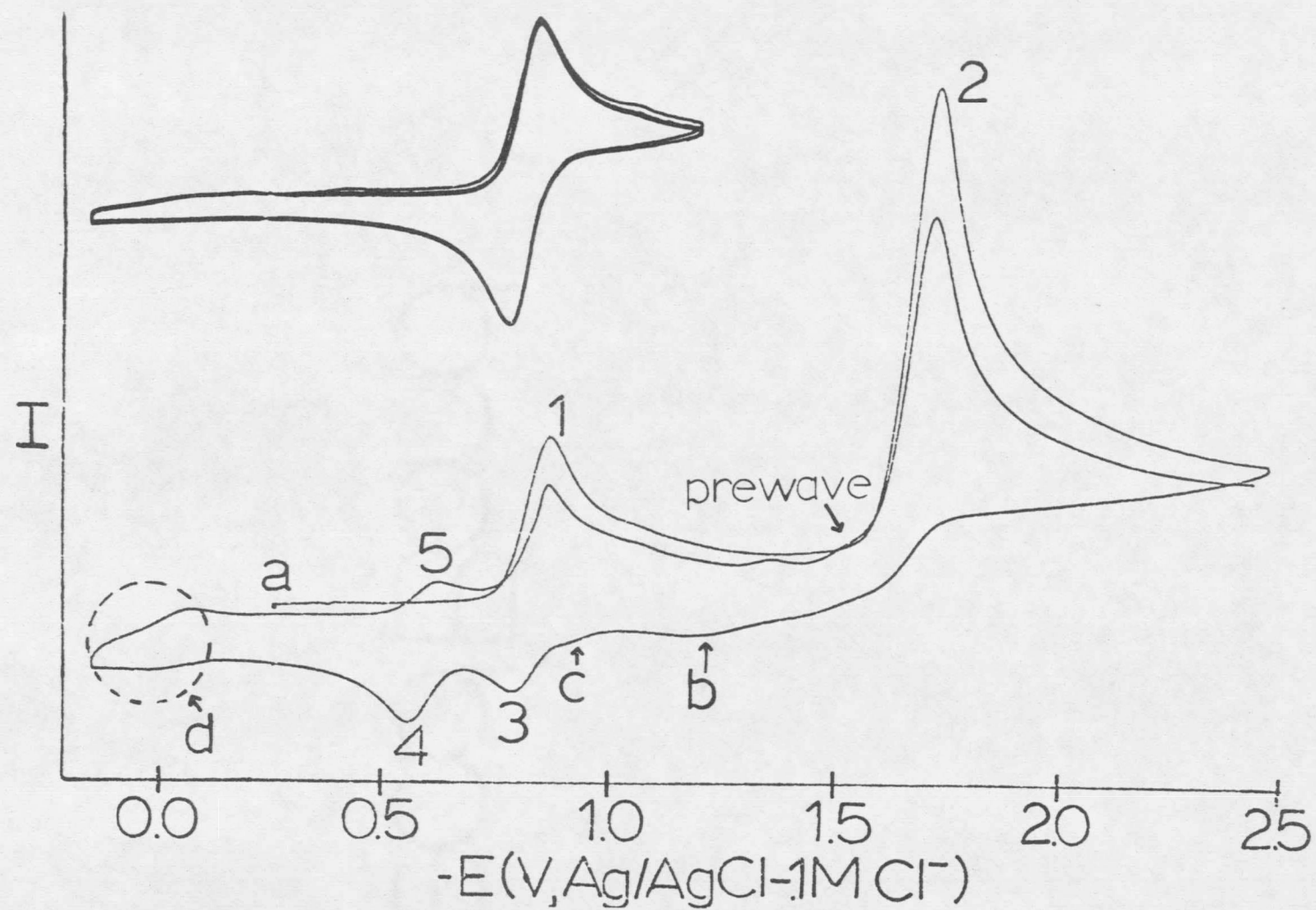
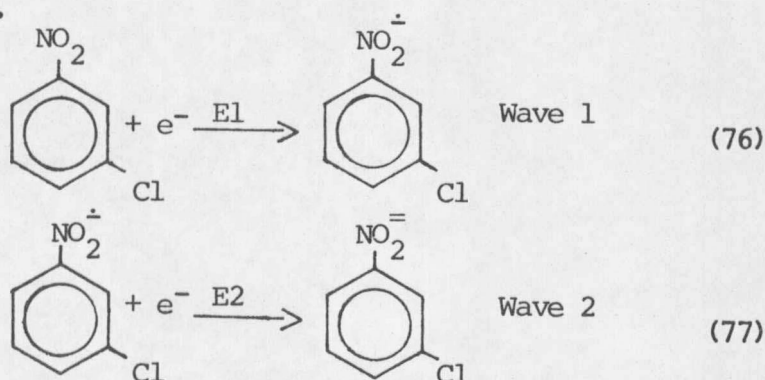
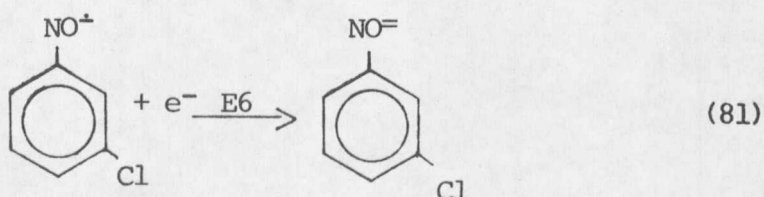
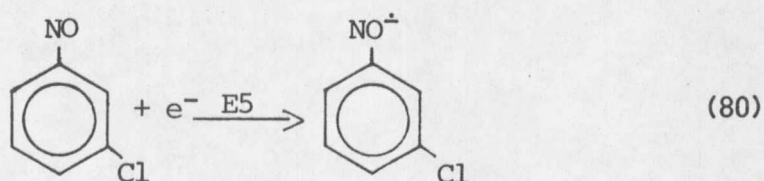
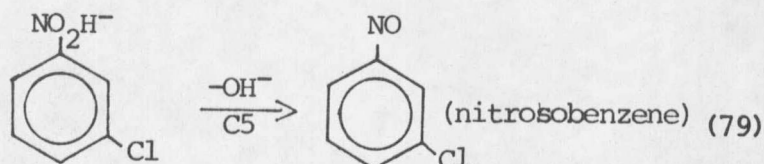
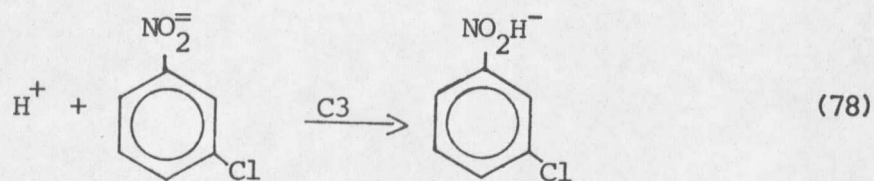


Figure 8. Cyclic voltammograms of 3-CNB.

nonfaradaic charging current and possibly faradaic reduction of impurities until a potential is reached where electrons are transferred to the 3-chloronitrobenzene compound. The current increases with potential until it is limited by the rate of diffusion of 3-CNB to the electrode and the peak of wave 1 is reached. Before the next electron transfer, the current decreases toward a non-faradaic current. At 1.8 V, the second set of electrons are transferred. The processes to this point are represented by Equations 76 and 77.

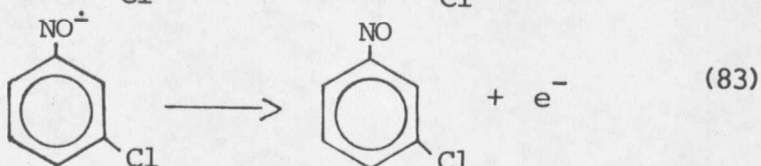
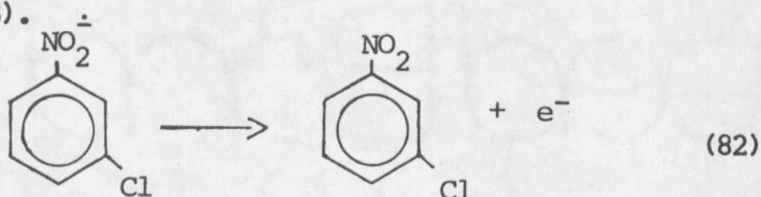


The reversibility of equation (76) is shown by the short sweep in Figure 7. However, wave 2 is much larger than wave 1, so it is apparent that wave 2 represents more than a single electron transfer. The electrochemical process is followed by a chemical process (or actually, two chemical processes), then further reduction. Equations 77-81 represents the chemistry associated with wave 2. The cathodic limit is reached and the direction of the potential sweep is reversed.



At point b, a small bump is observed. This is proposed to represent an oxidation of the protonated dianion which will be described throughout the discussion as the oxidative "bump" by the C3E2 process (see Mechanism, Figure 7). The letter "C" refers to a chemical process and E or E' to an electrochemical process. Point C is a shoulder on wave 3 and is proposed to result from direct oxidation of the protonated dianion by the E2' process. Wave 3 corresponds to the

oxidation of the 3-chloronitrobenzene radical anion and wave 4 represents the oxidation of the 3-chloronitrosobenzene radical anion (Equations 82 and 83).



On the second negative sweep wave 5 appears to be the reduction of 3-chloronitrosobenzene to its radical anion. The reversible wave at point d represents the amount of chloride which is lost from the substrate. It is due to the formation of the mercurous chloride complex which occurs when mercury is oxidized in the presence of chloride ion. In Figure 8, point d is not very large but it is present, so some chloride is lost. If this wave were larger, this would be indicative of a greater amount of chloride loss and a wave for formation of the nitrobenzene dianion would have appeared after wave 2. By correlating the potential of the dianion of nitrobenzene from the voltammogram of nitrobenzene with the wave which would have appeared, a positive identification can be proposed. In the case of more highly chlorinated compounds, the first irreversible wave of the actual compounds can be correlated with waves of the more highly

chlorinated compounds and the reduction pathway can be formulated.

In presenting the discussion, the main interest lies in the determination of processes occurring at the "irreversible" waves. However, these waves will be shown to be not truly irreversible. They are reversible waves followed by a reversible chemical step (Equation 79 for example) which is a $E_R C_R$ process (R for reversible) but the chemical equilibrium is not favorable for the reversibility of the chemical reaction so it does not occur rapidly. This causes the waves to appear as irreversible waves and they will be referred to as "irreversible" waves in order to distinguish them from the "reversible" waves which are quite obviously reversible (waves 1 and 3, waves 4 and 5). Waves 1 and 3 will appear in all voltammograms and will often be referred to as the "reversible couple." Rapid chloride loss does not occur with the electron transfer to form wave 1. It should be noted by the reader that wave 1 is the formation of the radical anion and there will be no discussion of it in the interpretation of the voltammograms.

It will be necessary to refer to the general mechanism on occasion. To avoid redundancy, the names of compound will be abbreviated with the first use of the name. The solvents will be abbreviated as was done previously.

Due to difficulty in determining potentials of small waves,

changes in conditions between a series of voltammograms, and shifting of potentials due to other close waves or competition between processes, the exact mechanistic pathway is sometimes difficult to determine. Allowances must be made when the potential of a wave and the potential of the proposed corresponding authentic wave do not match exactly. When a proton source is added, changes up to 60 mV are noted due to a change in the liquid junction potential. It is necessary to compare the potentials of waves with the authentic potentials of less chlorinated compounds. The change in potential between the wave and the authentic wave will appear after the compound with a negative sign if the authentic wave is more negative than the wave in the voltammogram being examined or a positive sign if it is more positive than the wave. For example, a wave has a potential of -1.78V and its formation is due to the formation of the 2-CNB dianion (+40mV) or 3-CNB (+10mV). This tells us the 2-CNB dianion forms 40mV more positive than the wave and the 3-CNB dianion wave appears 10mV more positive than the wave. In this case, the 3-CNB dianion is probably responsible for the formation of the wave in the voltammogram of a more chlorinated compound.

When a proton source is added, some waves will shift anodically. When this occurs, some waves will decrease while other waves will be obscured by waves shifting on top of one another. The numbering

system will remain the same as it was in the voltammogram without a proton source. Since two waves may now appear as one wave, the number of the wave will be the lowest number. Therefore, some voltammograms will not have sequential numbering.

The data are divided into three sets in the discussion of each section. The two sections are 1) without addition of a proton source and 2) with addition of a proton source. The three divisions are Series 1: no ortho chlorines in the compound; Series 2: one ortho chlorine in the compound and Series 3: two ortho chlorines in the compound. The voltammograms in each group will show particular characteristics, and later, the characteristics will be carried into sigma rho plots.

Cyclic Voltammograms without Proton Addition

Series 1: No Ortho Chlorines

Nitrobenzene. The cyclic voltammogram of nitrobenzene (NB) in DMSO is shown in Figure 9a. Wave 1 has already been discussed (radical anion formation). The second wave (2), appears to be an "irreversible" one electron transfer to form the NB dianion with further reduction to the nitrosobenzene dianion. Evidence for the nitroso dianion is due to the ratio of peak heights between waves 1 and 2 (1:3), proving that there is more than one electron involved. According to previously observed mechanisms,^{12,17,20} the dianion

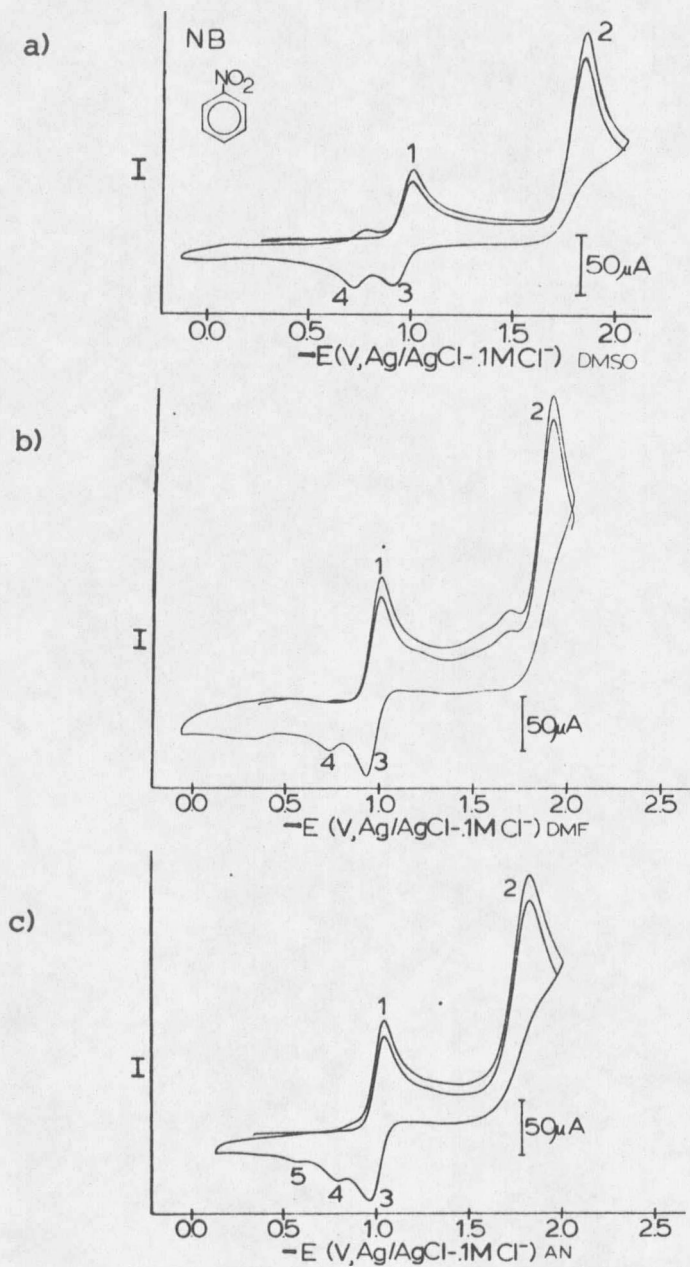


Figure 9. Cyclic voltammograms of nitrobenzene in a) DMSO; b) DMF; c) AN.

abstracts a proton and then loses hydroxide ion to form nitrosobenzene, which is in turn reduced. The oxidative sweep shows two waves. Wave 3 appears to be the oxidation of the NB radical anion while wave 4 corresponds to the nitrosobenzene radical anion oxidation. When the cathodic limit is moved more negative, a small wave appears just negative of wave 3. This is probably the oxidation of the protonated dianion to the protonated radical by the E2' process.

In DMF, the cyclic voltammogram appears similar but not identical (Figure 9b). The anodic shoulder on wave 2 was not seen in DMSO. This may be reduction of the protonated radical to the protonated dianion but there is no prewave on wave 1 corresponding to preprotonation of the parent compound. It may also result from some nitrosobenzene dianion which forms rapidly as the nitrobenzene dianion starts to form. Since the second sweep does not yield a reduction wave for nitrosobenzene, the assumption is made that the nitrosobenzene formed is used in another reaction. When the nitrosobenzene dianion forms, it can quickly be protonated and yield the phenylhydroxylamine anion. The phenylhydroxylamine anion and the nitrosobenzene which continues to form can react to give azoxybenzene and hydroxide ion. There is a small new wave just cathodic of wave 1 on the second sweep which may be the reduction of azoxybenzene.

In AN, Figure 9c, the cyclic voltammogram of NB appears to be identical to those observed in DMSO except for an additional small oxidative wave anodic of wave 4. The wave doesn't correlate with any known processes for nitro or nitrosobenzene and therefore, no process assignment can be made.

3-chloronitrobenzene. The cyclic voltammogram of 3-chloronitrobenzene in DMSO is shown in Figure 10a. Wave 2 is a multiple electron transfer forming what appears to be the 3-CNB dianion. There appears to be very little chloride loss since there is no wave for the formation of the nitrobenzene but there is a small chloride wave which does indicate some chloride loss. This probably occurs very slowly so no nitrobenzene dianion wave is observed. The oxidative sweep yields the oxidative "hump" (C3E2 process) described previously. There is a cathodic shoulder on wave 3 which may indicate direct oxidation by the E2' process while wave 3 itself appears to be the oxidation of the 3-CNB radical anion. Wave 4 is probably the oxidation of the 3-chloronitrosobenzene radical anion with its corresponding reduction wave appearing on the second sweep. On the second sweep, a small prewave appears prior to wave 2 which is probably preprotonation of the radical anion. There is also a small wave anodic of this prewave which may be the azoxybenzene reduction.

In DMF, the general mechanism is the same as above except for a

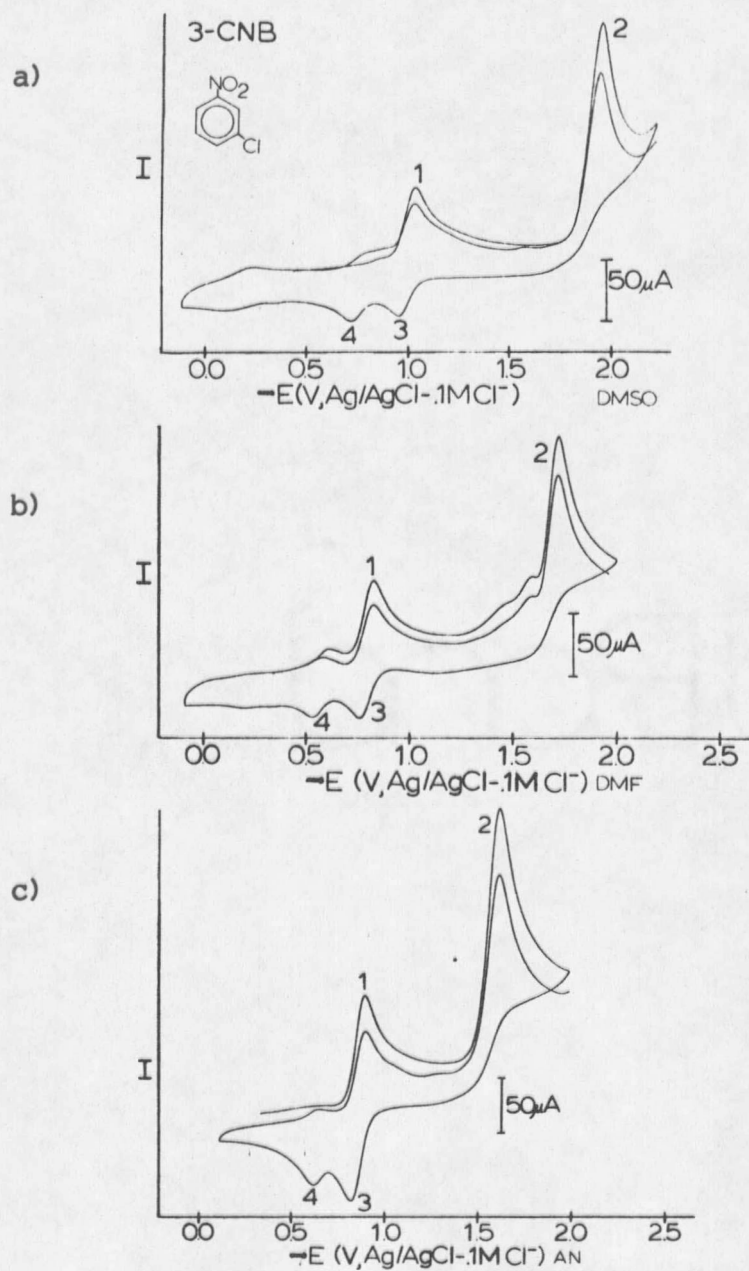


Figure 10. Cyclic voltammograms of 3-chloronitrobenzene in a) DMSO; b) DMF; c) AN.

set of prewaves prior to wave 2 (Figure 10b). One of these waves may be a preprotonation of the radical anion and the other could be a result of an adsorbed product. The nitrobenzene radical anion is known to strongly adsorb on a platinum electrode in sulfuric acid.⁹⁴ Bard and Faulkner described behavior of adsorbed species at the electrode which may appear as prewaves, postwaves, sharp irreproducible waves, or rounded or sharp peaks which are a distance from the actual diffusion peak.⁹⁵ The position and shape of the prewave depends on the concentration of species, the free energy of adsorption of the species and the strength of adsorption. When the product is strongly adsorbed, a prepeak results. When a reactant is strongly adsorbed, a post-peak results. Weakly adsorbed products and reactants usually yield normal voltammograms. However, as the free energy of adsorption, ΔG° , increases weakly and strongly adsorbed reactants are more difficult to reduce so that the reduction occurs at more cathodic potentials.⁹⁶ For weakly and strongly adsorbed products, an increase in ΔG° results in a decrease in the energy required for reduction to the adsorbed state and the wave moves anodically. In this case, the prewaves on peak 2 may be the result of a strongly adsorbed product since ΔE_p from the prewave to wave 1 is 227 mV, corresponding to 2×10^4 J/mole. The prewave on wave 1, that is round and more distant, may be the result of a strongly

absorbed product and a larger ΔG° of that species.

There is no apparent loss of chloride ion and, consequently, no wave for the formation of the nitrobenzene dianion. In this case, the nitro oxidation wave is about the same size as the wave for the oxidation of the radical anion.

In AN, the voltammogram appears qualitatively the same as in DMSO and is shown in Figure 10c. The amount of nitroso formation is much less than in DMF and DMSO. The size of the nitroso wave may represent the effect of the solvent on the ease of hydroxide loss from the protonated dianion if it assumed that the amount of protonated dianion and the amount of hydroxide loss are equal. It appears that more hydroxide is lost in DMSO than the other solvents.

4-chloronitrobenzene. The cyclic voltammogram of 4-chloronitrobenzene in DMSO, figure 11a, has only one irreversible wave. The mechanism is the same as was described for 3-CNB in DMSO. There is a slightly larger chloride wave and a wave is present cathodic of wave 2 which is probably the NB dianion formation. The oxidative "hump" and oxidation by the E2' process are both present.

In DMF, Figure 11b, there are two irreversible processes. Wave 2 corresponds to the formation of the 4-CNB dianion. Wave 3, which is quite small, represents the formation of the dianion of NB. On the oxidative sweep, wave 4 is part of the reversible couple and wave 5

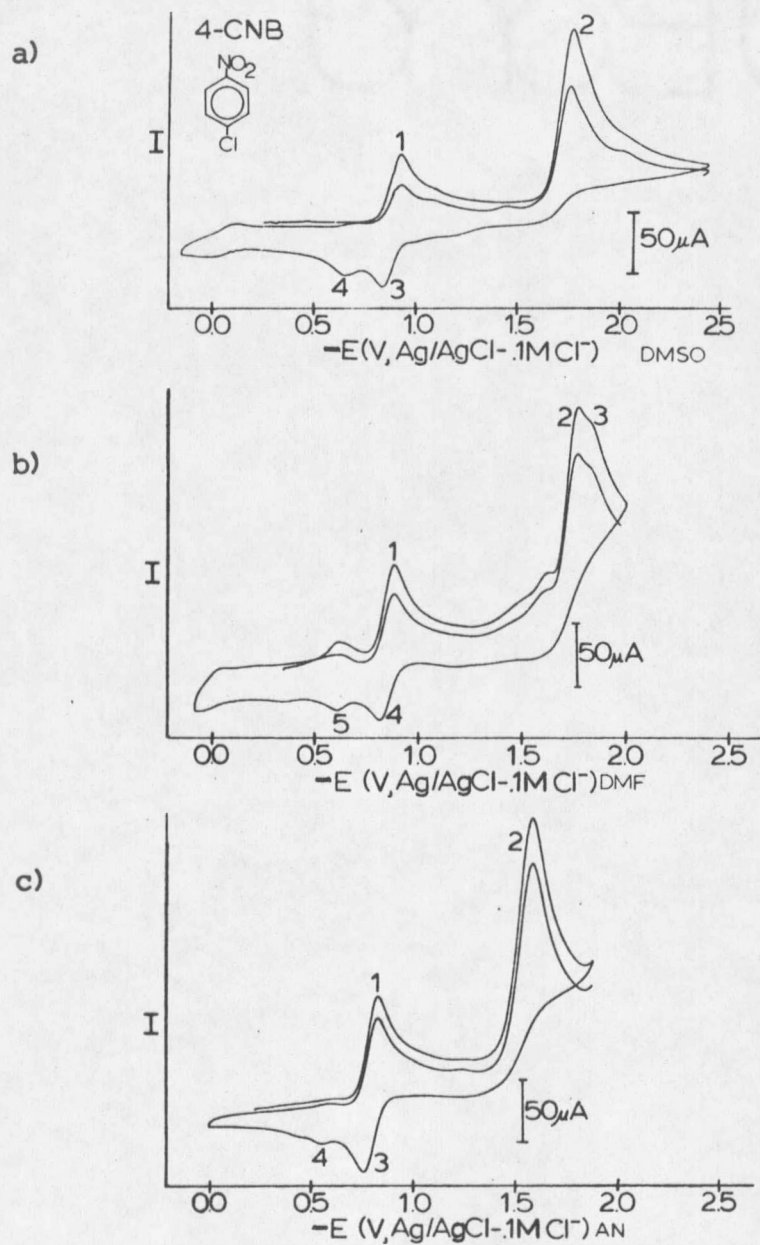


Figure 11. Cyclic voltammograms of 4-chloronitrobenzene in a) DMSO; b) DMF; c) AN.

corresponds to the oxidation of the 4-chloronitrosobenzene radical anion. The oxidative wave for the nitrosobenzene radical anion would fall between waves 4 and 5. Note that the minimum between two waves is not particularly sharp, so a very small nitrosobenzene radical anion oxidation wave could be present. The set of prewaves on waves 1 and 2 are again present. These appear to be characteristic of DMF.

In AN, the cyclic voltammogram (Figure 11c) is very similar to the one shown for DMSO (Figure 11a). However, nitroso formation (based on relative size of waves) is even less. No further discussion of this mechanism is necessary.

The series 1 compounds without ortho chlorines show a characteristic loss of para chlorines before meta chlorines. The voltammograms in DMF have a tendency for prewaves. In AN there is a marked decrease in nitroso formation and fewer irreversible waves are present.

3,4-dichloronitrobenzene. The cyclic voltammogram of 3,4-dichloronitrobenzene in DMSO is shown in Figure 12a. There are two irreversible processes. Wave 2 corresponds to 3,4-DCNB dianion formation with subsequent loss of chloride, yielding the less chlorinated radical anion. Wave 3 appears to be formation of the less chlorinated dianion. This is either the 3-CNB dianion (+22mV) or the 4-CNB dianion (-21mV). Since the wave is between the waves for the two possible compounds, competition between the two processes (loss of

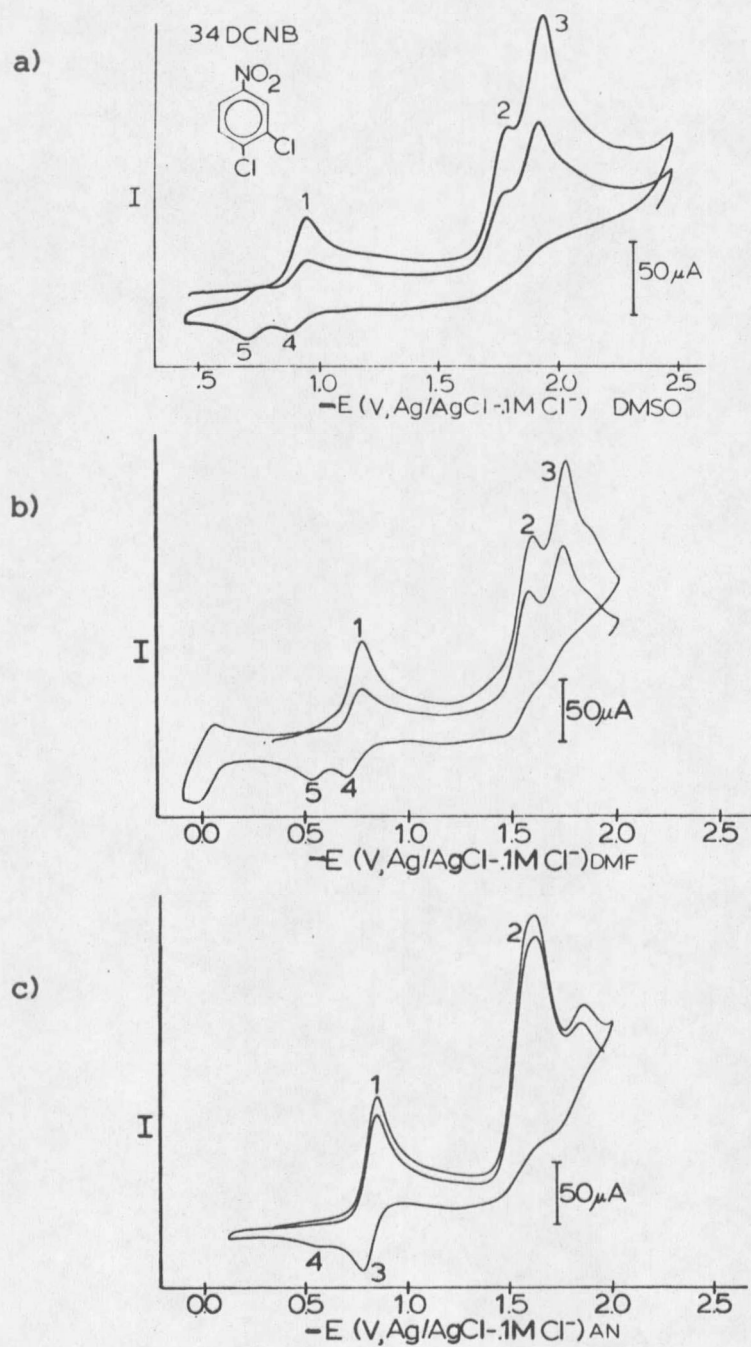


Figure 12. Cyclic voltammograms of 3,4-dichloronitrobenzene in a) DMSO; b) DMF; c) AN.

para vs meta chlorines due to adjacent chloride interactions) may be occurring but CNDO/2 calculations by Beland⁹⁰ predict the probability of loss of the para chlorine to be 88%. There is one nitroso wave on the oxidative sweep which appears to be 3-chloronitrosobenzene.

In DMF, the voltammogram of 3,4-DCNB (Figure 12b) is very similar to the one described above. The potential of wave 3 correlates best with the potential for the formation of the 3-CNB dianion though some competition may be occurring. There is a cathodic shoulder on wave 3 which may be the formation of the nitrobenzene dianion. Both waves 1 and 2 show a prewave which may represent preprotonation of the nitro group and the radical anion, respectively. Notice the difference between the front shoulder on wave 1 that is ascribed to preprotonation and a front wave (Figure 10b) that is probably surface adsorption. Wave 5 corresponds to the oxidation of the 3-chloronitrosobenzene radical anion.

In AN, the voltammogram of 3,4-DCNB is quite different (Figure 12c). There are two irreversible waves but the first of these is larger in proportion to those shown in Figure 11a and Figure 12b as well as appearing rounded on top. This indicates more than one process occurring near the same potential. The front part of the wave appears to be the formation of the 3,4-DCNB dianion and the back of the wave agrees with the potential of the 3-CNB dianion. The wave

cathodic of wave 2 may correspond to the formation of the NB dianion (-40mV) but this wave may also be from unknown sources since a wave similar to it is seen in other voltammograms that can't have NB formation. It is also more negative than the NB dianion. There is a small wave(s) which may be the oxidation of the 3-chloronitrosobenzene radical anion.

3,5-dichloronitrobenzene. The cyclic voltammogram of 3,5-dichloronitrobenzene in DMSO is shown in Figure 13a. There are two irreversible processes. The first, wave 2, corresponds to the formation of the 3,5-DCNB dianion and the second wave (3) is probably the 3-CNB dianion. The shoulder on wave 4, the radical anion oxidation, appears to be the E2' process. Wave 5 corresponds to the 3-chloronitrosobenzene radical anion oxidation. There is a small wave just anodic of wave 2 on the second sweep which may be azoxybenzene.

In DMF, the voltammogram of 3,5-DCNB appears more complex (Figure 13b). There are three irreversible waves and one or two anodic shoulders on the first irreversible waves. The two shoulders probably represent surface adsorption and/or preprotonation of the radical anion. Waves 2,3, and 4 correspond to the formation of dianions for 3,5-DCNB, 3-CNB and possibly NB, respectively. Nitrobenzene may not be present since the chloride wave indicates a relatively small amount of chloride ion is lost. On the anodic sweep there is a cathodic

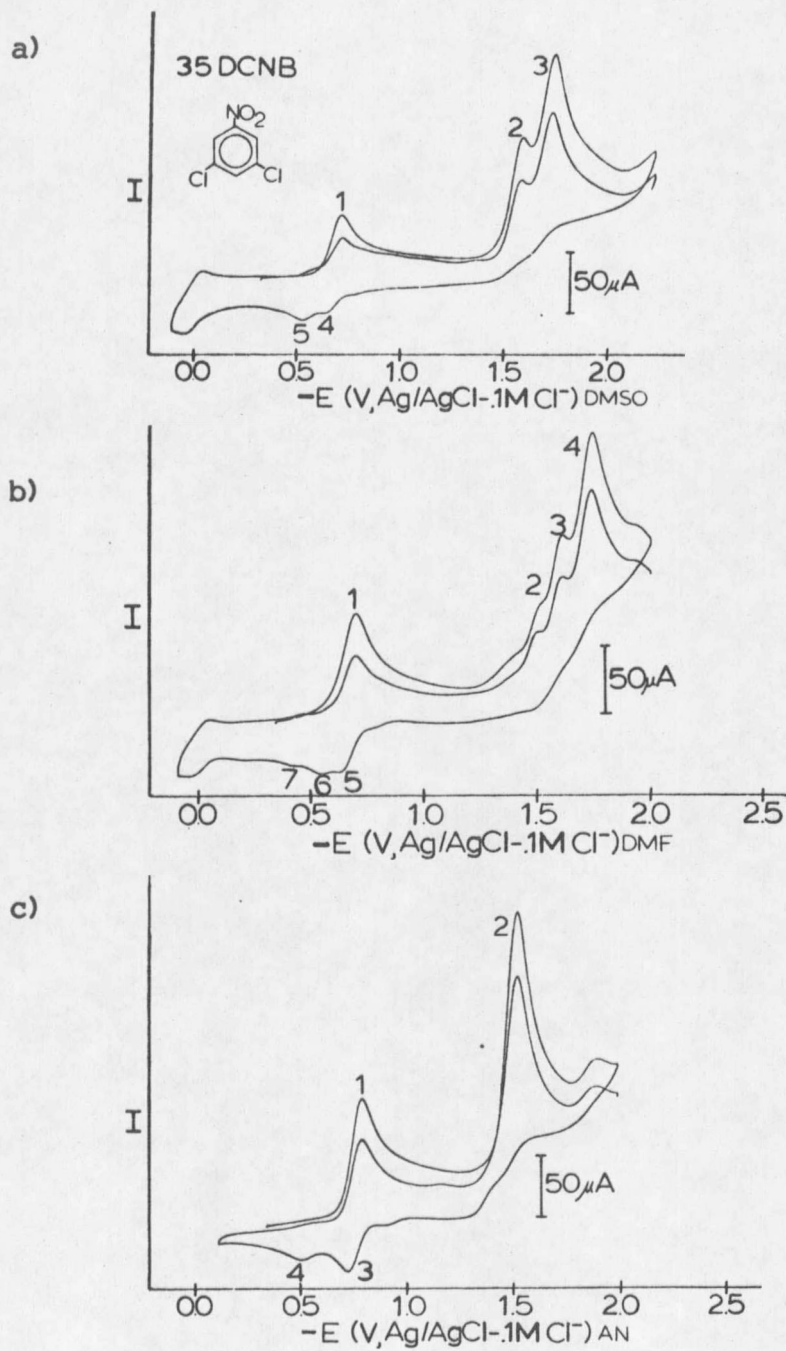


Figure 13. Cyclic voltammogram of 3,5-dichloronitrobenzene in a) DMSO; b) DMF; c) AN.

shoulder on wave 5, corresponding to the oxidation of the 3-CNB radical anion. Waves 6 and 7 correspond to the oxidation of the radical anions of 3-chloronitrosobenzene and 3,5-dichloronitrosobenzene, respectively. Nitroso formation appears relatively weak indicating hydroxide loss from the protonated dianion in DMF is slow.

In AN, Figure 13c, there is one irreversible wave. Wave 2 appears to be the formation of the 3,5-DCNB dianion; but, the 3-CNB dianion wave may have shifted and both waves may be near the same potential. Note how the height of wave 2 is very large compared to wave 1. The wave separation in AN is always less than that observed in DMF or DMSO. This will be discussed in the conclusion. Waves 3 and 4 correspond to the oxidations of the anion radicals of 3,5-DCNB and 3,5-dichloronitrosobenzene, respectively. There is a small amount of reduction of the nitroso species on the second sweep but this increases with sweep rate indicating the nitroso product is consumed in a slow chemical reaction. There is another wave that occurs on the second sweep just prior to the irreversible wave that may be azoxybenzene formed from the reaction of the nitroso species and phenylhydroxylamine or dimerization of the nitroso species.

3,4,5-trichloronitrobenzene. The cyclic voltammogram of 3,4,5-trichloronitrobenzene in DMSO, shown in Figure 14a, has three irreversible processes. After the dianion formation at wave 2, wave 3

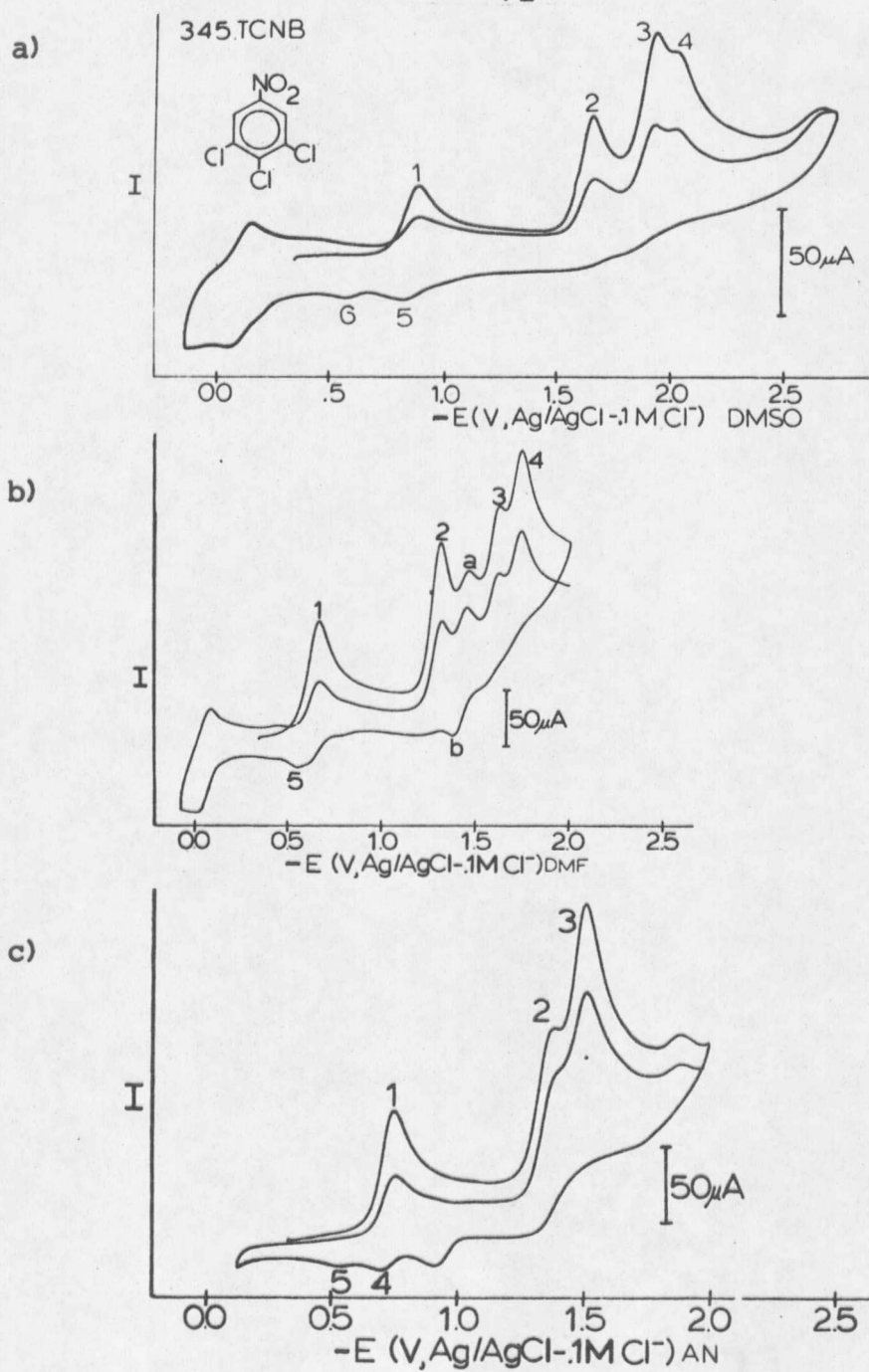


Figure 14. Cyclic voltammograms of 3,4,5-trichloronitrobenzene in a) DMSO; b) DMF; c) AN.

corresponds to loss of the para chlorine yielding the 3,5-DCNB dianion. Loss of the one meta chlorine with further reduction yields wave 4, the 3-CNB dianion. There are two nitroso waves in the voltammograms. Wave 5 corresponds to the oxidation of the 3,5-dichloronitrosobenzene radical anion. Wave 5 has an anodic shoulder that is probably the 3-chloronitrosobenzene radical anion oxidation. Wave 3 may also represent competition between loss of the meta and para chlorines since the 3,4-DCNB dianion is very close ($\sim 20\text{mV}$) to the potential of the wave but the formation of the 3,5-DCNB dianion probably dominates.

In DMF, Figure 14b, the voltammogram of 3,4,5-TCNB is very strange. The following mechanistic characteristics are present: reduction of 3,4,5-TCNB to its dianion (wave 2), followed by loss of the para chlorine and further reduction to give the 3,5-DCNB dianion (wave 3), then loss of a meta chlorine and reduction yielding the 3-CNB dianion (wave 4). The oxidative sweep yields a small prewave on the negative shoulder of wave 5 that is probably the E2' process (oxidation of the protonated dianion to the protonated radical anion). There is a nitroso wave on the anodic shoulder of wave 5 (wave 6) and a nitroso wave more anodic. This corresponds to oxidations of the 3-chloronitrosobenzene radical anion and the 3,5-dichloronitrosobenzene radical anion, respectively. The waves labeled "a" and "b" may be the

reduction and oxidation of the 3,4,5-trichloronitrosobenzene dianion which is observed in voltammograms of the nitroso compound⁸⁸ but has not been seen previously in this study. These waves may also be due to surface adsorption and/or to the oxidation of wave 3. They do seem to be characteristic of compounds with two meta chlorines in DMF though they didn't appear in 3,5-DCNB itself.

In AN, the voltammogram of 3,4,5-trichloronitrobenzene yields two irreversible waves (Figure 14c). Wave 2 appears to be the formation of the 2,4,5-TCNB dianion and wave 3 corresponds to the formation of the 3,5-DCNB dianion. If there is formation of the 3-CNB dianion, the wave has shifted under wave 3. The wave cathodic of wave 4 may be the protonated dianion oxidation (E_2'), while wave 5 corresponds to the oxidation of the 3,5-dichloronitrosobenzene radical anion. Note that wave 5 is very small indicating hydroxide loss from the protonated dianion is slow.

Series 2: One Ortho Chlorine

2-chloronitrobenzene. The cyclic voltammogram for 2-chloronitrobenzene in DMSO is shown in Figure 15a. There are two irreversible processes. Wave 2 appears to be the one-electron addition to yield the 2-CNB dianion. At this point, either chlorine can be lost, or the 2-CNB dianion can be reduced to its nitroso compound. Wave 3 corresponds to the formation of the NB dianion indicating chloride is

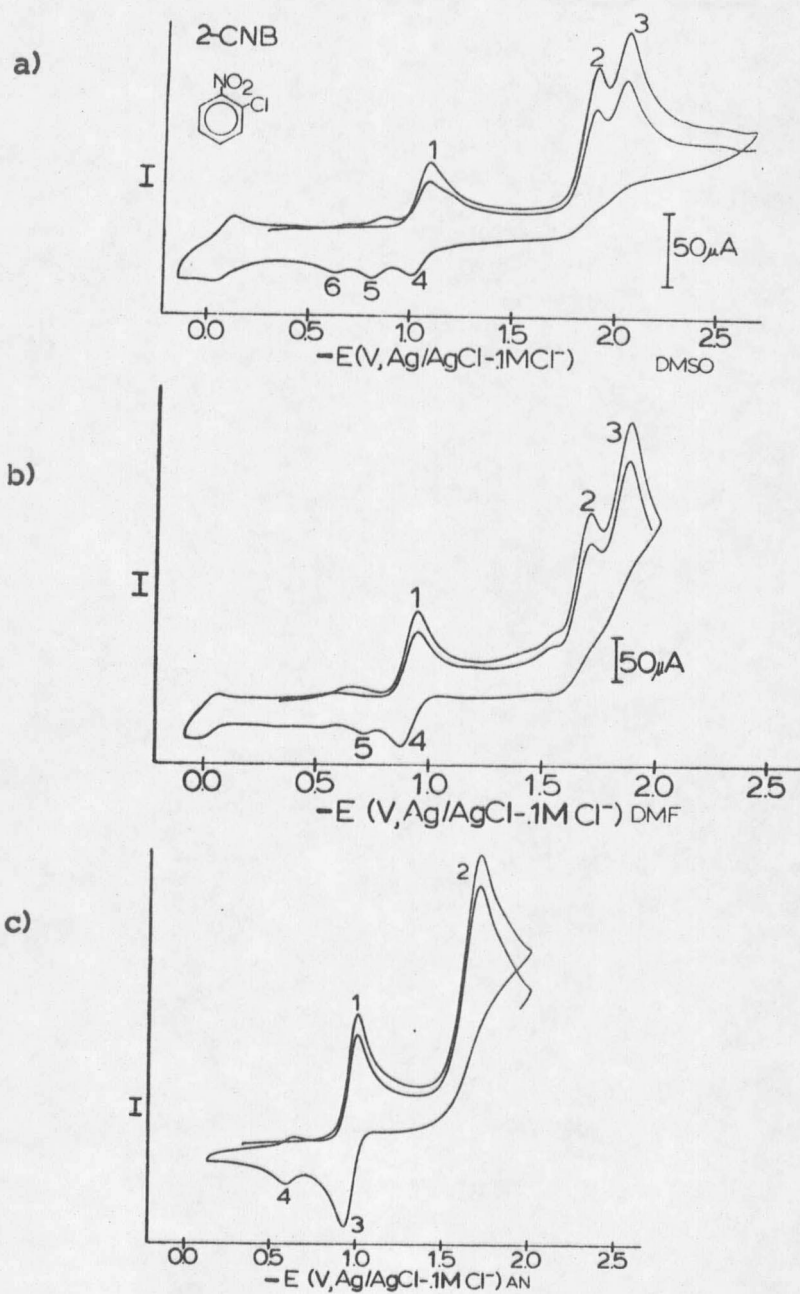


Figure 15. Cyclic voltammograms of 2-chloronitrobenzene in a) DMSO; b) DMF; c) AN.

lost. The large chloride wave confirms this. The oxidative sweep has two waves besides wave 4, the oxidative wave of the reversible couple. Waves 5 and 6 correspond to the oxidations of the nitrosobenzene radical anion and the 2-chloronitrosobenzene radical anion, respectively. The reduction waves for the nitroso compounds are present on the second sweep.

In DMF, the voltammogram (Figure 15b) appears very similar to the corresponding voltammogram in DMSO. The prewaves on waves 1 and 2 are present. When the cathodic limit was held on the second prewave of wave 2, the 2-chloronitrosobenzene radical anion oxidation wave appears. It appears that the prewaves are preprotonation waves and surface adsorption waves, that reduce at more positive potentials than the unprotonated dianion and dissolved species. The nitroso compound can be formed from the protonated dianion.

In AN, the cyclic voltammogram has one irreversible wave (Figure 15c). Noting that the ratio of peak heights of wave 1 to wave 2 is 1:2, it appears that the processes occurring at the potential of wave 2 are the one-electron transfer to the dianion, protonation with loss of hydroxide ion and formation of the nitroso anion and dianion for a total electron transfer between 1 and 3 electrons. Only part of the material is going to the nitroso dianion which indicates hydroxide loss may be slow but chloride loss is even slower. The 2-CNB compound

does not lose chloride very readily in AN.

2,3-dichloronitrobenzene. The cyclic voltammogram of 2,3-dichloronitrobenzene in DMSO is shown in Figure 16a. There are three irreversible waves, the first representing the formation of the 2,3-DCNB dianion. Wave 3 corresponds to the formation of the 3-CNB dianion and wave 4 to nitrobenzene dianion formation. This is interesting since in the 3-CNB voltammogram in DMSO, the nitrobenzene dianion did not form, indicating there was no loss of the meta chlorine. Since the nitrobenzene dianion wave is present, the meta chlorine is lost indicating that there is a greater probability for loss of the meta chlorine when it is adjacent to another chlorine. There is a small wave on the anodic shoulder of wave 5. This corresponds to the oxidation of the nitrosobenzene radical anion while wave 6 corresponds to the 3-chloronitrosobenzene radical anion oxidation. The small "peak" on the cathodic shoulder of wave 2 may be the formation of the nitrobenzene radical anion or of the 2-CNB radical anion. Very little nitrobenzene is formed so it would be surprising to see a wave for the reduction of its radical anion, but the existence of the 2-CNB radical anion is also surprising. Reversal of the sweep direction after wave 2 did not show the "peak" that indicates that the meta chlorine was not yet lost. However, there may be enough competition between loss of the ortho and meta

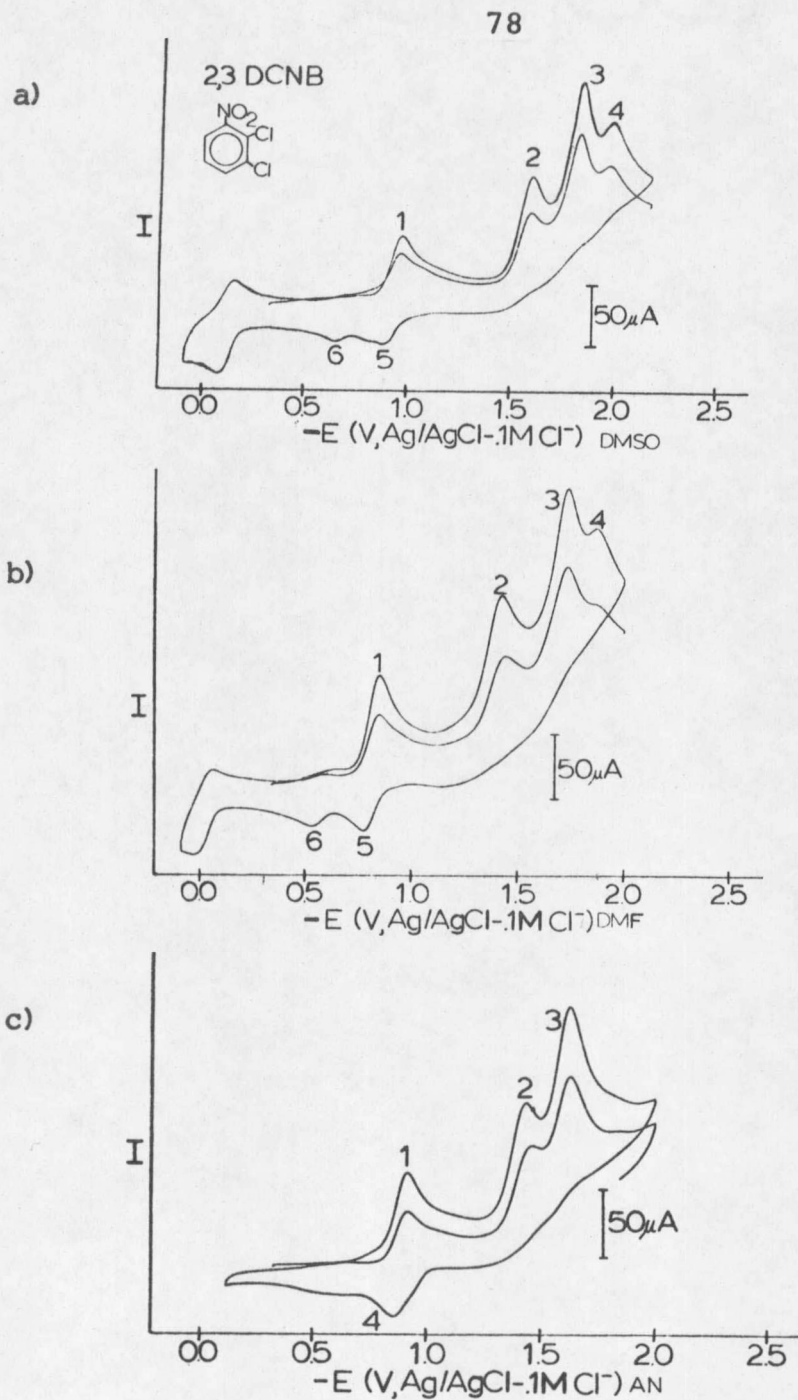


Figure 16. Cyclic voltammograms of 2,3 dichloronitrobenzene in a) DMSO; b) DMF; c) AN.

chlorines to observe the 2-CNB radical anion.

In AN, there are two irreversible waves (Figure 16c). Wave 2 appears to be the formation of the 2,3-DCNB dianion and wave 3 corresponds to the 3-CNB dianion. There is no formation of the nitrobenzene dianion. This may be due to an increased effective water concentration (note waves 2 and 3 are closer together than in DMSO or DMF), which has shifted the nitrobenzene dianion under wave 3. There is very little nitroso formation indicating the loss of hydroxide ion is slow. There is a cathodic shoulder on wave 4 that may be the E2' process or the oxidation hump shifted anodically.

2,4-dichloronitrobenzene. The cyclic voltammogram of 2,4-dichloronitrobenzene in DMSO (Figure 17a) yields three irreversible processes. Wave 2 represents the dianion of 2,4-DCNB. Waves 3 and 4 correspond to the dianions of the less chlorinated compounds, 4-CNB and NB, respectively. Wave 6 corresponds to the oxidation of the 4-chloronitrosobenzene radical anion. It appears that the ortho chlorine is lost prior to the para chlorine since the 4-CNB dianion (+15mV) is apparently responsible for wave 3 and the 2-CNB dianion is +57mV from wave 3. The size of the chloride wave indicated both chlorides are lost.

In DMF, the same three irreversible waves are present but in different proportions to one another (Figure 17b). The wave for nitro-

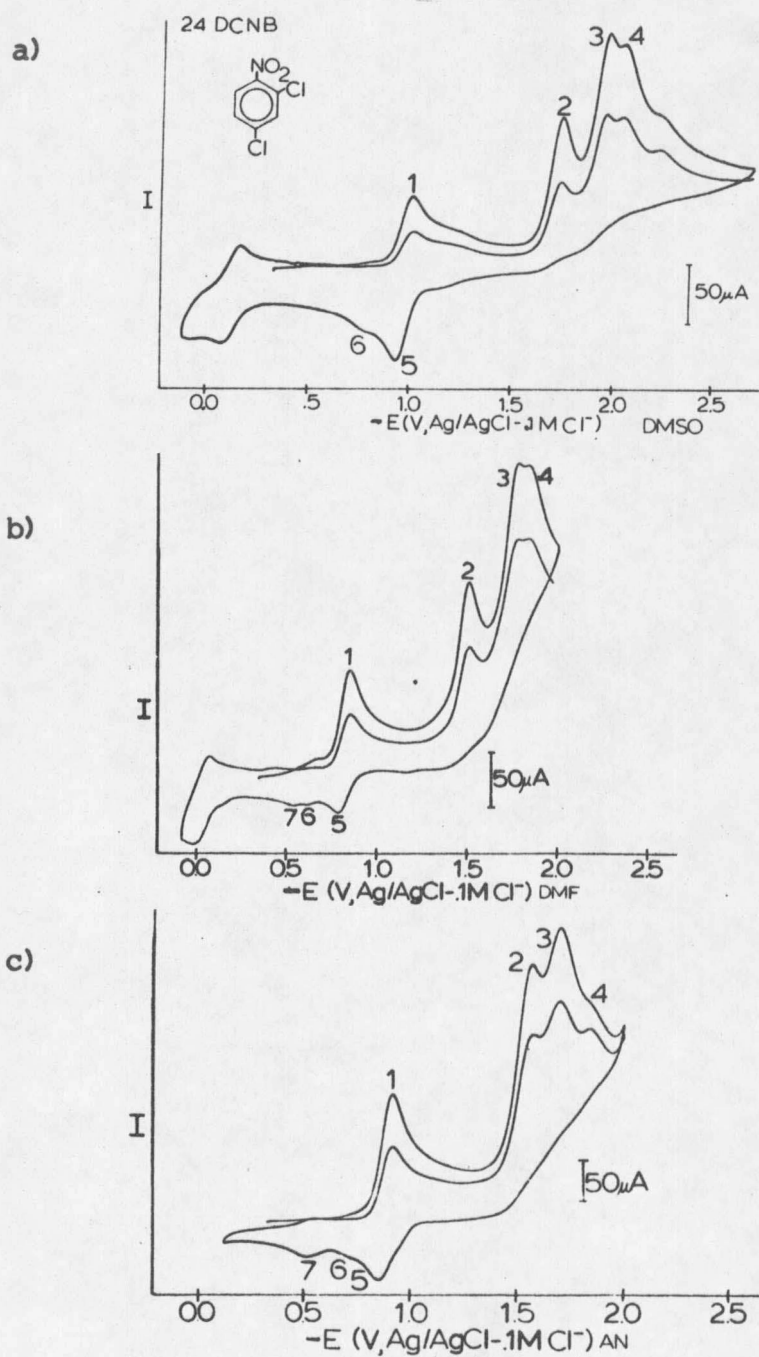


Figure 17. Cyclic voltammograms of 2,4-dichloronitrobenzene in a) DMSO; b) DMF; c) AN.

benzene dianion formation has increased. This may mean that more of the 4-CNB dianion was reduced to the nitrobenzene dianion, indicating loss of the para chlorine may be slightly easier in DMF. The oxidative sweep yields a small wave cathodic of wave 5 that is probably the oxidative "hump". Waves 6 and 7 correspond to the oxidations of radical anions of 4-chloronitrosobenzene and 2,4-dichloronitrosobenzene, respectively.

In AN, Figure 17c, there are two irreversible processes with the third of these processes being more pronounced on the second sweep. Wave 2 corresponds to the formation of the dianion of 2,4-DCNB. Wave 3 may be either the formation of the 2-CNB dianion (-9mV) or the 4-CNB dianion (-3mV). These are too close together to make an assignment. Wave 4 corresponds to the formation of the nitrobenzene dianion. There is a cathodic shoulder on wave 5 which may be the oxidation of the protonated dianion (E_2^H). Waves 6 and 7 are the oxidation waves of the 4-chloronitroso and 2,4-chloronitrosobenzene radical anions.

2,5-dichloronitrobenzene. The cyclic voltammogram of 2,5-dichloronitrobenzene, shown in Figure 18a, has two irreversible processes. Wave 2 corresponds to the formation of the dianion of 2,5-DCNB. Wave 3 is probably the 3-CNB dianion formation since the 2-CNB dianion (+55 mV) is further away than the 3-CNB dianion (+30mV)

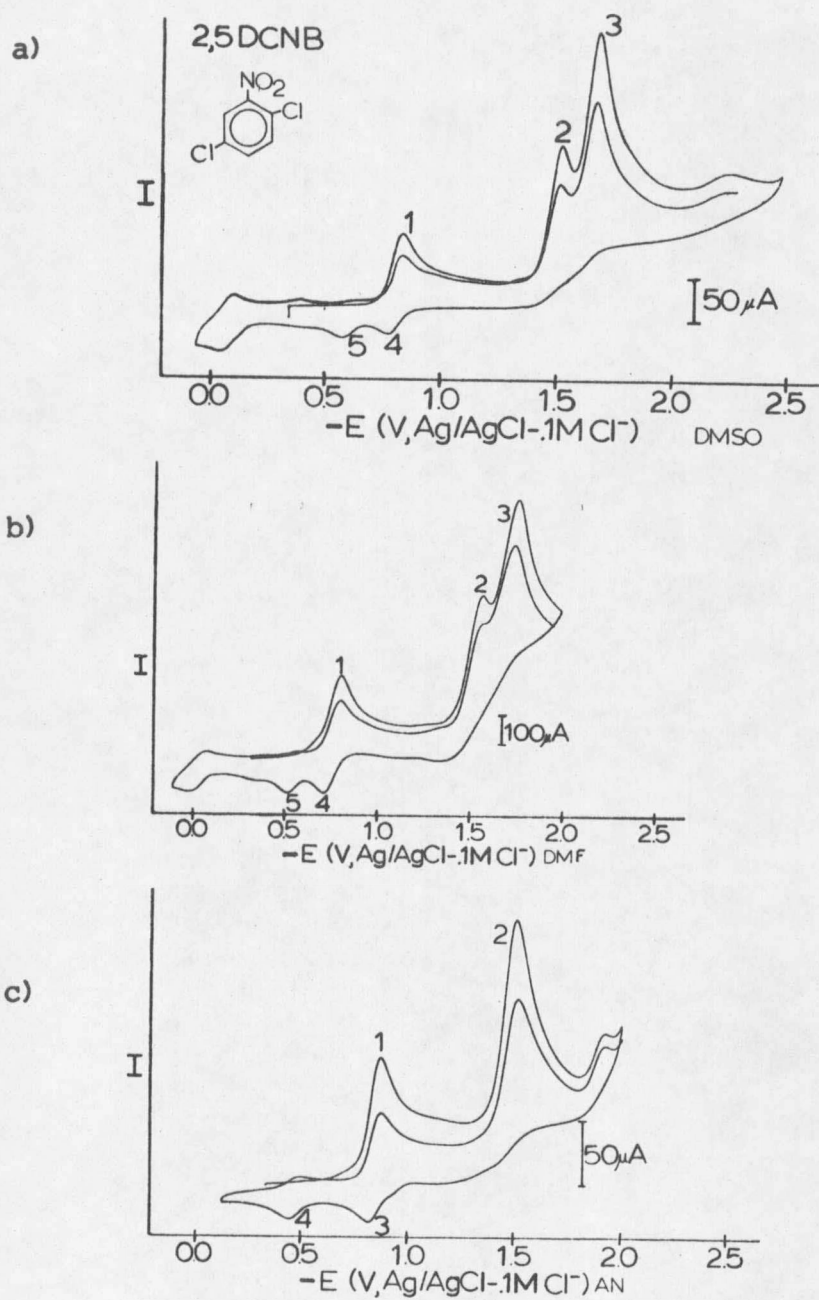


Figure 18. Cyclic voltammograms of 2,5-dichloronitrobenzene in a) DMSO; b) DMF; c) AN.

and it would be followed by a wave for the formation of the nitrobenzene dianion. There is no nitrobenzene dianion wave. The 3-CNB dianion could be shifted slightly due to competition between chlorines, or more likely, to the presence of trace amounts of water. The oxidative sweep shows one apparent nitroso wave (5) which is probably the oxidation of the 3-chloronitrosobenzene radical anion. The second sweep yields a small bump at approximately the starting potential (-.33V) from an unknown process and a small wave cathodic of wave 2, which may be the radical anion formation of 3-CNB. There is a small prewave on wave 2 which may indicate preprotonation.

In DMF, the voltammogram shown in Figure 18b looks much like Figure 18a. In this case, the wave for the formation of the 3-CNB which follows the 2,5-DCNB dianion is more cathodic (-52mV) than authentic 3-CNB. This may be due to a change in conditions, such as the solvent being more anhydrous or the compound itself containing less moisture than 3-CNB compound. The nitroso oxidation wave (5) is probably the 3-chloronitrosobenzene radical anion. The oxidative "hump" is also present.

In AN, Figure 18c, there is one irreversible wave corresponding to the formation of the 2,5-DCNB dianion. There does not appear to be any wave for a less chlorinated compound. The wave which follows wave 2 does not correspond to any known waves. The cathodic shoulder

on wave 3 is probably the E2' process and the oxidative "hump" may be present. The nitroso wave appears as a reversible couple and corresponds to the 2,5-dichloronitrosobenzene radical anion. The 3-CNB dianion may have shifted into wave 2 but if this were true, there would be a nitroso wave for the 3-chloro compound. It would appear between waves 3 and 4 but there is no wave there.

2,3,4-Trichloronitrobenzene. The cyclic voltammogram of 2,3,4-trichloronitrobenzene in DMSO (Figure 19a) yields three irreversible waves. The first process, wave 2, corresponds to the formation of the 2,3,4-TCNB dianion. The second process, wave 3, correlates with the formation of the 2,3-DCNB dianion (+50mV), but the 2,4-dianion is the same distance the other direction from it (-48mV). Competition probably results between loss of meta and para chlorines. Wave 4 is evidently the formation of the 3-CNB dianion while wave 6, a nitroso wave, corresponds with the 2,3-dichloronitrosobenzene radical anion oxidation. The E2' process and the oxidative "hump" are both present. There is a small prewave on wave 1 which is probably preprotonation.

In DMF, the voltammogram for 2,3,4-trichloronitrobenzene (Figure 19b) seems to follow the same mechanism as described for the compound in DMSO. There is a prewave prior to wave 1 which is probably surface adsorption.

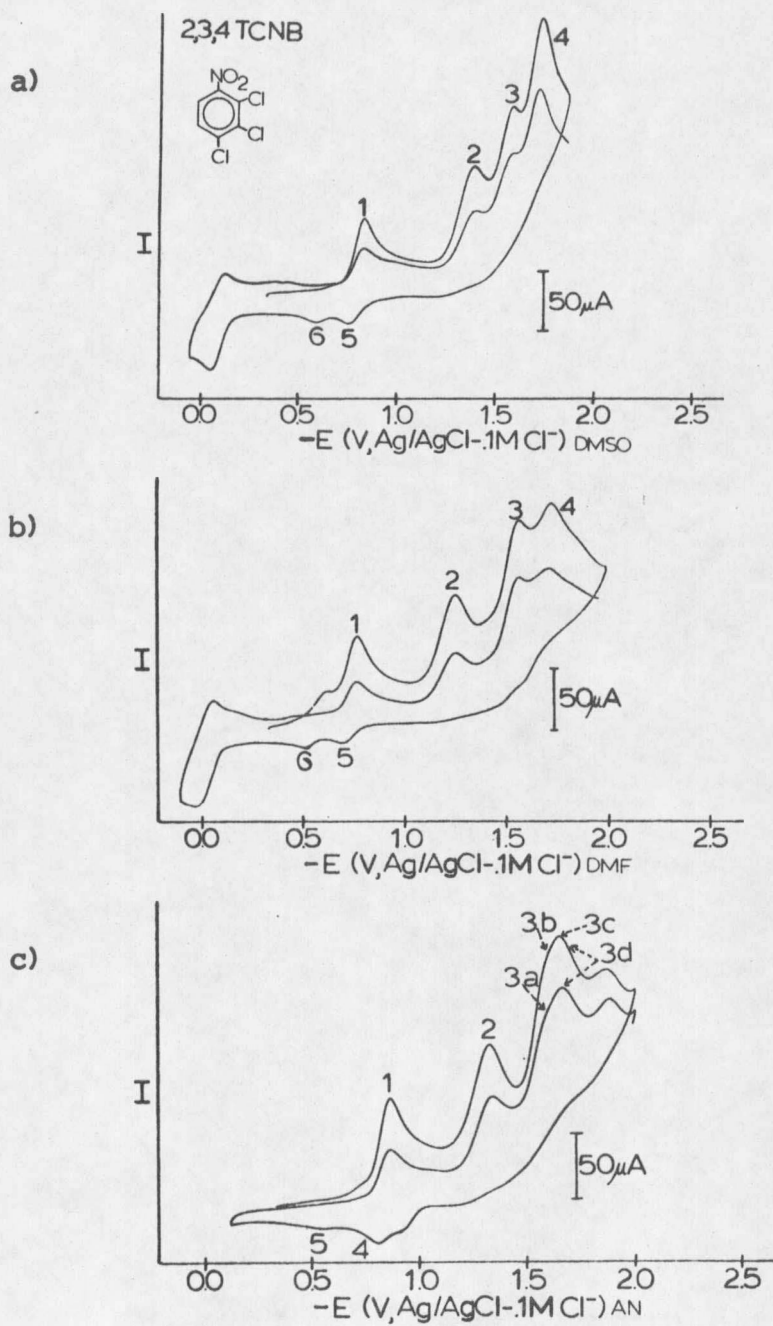


Figure 19. Cyclic voltammograms of 2,3,4-trichloronitrobenzene in a) DMSO; b) DMF; c) AN.

In AN, Figure 19c, the voltammogram for 2,3,4-trichloronitrobenzene has three irreversible waves. The first process, wave 2, corresponds to the formation of the dianion of 2,3,4-TCNB and the second process, wave 3, is broad and rounded. This is characteristic of overlapping waves. The front part of the wave appears to be the formation of the 2,4-DCNB dianion (3a) (note fluctuation on second sweep). The 3,4-DCNB dianion (3b) (note slight bump on first sweep) and the back of the wave is the 3-CNB dianion (3c) (+30mV) and/or the 4-CNB dianion (3d) (-40mV). The potential of the 3-CNB dianion is closest to the potential of the wave, but there may be competing processes since loss of the meta chlorine may be greater in this case due to the presence of adjacent chlorines. This was seen previously and it does appear that both dianions are formed with more of the 2,4-DCNB and the 4-CNB dianions being formed on the second sweep. The oxidative sweep yields the oxidative "hump" and the wave for the E2' process. There is a small nitroso wave (5) which appears to correspond to the 3,4-dichloronitrosobenzene radical anion.

2,3,5-Trichloronitrobenzene. The cyclic voltammogram of 2,3,5-trichloronitrobenzene in DMSO is shown in Figure 20a. Wave 2 corresponds to the formation of the dianion of 2,3,5-TCNB which includes the rapid loss of chloride ion. This was exhibited by setting the cathodic limit just passed the potential of wave 2 and

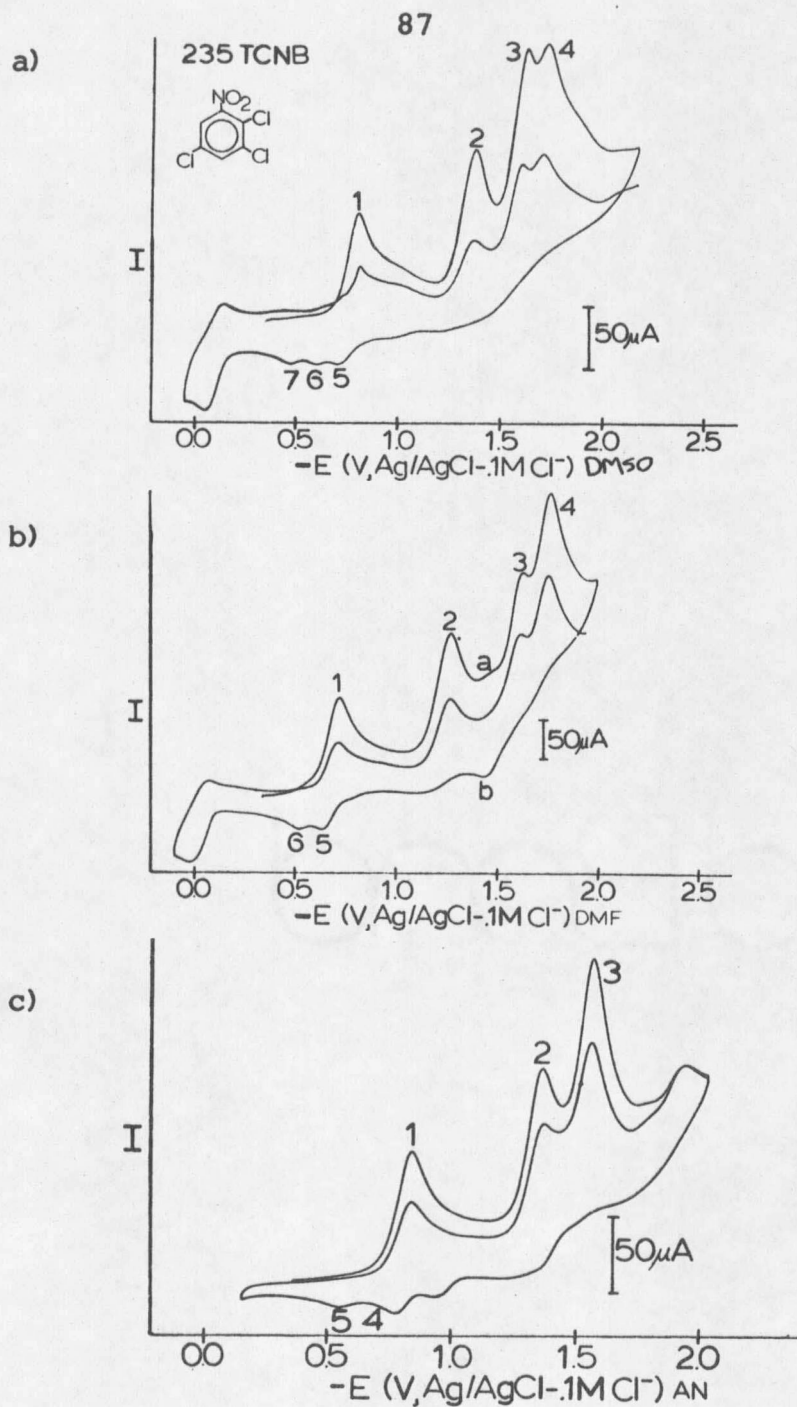


Figure 20. Cyclic voltammograms of 2,3,5-trichloronitrobenzene in a) DMSO; b) DMF; c) AN.

noting the formation of the mercurous chloride wave. Wave 3 appears to be the formation of the 3,5-DCNB dianion. Upon setting the cathodic limit just past this wave, the 3,5-dichloronitrosobenzene wave forms and a small bump corresponding to the 3-chloronitrosobenzene radical anion oxidation appears. There is probably competition between loss of the meta and ortho chlorine since the potential of wave 3 lies between that for the formation of the 2,5-DCNB and 3,5-DCNB dianions. The potential of wave 4 does not correspond to any of the possible mono-chloro compounds but it may be the formation of the 3-CNB dianion which has shifted due to an increase in residual water concentration. Waves 6 and 7 correspond to the 3-chloro- and 3,5-dichloronitrosobenzene radical anion oxidations. The second sweep shows a sharp peak at wave 1. This may be due to a surface adsorption phenomena. There is also a cathodic shoulder on wave 1 which is probably an impurity. The oxidative "hump" is also present.

In DMF, the voltammogram of 2,3,5-TCNB (Figure 20b) shows waves for the formation of the 2,3,5-TCNB dianion, 3,5-DCNB dianion and 3-CNB dianion. Between waves 2 and 3, there is a flat shoulder (labeled "a") and the oxidative sweep yields the corresponding wave ("b"). This may be the reduction and oxidation of the 2,3,5-trichloronitrosobenzene dianion or a surface adsorption wave. It is

also possible that "a" is a surface wave and "b" is the oxidation of wave 3, the 3,5-DCNB dianion. This wave was also seen in 3,4,5-TCNB in DMF (Figure 13b). The oxidative "hump" and a wave due to the E2' process are present as well as a nitroso wave (6) that may be a representative of 3,5-dichloro or 3-chloronitrosobenzene.

In AN, 2,3,5-TCNB yields two irreversible waves (Figure 20c). The dianion formation (wave 2) is followed by loss of a ortho chlorine to give the 3,5-DCNB dianion (wave 3). On the oxidative scan, the wave cathodic of wave 4 is probably the oxidation of the protonated dianion (E2'), while waves 4 and 5 represent oxidations of the 2,3,5-TCNB radical anion and the 2,3,5-trichloronitrosobenzene radical anion, respectively. The wave following wave 3 is from unknown sources.

2,4,5-Trichloronitrobenzene. The cyclic voltammogram of 2,4,5-trichloronitrobenzene in DMSO is shown in Figure 21a. Wave 2 represents the formation of the dianion of the trichloro compound. Waves 3 and 4 are electrochemical reductions that yield either the 2,5-dichloro dianion (+20mV) or the 3,4-dichloro dianion (-91mV) and the 2-CNB dianion (-69mV) or the 3-CNB dianion (-57mV). It appears there is loss of the para chlorine forming the 2,5-DCNB dianion, followed by loss of the ortho chlorine yielding the 3-chloro dianion. The oxidative sweeps shows the reversible radical anion oxidation

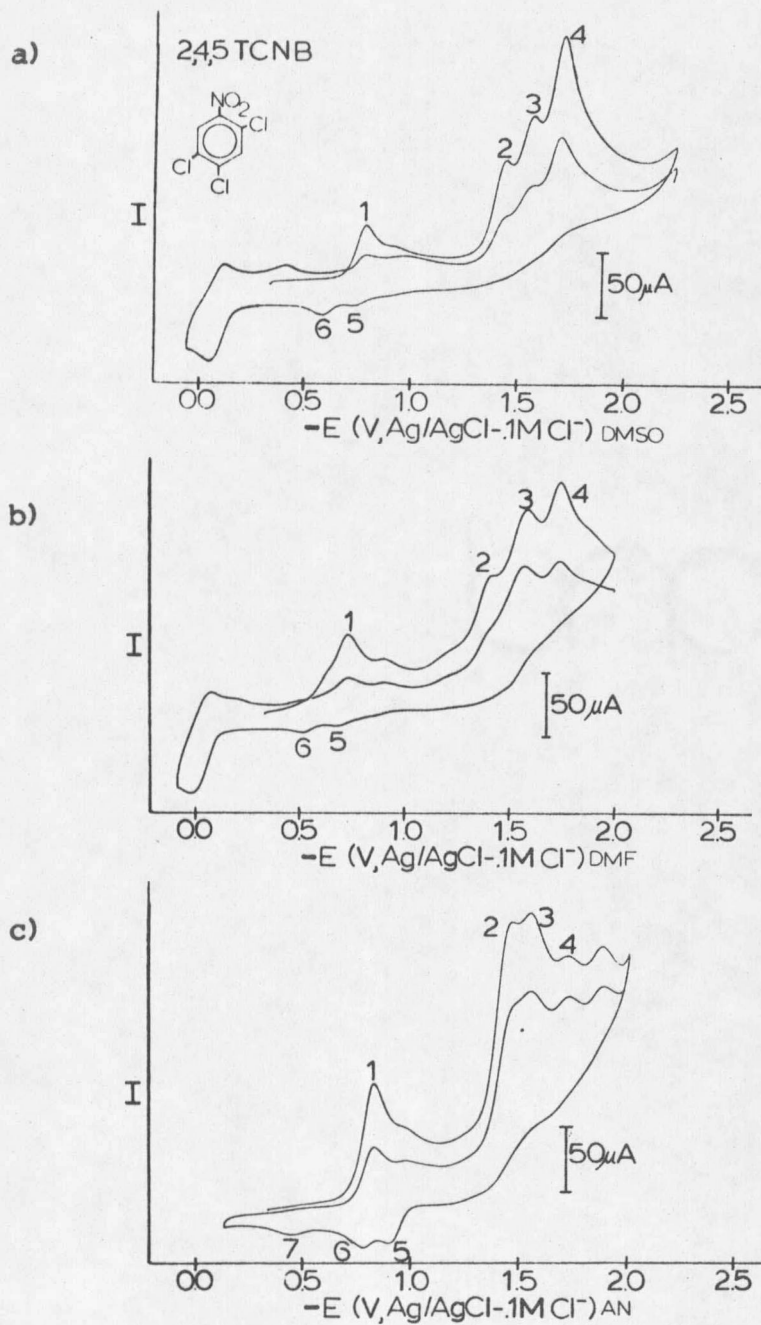


Figure 21. Cyclic voltammograms of 2,4,5-trichloronitrobenzene in a) DMSO; b) DMF; c) AN.

(wave 5) and the oxidation of a nitroso compound, most likely the 2,5-dichloronitrosobenzene radical anion (wave 6). The cathodic shoulder on wave 1 is probably an impurity or a surface adsorption wave.

In DMF, Figure 21b, some new waves appear. Wave 1, the reversible anion radical formation, has an anodic shoulder and a small wave cathodic of it but still some distance from wave 2. The anodic shoulder may be preprotonation of the trichloro compound or it may be surface adsorption. The cathodic shoulder is most likely an impurity. Wave 2, the formation of the trichloro dianion, appears to have a prewave which may be due to protonation of the radical anion. The reduction process at wave 3 yields the 2,5-dichloro dianion (+20mV) or the 3,4-dichloro dianion (+9mV). Wave 4 is either the formation of the 3-CNB dianion (+31mV) or the 4-CNB dianion (-24mV). These are too close together for speculation. There is not much oxidation occurring but a small nitroso wave is present that corresponds with the oxidation of the 3,4-dichloronitrosobenzene radical anion.

In AN, Figure 21c, the voltammogram of 2,4,5-TCNB shows a cathodic shoulder on wave 1. This seems to be an impurity since it was present in DMSO and DMF with this compound. Wave 2 corresponds to the formation of the 2,4,5-TCNB dianion and wave 3 may be either

the 3,5-DCNB dianion (+36mV) or the 2,4-DCNB dianion (-18mV). Wave 4 yields the 2-CNB dianion (+17mV) or the 4-CNB dianion (+16mV). The 3,4-DCNB dianion is much further away from wave 3 than the other two compound (-85mV) and the 3-CNB dianion is about the same distance from wave 4 (-89mV). It is apparent that the meta chlorine is lost at some point in the mechanism. There may be competition between all three positions that shifts the waves so they appear between potentials of authentic compounds. The wave that appears after wave 4 has appeared in many voltammograms in AN and is probably an impurity since it is too negative to be NB or an azo compound. Wave 5 appears to be superimposed on an impurity since the wave was smaller and shifted -32 mV with shorter sweep times. The potential of wave 5 is between the potentials of the 2,4-DCNB radical anion (-26mV) and the 2,5-DCNB (+17mV) dianion wave indicating it is a dominating process and the loss of chlorine is small compared to it. This is a small nitroso wave (7) which may be the oxidation of the 2,5-dichloronitrosobenzene radical anion.

2,3,4,5-Tetrachloronitrobenzene. The cyclic voltammogram of 2,3,4,5-tetrachloronitrobenzene (Figure 22a) has four irreversible processes. The first of these, wave 2, corresponds to the dianion formation of 2,3,4,5-TeCNB. Wave 3 appears to be the 2,3,4-TCNB dianion (+7mV) or the 2,3,5-TCNB dianion (+45mV) formation. Wave 4

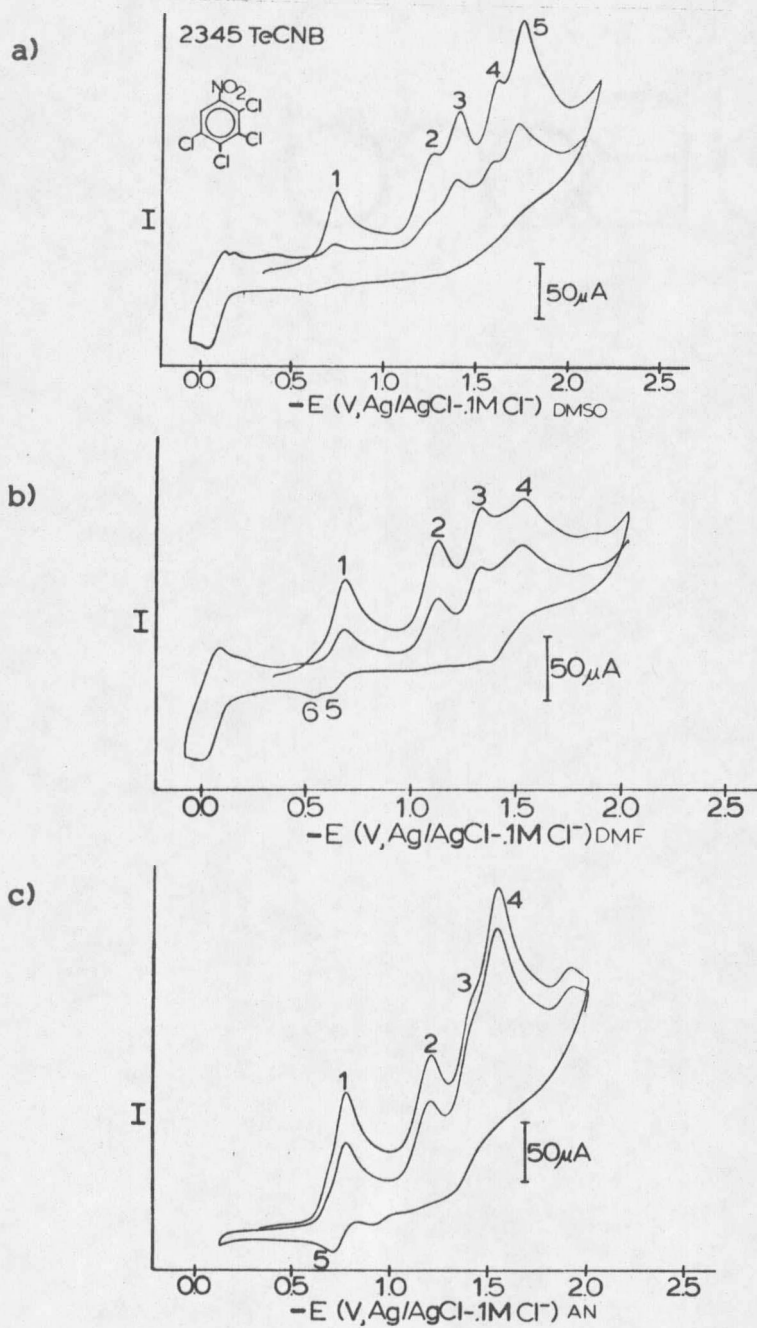


Figure 22. Cyclic voltammograms of 2,3,4,5-tetrachloronitrobenzene in a) DMSO; b) DMF; c) AN.

may be either the formation of the 2,3-DCNB dianion (+69mV) or the 3,5-DCNB dianion (-38mV). Wave 5 appears to be the 3-CNB dianion. The waves on the oxidative sweep are very small. When the cathodic limit is moved anodically, there is a wave for the oxidation of the 2,3,4,5-TeCNB radical anion. The radical anion oxidation is not present on longer sweeps due to rapid chloride loss. The radical anion may be losing chloride immediately (instead of the dianion) that would be an irreversible process. Expected products from this reduction are the 2,3,5-TCNB dianion, the 3,5-DCNB dianion and the 3-CNB dianion. Competition between position of chloride loss would also yield the 2,3,4-DCNB dianion and the 2,3-DCNB dianion.

In DMF, Figure 22b, the voltammogram exhibits loss of chloride ion to yield the 3,4,5-TCNB dianion (+22mV). This is a different product than was seen in DMSO. The 2,3,5-DCNB dianion is +52mV away from wave 3 and the 2,3,4-DCNB dianion is +62mV away from the wave, so it appears that the 3,4,5-DCNB dianion is formed. It is reduced according to the mechanism described for 3,4,5-TCNB in DMF. There is a small reversible wave between waves 3 and 4 that was described previously. Preprotonation of the radical anion and the oxidative "hump" are present.

In AN, Figure 22c, there is very rapid chloride loss. Wave 2 is the formation of the 2,3,4,5-TeCNB dianion with rapid chloride loss

followed by wave 3 that appears as a anodic shoulder on wave 4. The chemical processes are apparently occurring so rapidly (due to perhaps more available water in AN) that the electrode processes are shifted on top of one another. This is a known effect of the rapid kinetics of a following chemical step on an electrochemical process. Waves 3 and 4 corresponds to the formation of the 3,4,5-TCNB dianion and the 3,5-DCNB dianion. At faster sweep rates, the E2' wave is large. There is no nitroso formation that further indicates the chloride loss is more rapid than hydroxide loss in this case.

Series 3: Two Ortho Chlorines

2,6-dichloronitrobenzene. The cyclic voltammogram of 2,6-dichloronitrobenzene in DMSO is shown in Figure 23a. There are three irreversible processes. Wave 2 may be the formation of the 2,6-DCNB dianion. Wave 3 and wave 4 are dianions for less chlorinated compounds (2-CNB and NB, respectively). The oxidative sweep yields 2,6-DCNB (wave 5), 2-chloronitrosobenzene (wave 6) and nitrosobenzene (wave 7).

In DMF, Figure 23b, the irreversible processes are the same as in DMSO but there is more separation between the waves. This is very characteristic of voltammograms in DMF and may be due to less residual water in the solvent. Wave 2, the 2,6-DCNB dianion formation appears to be broader than usual. This may be due to the extremely rapid

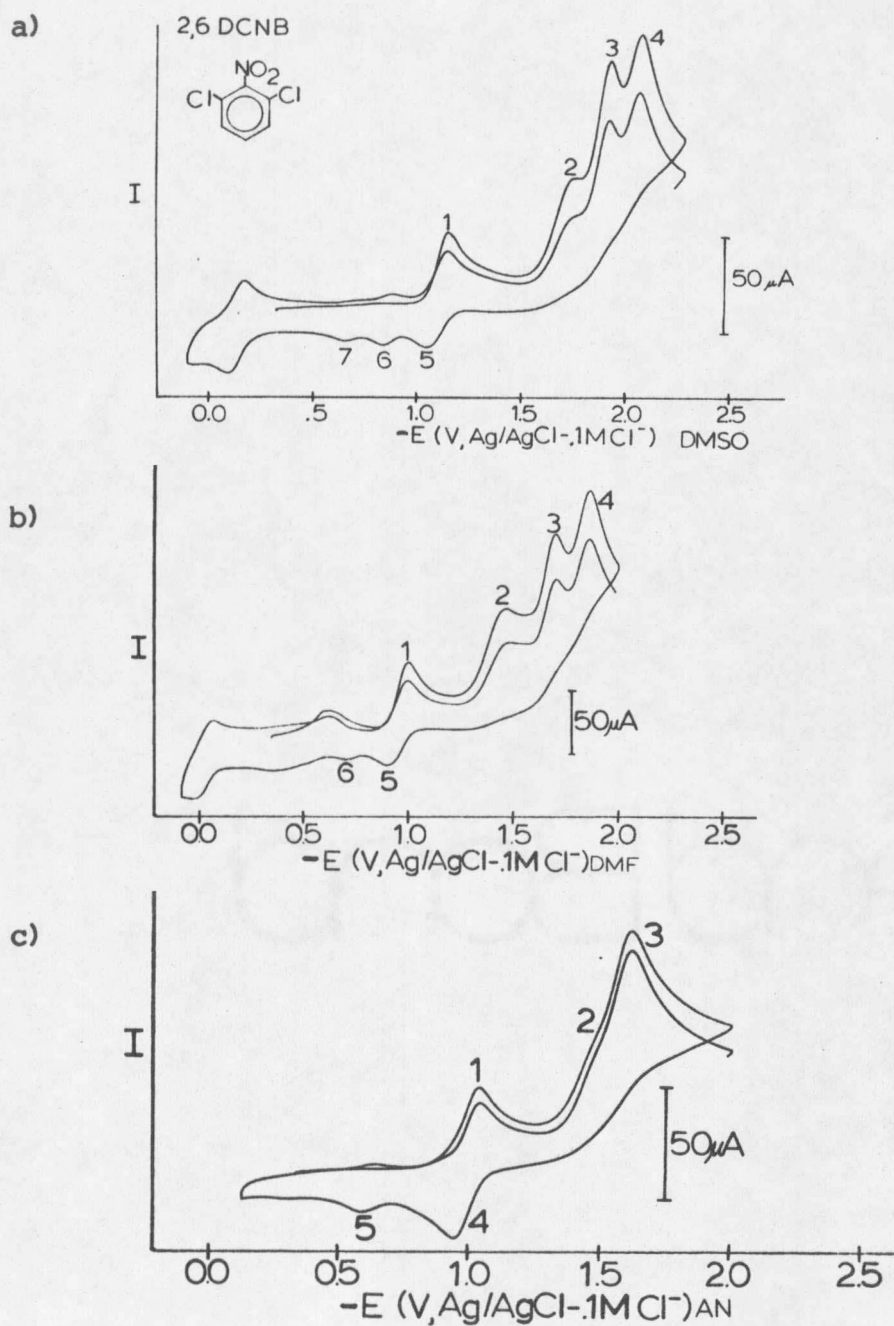


Figure 23. Cyclic voltammograms of 2,6-dichloronitrobenzene in a) DMSO; b) DMF; c) AN.

chloride loss observed. Waves 3 and 4 correspond to the formations of the 2-CNB dianion and the NB dianion, respectively. There is a small nitroso wave (6) that is most likely the oxidation of the 2-chloronitrosobenzene radical anion. The prewave to wave 1 is very characteristic of the previously described surface adsorption. The broad "belly" anodic of wave 6 on the oxidative sweep may be a surface effect or an electroactive impurity.

In AN, there are two irreversible processes (Figure 23c). Wave 2 appears as a shoulder on wave 3 indicating rapid chloride loss from the 2,6-DCNB dianion (wave 2) and subsequent formation of the 3-CNB dianion (wave 3). This is the same effect noted earlier for a rapid chemical process following an electrochemical process. The oxidative processes appear to be the oxidation of the 2,6-DCNB radical anion (wave 4) and the 2-chloronitrosobenzene radical anion (wave 5). Wave 4 has a anodic shoulder on it that makes the wave broad and rounded. The shoulder is apparently due to the oxidation of the nitrosobenzene radical anion or the 2-CNB radical anion.

2,3,6-trichloronitrobenzene. The cyclic voltammogram of 2,3,6-trichloronitrobenzene in DMSO (Figure 24a) appears to have lost an ortho and/or a meta chlorine to yield the 2,5-DCNB dianion (+16mV) and/or the 2,3-DCNB dianion (+33mV) at wave 3. Wave 2, the formation of the 2,3,6-TCNB dianion, is quite broad and may indicate

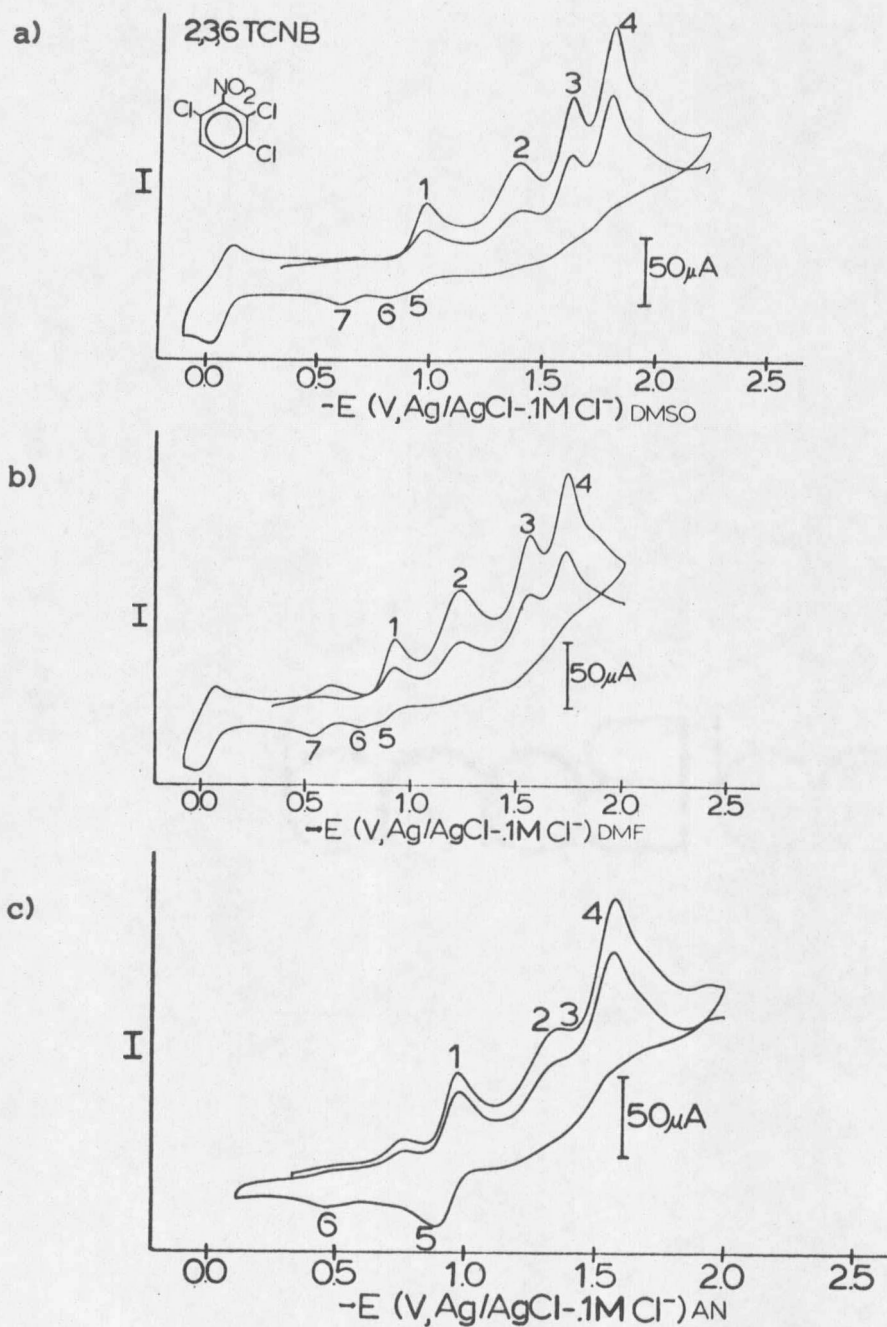


Figure 24. Cyclic voltammograms of 2,3,6-trichloronitrobenzene in a) DMSO; b) DMF; c) AN.

competition in the loss of chlorine between the ortho and meta chlorine. Wave 3 corresponds to the 3-CNB dianion that indicated the 2,5-DCNB dianion formation was probably dominate. However, wave 4 corresponds with the NB dianion that is not formed from the 3-CNB dianion unless adjacent chlorines are present. If some 2,3-DCNB dianion was formed, loss of the meta chlorine could result and yield the small wave for the NB dianion. There could also have been competition between 2,5-DCNB and 2,6-DCNB but this is not as likely. The oxidative sweep yields two waves for nitro radical anion oxidations. Wave 5 corresponds to the 2,3,6-TCNB radical anion oxidation and wave 6 is apparently the 2,5-DCNB radical anion oxidation. Shorter sweeps produced this wave and appeared to prove the existence of the 2,5-DCNB radical anion. Wave 7 corresponds to the oxidation of the 2,5-dichloronitrosobenzene radical anion.

In DMF, the voltammogram of 2,3,6-TCNB (Figure 24b) follows the same mechanism as described for DMSO except for the prewave to wave 1 which is probably surface adsorption.

In AN, Figure 24c, the voltammogram of 2,3,6-TCNB yields two irreversible waves. There is a prewave to wave 1 that is reversible at slow sweep rates when the cathodic limit is moved to a potential just negative of wave 1. At faster sweep rates, the process disappears. This may be preprotonation or a surface adsorption wave.

There is also a prewave on wave 2 that is probably formation of the protonated dianion (reduction of the protonated radical anion). Wave 2 is the formation of the 2,3,6-TCNB dianion. Note that the wave is very broad. The wave labeled (4) is too cathodic to be dichloro compounds so it appears that the cathodic part of wave 2 is wave 3, which is loss of chloride forming a dichloro compound. Wave 4 corresponds to the 3-CNB dianion formation. Wave 6 corresponds to the oxidation of the 2,3-dichloronitrosobenzene radical anion. The shoulder between waves 5 and 6 could be the oxidation of the 3-chloronitrosobenzene radical anion.

2,4,6-Trichloronitrosobenzene. The cyclic voltammogram of 2,4,6-trichloronitrosobenzene, shown in Figure 25a, yields four irreversible processes. Wave 2 appears to be the dianion formation of 2,4,6-DCNB while wave 3 is the formation of the 2,4-DCNB, and wave 4 corresponds to the 4-CNB dianion. The oxidative sweep yields the oxidative "hump", the E2' process wave, and waves 5 and 6. Wave 5 has two peaks. One appears as a cathodic shoulder but the waves are almost the same size. These waves appear to represent the oxidations of the radical anions of 2,4,6-TCNB and 4-CNB or 2,4-DCNB. The 2,4-DCNB radical anion probably is present because the cathodic part of wave 5 likely corresponds to the 2,4,6-DCNB radical anion oxidation since it must be about 60mV from its reversible couple. The 4-CNB radical

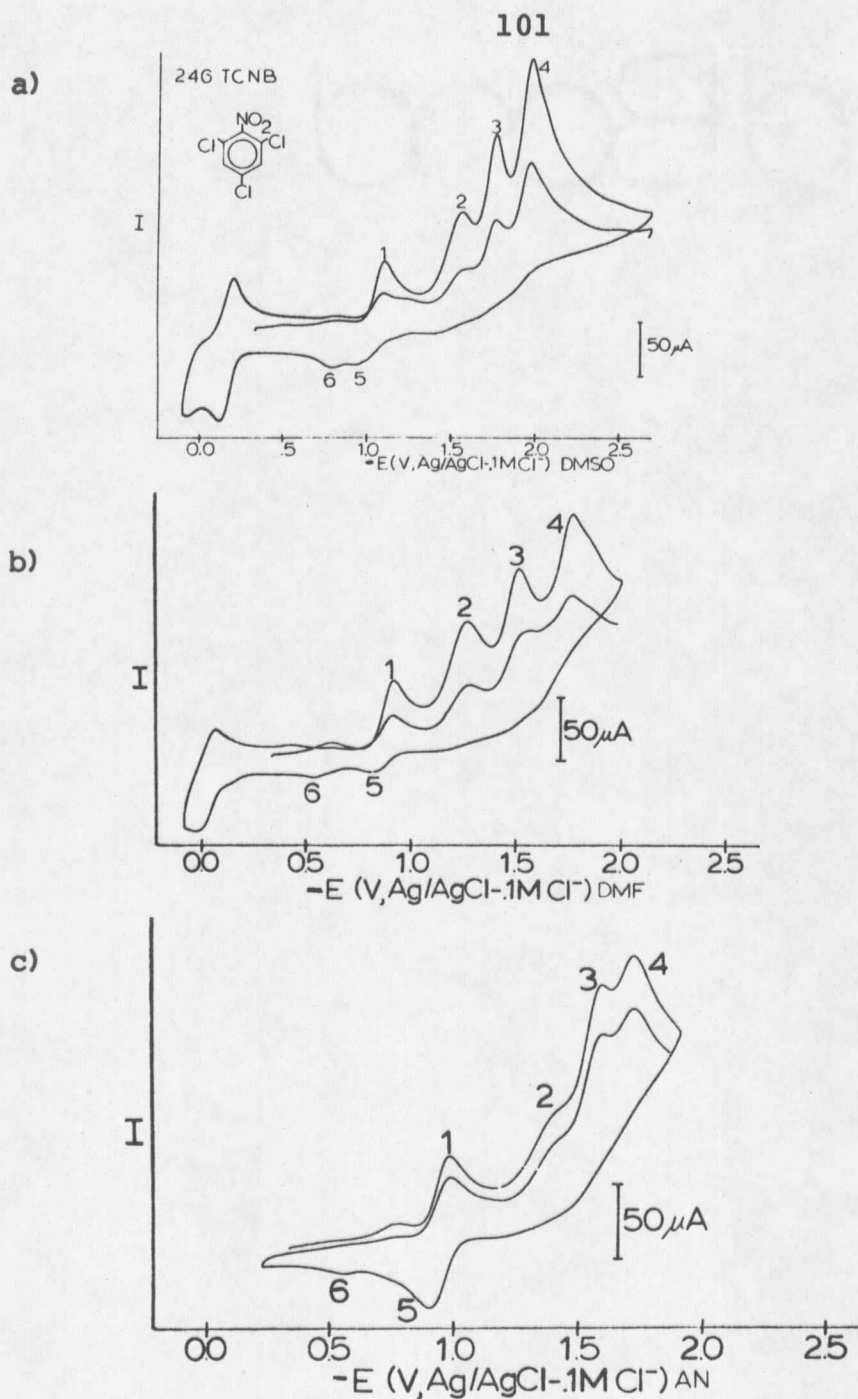


Figure 25. Cyclic voltammograms of 2,4,6-trichloronitrobenzene in a) DMSO; b) DMF; c) AN.

anion would fall at the same potential as the 2,4,6-DCNB radical anion. However, CNDO/2 calculations by Beland⁹⁰ predict a 89% probability of the 2,6-DCNB dianion forming. Wave 6 corresponds to the 4-chloronitrosobenzene radical anion oxidation.

In DMF, the pathway is the same as described for DMSO (2,4-DCNB formation) with only a slight amount of NB formation. The voltammogram is shown in Figure 25b. There is a prewave to wave 1 that is probably a result of a strongly adsorbed product.

In AN, Figure 25c, the mechanism of reduction is the same as in DMF without NB formation. There is preprotonation of the radical anion, and the nitroso waves are present (wave 6 and a cathodic shoulder on 6) and are probably 2,4-dichloronitrosobenzene and 4-chloronitrosobenzene, respectively. The oxidative "hump" may be present.

2,3,4,6-tetrachloronitrobenzene. The cyclic voltammogram of 2,3,4,6-tetrachloronitrobenzene in DMSO is shown the Figure 26a. Wave 2 corresponds to the formation of the 2,3,4,6-TeCNB dianion which reduces to 2,4,5-TCNB (-15mV) and forms its dianion at wave 3. The 2,4,6-TCNB dianion (-28mV) may be formed by competition between the ortho and meta chlorines. The reduction proceeds to the 2,5-DCNB dianion at wave 4 and the 3-CNB dianion at wave 5. Chlorine is lost very rapidly and a small amount of a chlorinated nitroso compound is

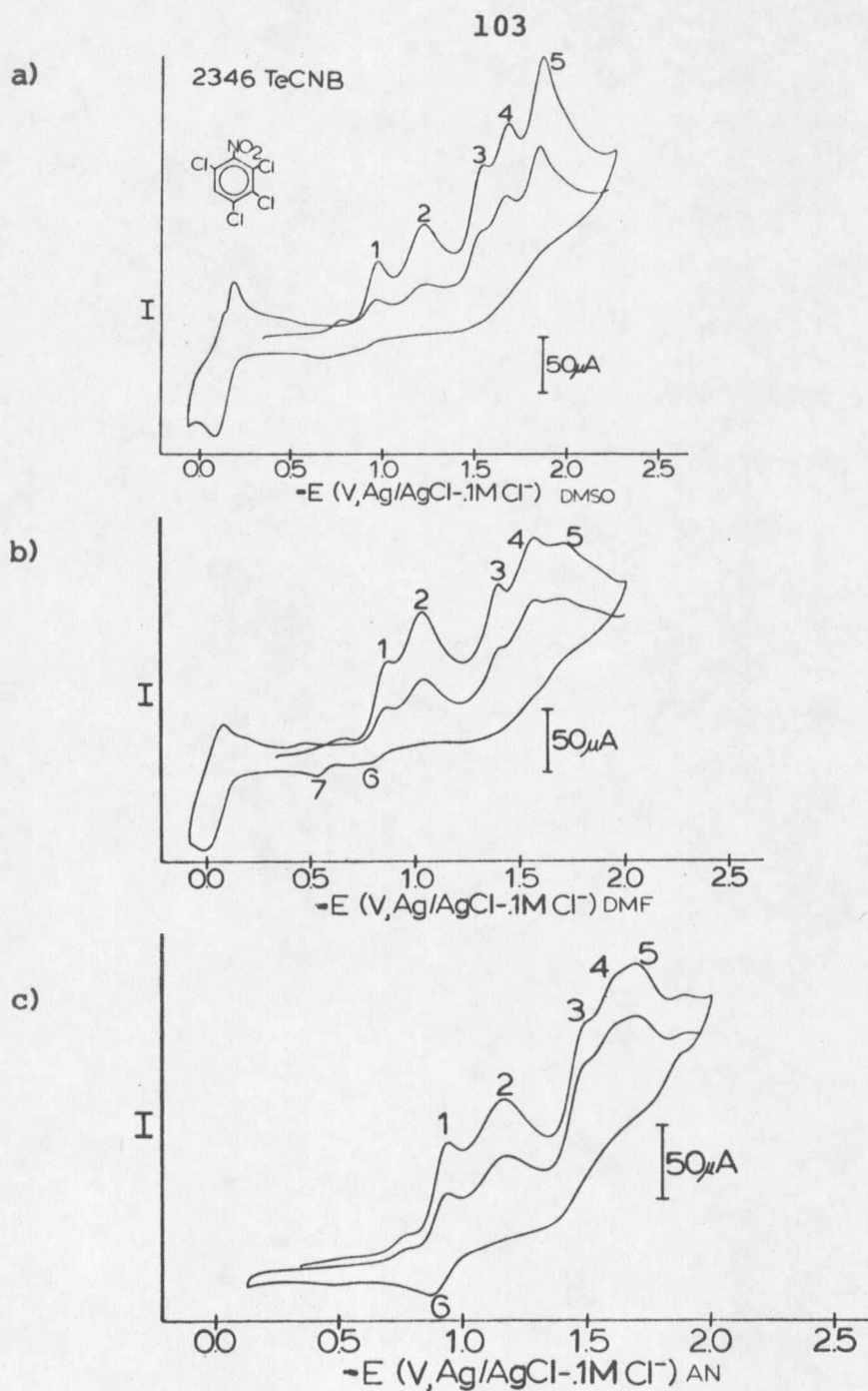


Figure 26. Cyclic voltammograms of 2,3,4,6-tetrachloronitrobenzene in a) DMSO; b) DMF; c) AN.

formed.

In DMF, Figure 26b, the reduction of 2,3,4,6-TeCNB yields the 2,4,5-TCNB dianion at wave 3 followed by formation of the 2,5-DCNB dianion (0mV) or the 3,4-DCNB dianions (-11mV) at wave 4, and wave 5 corresponds to the 3-CNB dianion. There is some preprotonation of the radical anion and a nitroso wave (7), that corresponds to the oxidation of the 3,4-dichloronitrosobenzene radical anion. There is a shoulder between wave 6 and 7 that is probably the 3-chloronitrosobenzene radical anion oxidation wave.

In AN, Figure 26c, 2,3,4,6-TeCNB yields a more definite pathway. Wave 2 is a broad wave that appears to be the 2,3,4,6-TeCNB dianion with preprotonation occurring on the front of the wave which may be linked to preprotonation of the radical anion or to surface adsorption. Wave 3 may be the formation of the 2,4,5-TCNB dianion and waves 4 and 5 correspond to the formation of the 3,4-DCNB dianion and the 4-CNB dianion, respectively. There is a small amount of nitroso formation that is probably the 3,4-dichloronitrosobenzene radical anion oxidation.

2,3,5,6-Tetrachloronitrobenzene. The cyclic voltammogram of 2,3,5,6-tetrachloronitrobenzene in DMSO is shown in Figure 27a. The full sweep shows five irreversible processes. Waves 2 and 3 appear to represent formation of the 2,3,5,6-TeCNB dianion and the 2,3,5-TCNB

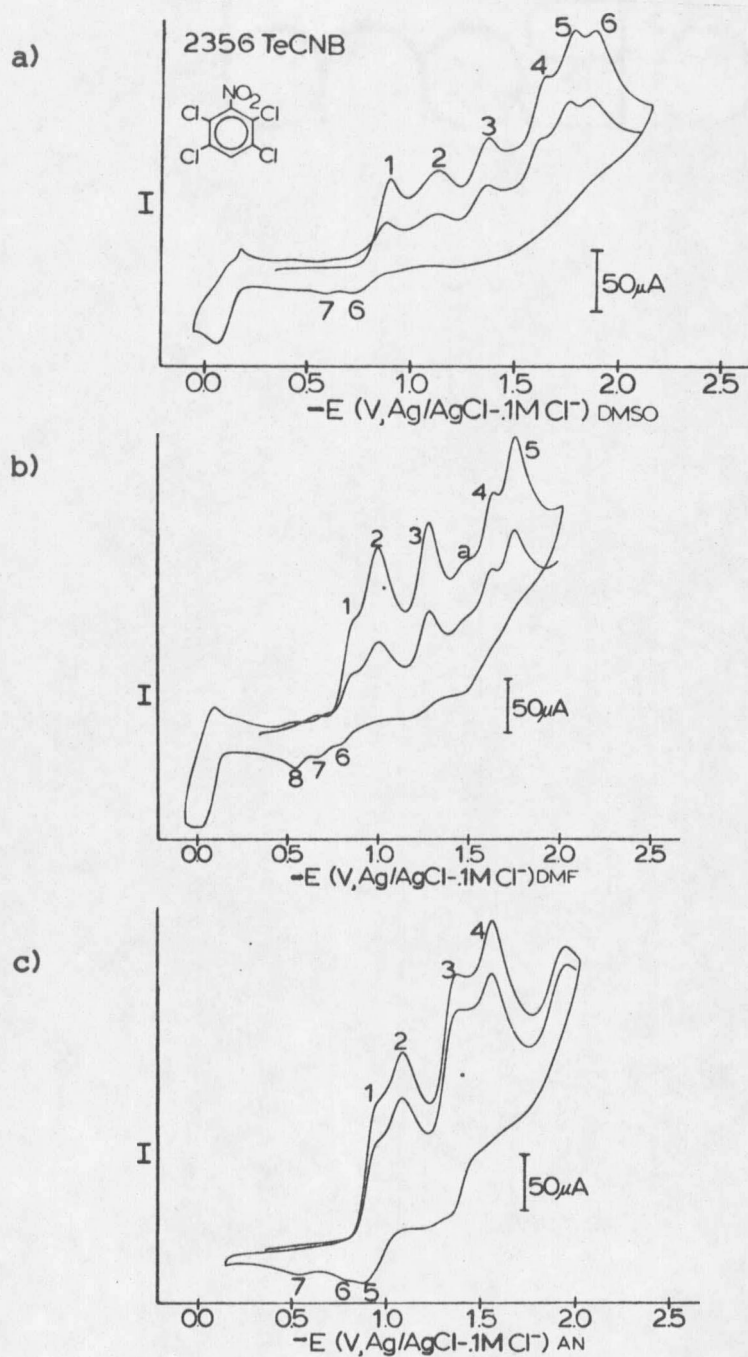


Figure 27. Cyclic voltammograms of 2,3,5,6-tetrachloronitrobenzene in a) DMSO; b) DMF; c) AN.

dianion (+7mv) or the 2,3,6-TCNB dianion (+14mV), respectively. Wave 4 may be the 2,6-DCNB dianion (+33mV), the 2,5-DCNB dianion (+36 mV), the 2,3-DCNB dianion (+103mV), or the 3,5-DCNB dianion (-13mV). From this data, it appears that the 2,3,5- and 2,3,6-TCNB dianions are too close to decipher the actual process and competition is occurring between loss of the ortho and meta chlorines. It also appears that there may be some competition between the 3,5- and 2,6-DCNB dianions but the 3,5-DCNB process dominates. Wave 5 corresponds with the 3-CNB dianion and wave 6 to the NB dianion. CNDO/2 calculations by Beland⁹⁰ do show that the probability of losing an ortho chlorine is only slightly favored over loss of a meta chlorine for this compound. Some competition could be involved. There appears to be some nitroso oxidation (wave 8) that may be the 3,5-dichloronitrosobenzene radical anion. This is another case where 3-CNB loses a chloride due to an adjacent chloride ion in the parent compound.

In DMF, Figure 27b, there are four irreversible processes. Wave 1 appears as a shoulder on wave 2 indicating rapid chloride loss as soon as the 2,3,5,6-TcCNB dianion starts to form. There is a small prewave on wave 1 which may be a surface wave. Wave 3 corresponds to the 2,3,5-TCNB dianion. Wave 4 is probably the 3,5-DCNB dianion and wave 5 corresponds with the formation of the 3-CNB dianion. The oxidative sweep shows a definite oxidative "hump" and two nitroso

waves (waves 7 and 8) but from this data, the waves cannot be matched with corresponding compounds. The peak labeled "a" is either the reduction of a nitroso dianion or a surface wave. There appears to be a small oxidation wave directly below it (sharp corner).

In AN, Figure 27c, waves 3 and 4 are closer together than in the other solvents. After formation of the 2,3,5,6-TCNB dianion (wave 2), loss of a chloride ion and further reduction yields the 2,3,5-TCNB dianion (+10mV) or the 2,3,6-TCNB dianion (-17mV). Wave 4 represents formation of the 2,5-DCNB dianion (+27mV) or the 3,5-DCNB dianion (+1mV). It appears that the 2,3,5-TCNB dianion is formed, then loss of the ortho chlorine yields the 3,5-DCNB dianion after reduction. In AN, the 3,5-DCNB compound does not have a wave for further reduction. The most cathodic wave is, apparently, an impurity. The oxidative "hump" and three other oxidation waves are present. Wave 5 corresponds to the oxidation of the 2,3,5,6-TCNB radical anion. It appears to have a cathodic shoulder that may be the E2' process. Wave 6 does not correspond to a nitroso compound but it may be the oxidation of the 2,3,5-TCNB radical anion (-2mV) or the 3,5-DCNB radical anion (+15mV). The wave is not well defined so it is difficult to determine an accurate potential. The reduction waves for the radical anions would appear under wave 1. Wave 7 corresponds to the 3,5-dichloronitrosobenzene radical anion

oxidation.

2,3,4,5,6-pentachloronitrobenzene. The cyclic voltammogram of 2,3,4,5,6-pentachloronitrobenzene is shown in Figure 28a. Wave 1 represents the formation of the radical anion and formation of the irreversible dianion with rapid loss of chloride ion. This makes the wave irreversible. Wave 2 appears to be the formation of the 2,3,4,5-TeCNB dianion. The rest of the voltammogram interpretation follows that for 2,3,4,5-TeCNB. There is a small prewave on wave 1 that may indicate some preprotonation. Chloride loss is too rapid in the penta-chloro compound for nitroso formation.

In DMF, Figure 28b, wave 1 is very large indicating formation of the radical anion and dianion with rapid chloride loss. However, the 2,3,4,5-TeCNB formed would be reduced immediately to its radical anion since the wave for the radical anion formation is positive of the first wave of the penta-chloro compound. Wave 1 corresponds to a three electron transfer. The rest of the voltammogram can be interpreted as it was for 2,3,4,5-TeCNB. Wave 1 has a prewave which may be surface adsorption. The small oxidative waves may be oxidations of 2,3,4,5-TeCNB radical anion (wave 5), the 3,5-di or the 3,4,5-TCNB radical anion (wave 6) and the 3- or 3,5-dichloronitrosobenzene radical anion (wave 7).

In AN, Figure 28c, PCNB appears to undergo reduction to the

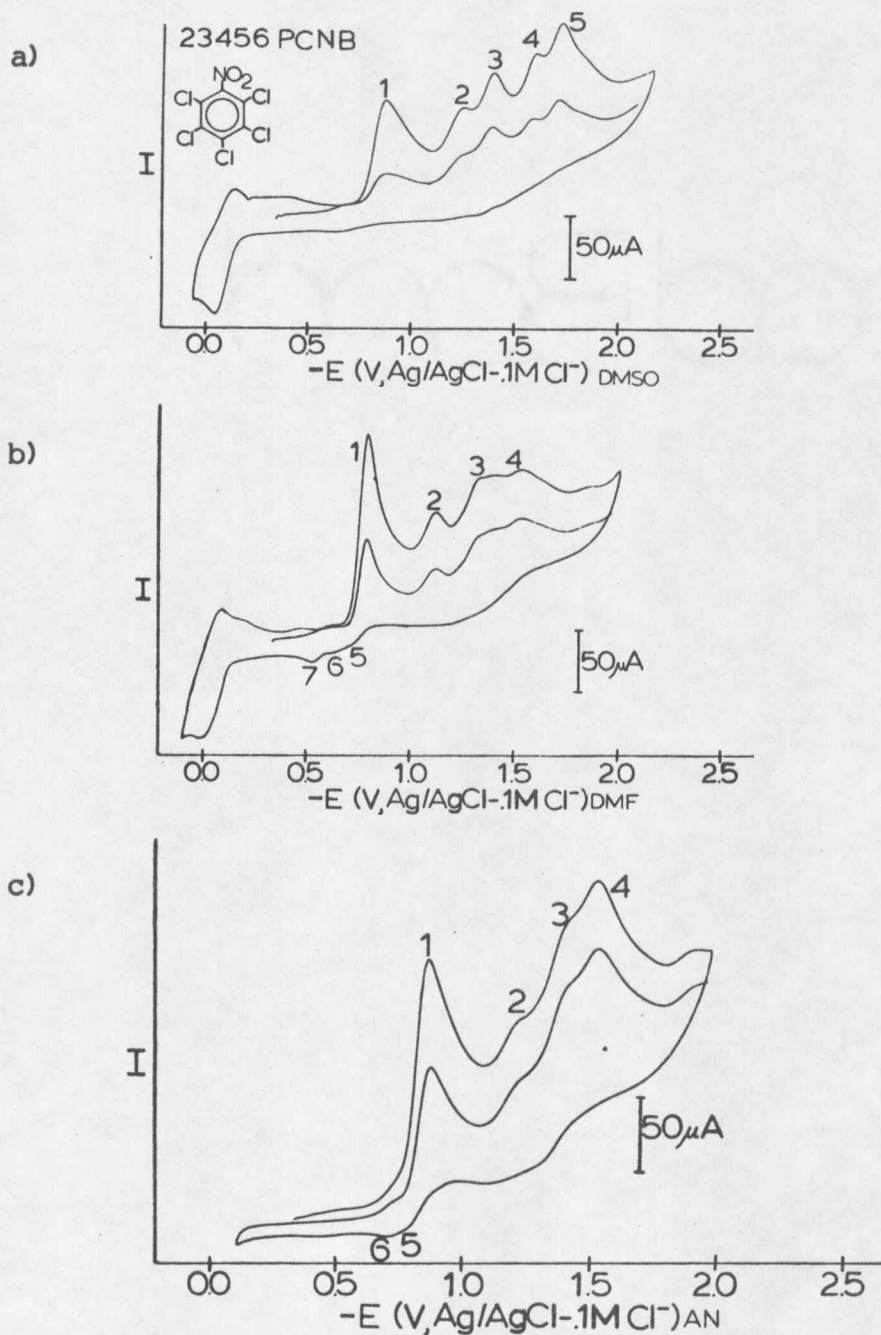


Figure 28. Cyclic voltammograms of 2,3,4,5,6-pentachloronitrobenzene in a) DMSO; b) DMF; c) AN.

2,3,4,5-TeCNB dianion. Wave 1 is the same as it was in DMF. The height of the wave is indicative of a three-electron transfer. The pathway of reduction is the same as was described for 2,3,4,5-TeCNB in AN. The oxidative "hump" and two small oxidative waves are present. These represent the 3,5-DCNB radical anion oxidation (wave 5) and the 2,3,4,5-TeCNB radical anion oxidation wave (6).

Cyclic Voltammograms with Proton Addition

Series 1: No Ortho Chlorines

Nitrobenzene. For nitrobenzene, Figure 29, addition of water to DMSO yielding a water concentration of .097 M produces new waves and changes in the potentials of some of the previously existing waves. The irreversible wave (2) shifts +48mV, however, the other waves do not. The first of the new waves is a cathodic shoulder on wave 3. It appears, for the nonaqueous experiment, when the cathodic limit is moved more negative, presumably allowing more product formation time. This wave is probably due to the E2' process. The wave anodic of wave 4 has not been previously seen. The oxidative wave appears to be due to a reaction of the mercury on the surface of the electrode with hydroxide ion, that is lost as nitroso compounds are formed. Since the addition of a proton source appears to increase the amount of nitroso formation, as is shown by wave 5, more hydroxide ion will

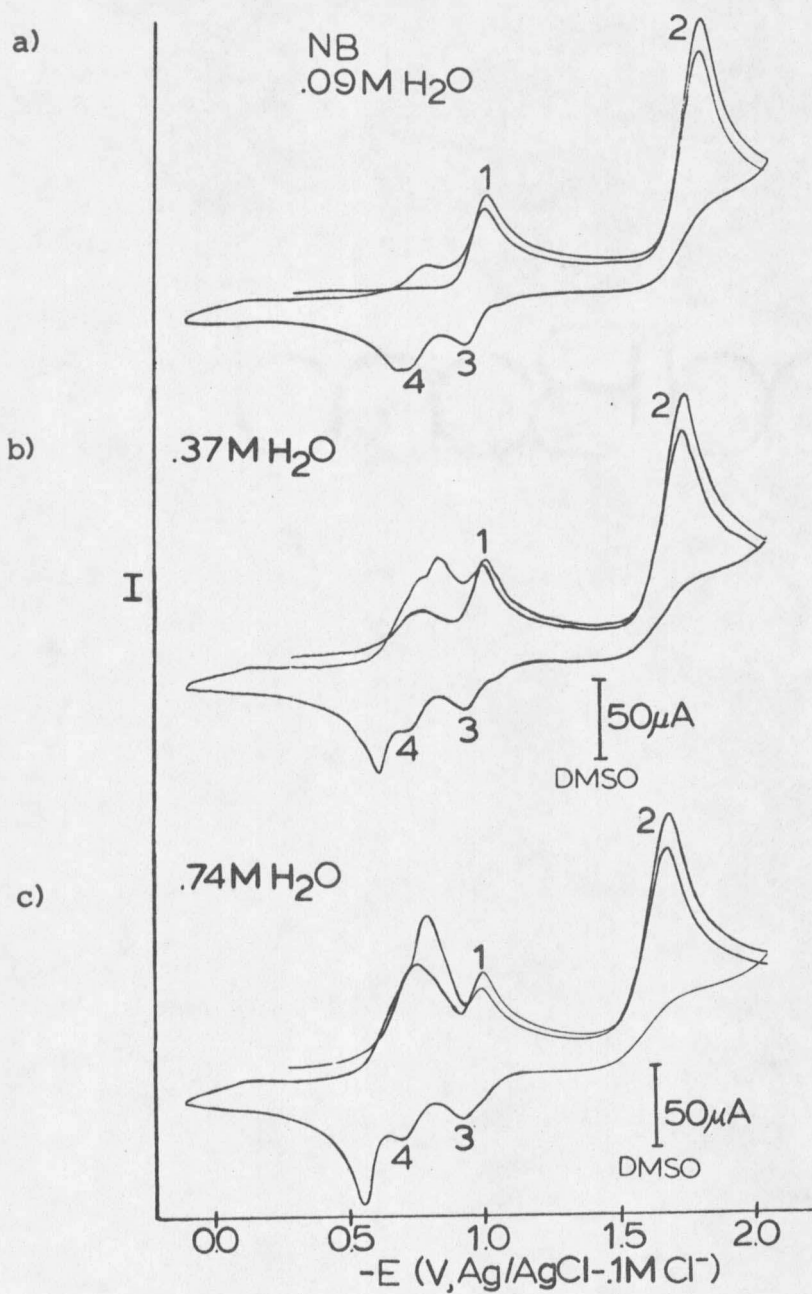


Figure 29. Cyclic voltammograms of nitrobenzene in DMSO with a) $.097 \text{ M H}_2\text{O}$; b) $.37 \text{ M H}_2\text{O}$; c) $.74 \text{ M H}_2\text{O}$.

be produced. This wave will be referred to as the mercury complex or mercuric oxide wave. It appears at low concentrations of proton source and increases to a large sharp wave at higher concentrations. It also shifts anodically as the concentration increases (see Figure 77 for a good example of this). Increasing the water concentration to .38 M, the irreversible wave (2) and wave 5 both shift approximately +68mV. Wave 5 is sharper and larger. There is a prewave on wave 1 on the first sweep, that is probably due to product adsorption on the electrode,⁹⁵ but the second sweep shows the wave takes on strange shapes and repetitive voltammograms have proved it is not reproducible. This is very characteristic of surface adsorption. Waves 1 and 3 remain steady but a cathodic shoulder on wave 3 shows anodic motion. Wave 2 decreases in height, indicating a shift in equilibrium. On the second sweep, wave 2 shifts positively towards the two large round waves that are due to the mercury complex. This could be due to competition between the protonated and unprotonated nitrobenzene radical anions. At .74 M H₂O, waves 2, 4 and 5 shift +56mV, +24mV and +52mV, respectively, while the cathodic shoulder on the steady wave 3 shifts +30mV. The wave anodic of wave 1 is large, indicating a significant increase in that process.

In DMF, Figure 30, there is a dramatic +275 mV anodic shift in the potential of the irreversible wave with .37 M water. Wave 4

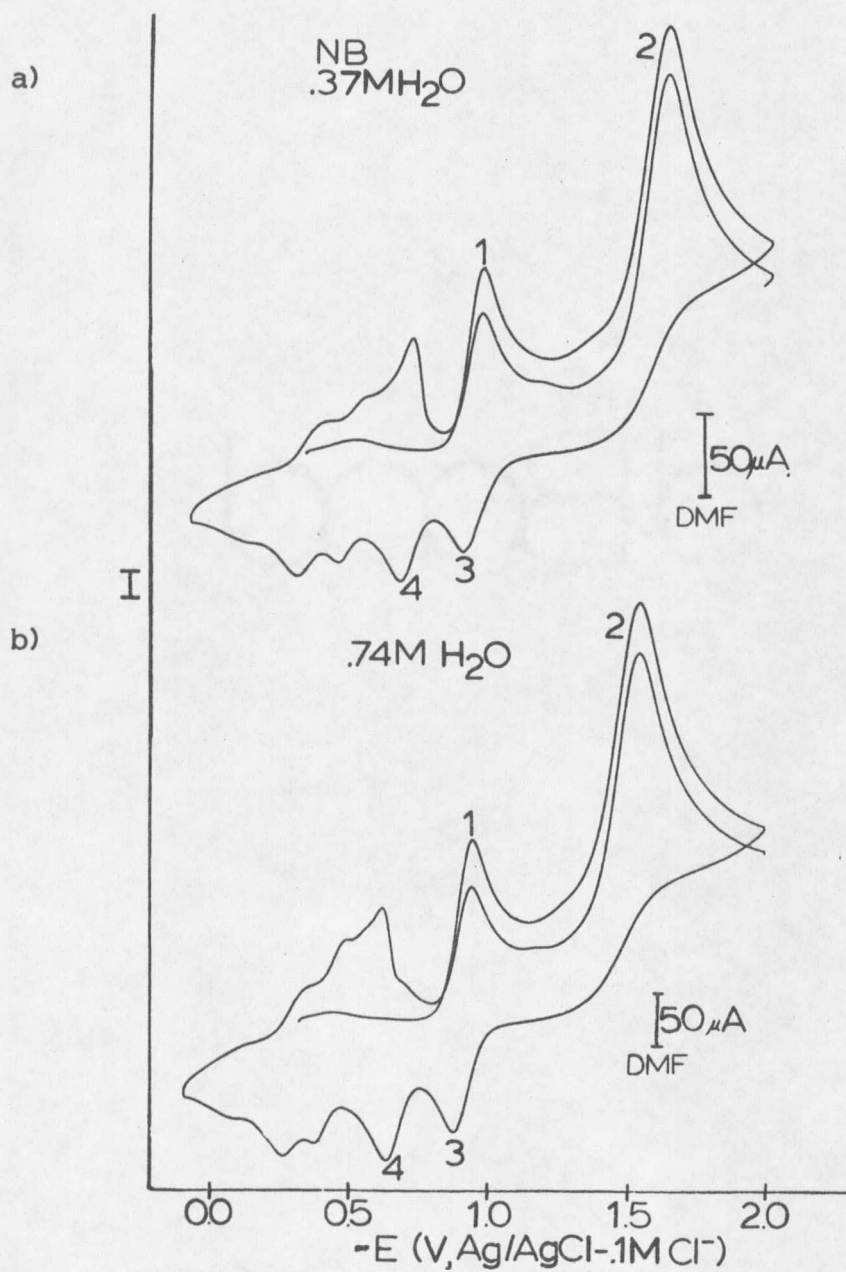


Figure 30. Cyclic voltammograms of nitrobenzene in DMF with a) .37 M H_2O ; b) .74 M H_2O

shifts +42mV, whereas the potentials of the radical anion reversible couple are constant. The mercury complex waves are present anodic of wave 4. It is not known whether both of these oxidation waves are due to the mercury complex or whether one may be surface adsorption. At .74 M, wave 2 shifts +83mV while wave 1 shows a small +17mV shift, that may be due to either liquid junction potential changes or to competition between the protonated and unprotonated species.

Figure 31 is the voltammogram for the addition of water to nitrobenzene in AN. At .37 M H_2O , wave 2 moves +422mV while waves 1 and 3 shift +50mV and +69mV, respectively. Wave 4, the nitroso wave, shifts +104mV. The mercury complex waves showed definite surface interactions. It is noteworthy that nitrosobenzene shows the surface interactions with water addition in AN. Nitrosobenzene in DMSO and DMF with water do not yield a surface wave. This helps us understand that there must be available protons for the mercury compounds to form and that AN must help make the protons more available. At .74 M, the mechanism of reduction unfolds. Waves 1, 2 and 4 move an additional +27mV, +142mV and +33mV, respectively, while wave 3 has split into two waves. The wave that has moved the least has to be the reversible couple since reversibility will not occur if the potentials are too far apart. The most cathodic of the two waves shifts +24mV. Wave 3, at .37 M H_2O , did show broadness. The new

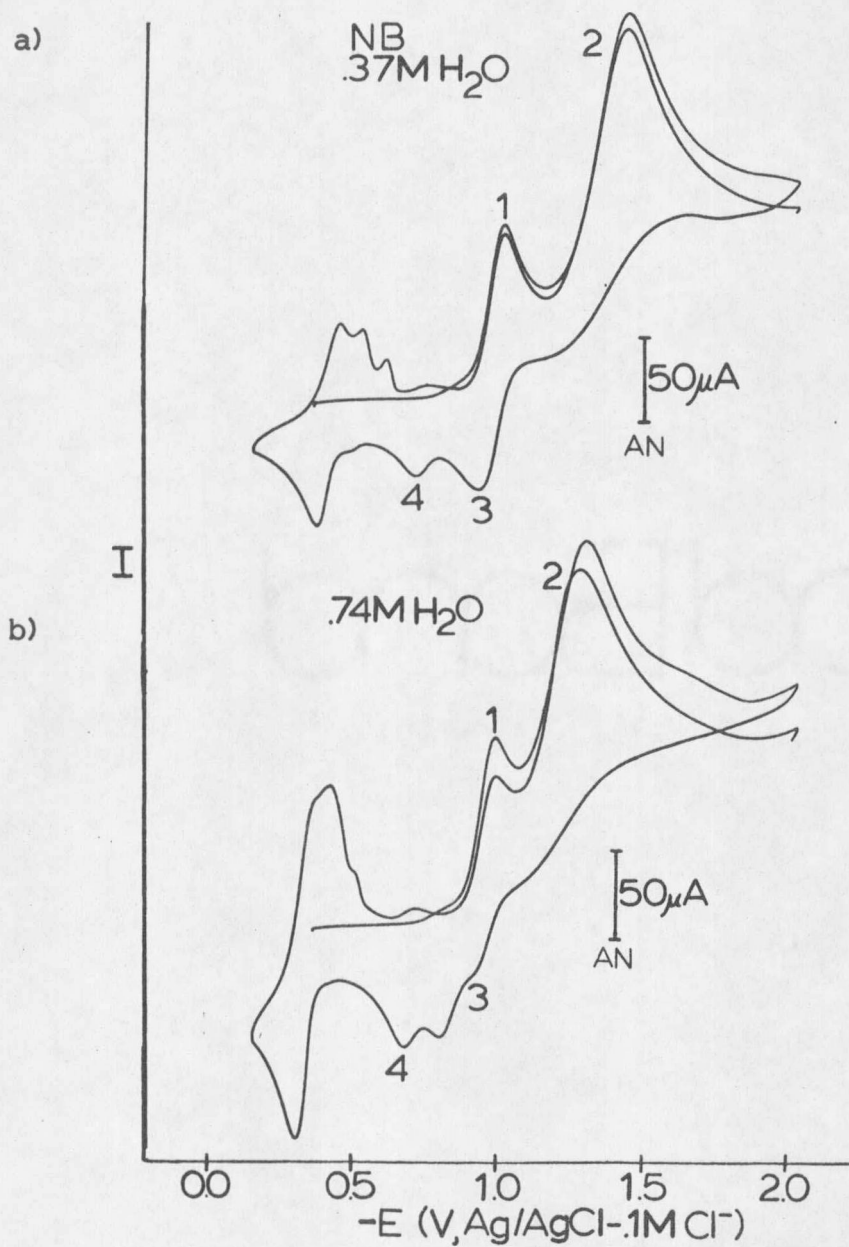


Figure 31. Cyclic voltammograms of nitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

wave is between waves 3 and 4. In the voltammograms of nitrobenzene, a wave was noted cathodic to the wave associated with the oxidation of the radical anion which is thought to be from the E2' process or the E2C3 process (oxidative "hump"). This wave may be shifting into wave 3 and is thus not at .37 M H₂O; but, moves anodically at .74 M H₂O so it is readily apparent. The shift of this wave has been seen in computer simulation studies by R. Geer.⁹⁷

3-Chloronitrobenzene. Cyclic voltammograms for the addition of water to 3-CNB in DMSO appear in Figure 32. At a water concentration of .34 M, waves 1 and 3 remains steady while wave 2 moves anodically by +78mV. Two new waves due to the mercury complex appear. At .74 M, wave 2 shifts +101mV. The wave for the reversible radical anion couple does not shift. The mercury complex waves take on a definite appearance of surface effects (sharpness, irreproducibility, odd-shaped). There is a large preprotonation wave prior to wave 1 that has increased from the lower water concentration. We find that the use of ethanol helps avoid the formation of mercury complexes.

Figure 33 shows the voltammograms for the addition of ethanol (100%) to 3-CNB in DMSO. At .32 M, waves 1 and 3 are constant while wave 2 shifts +110mV. Wave 3 shows a cathodic shoulder that has grown considerably and shifted anodically. This is probably due to the E2' or the C3E2 process since it is too negative to result from

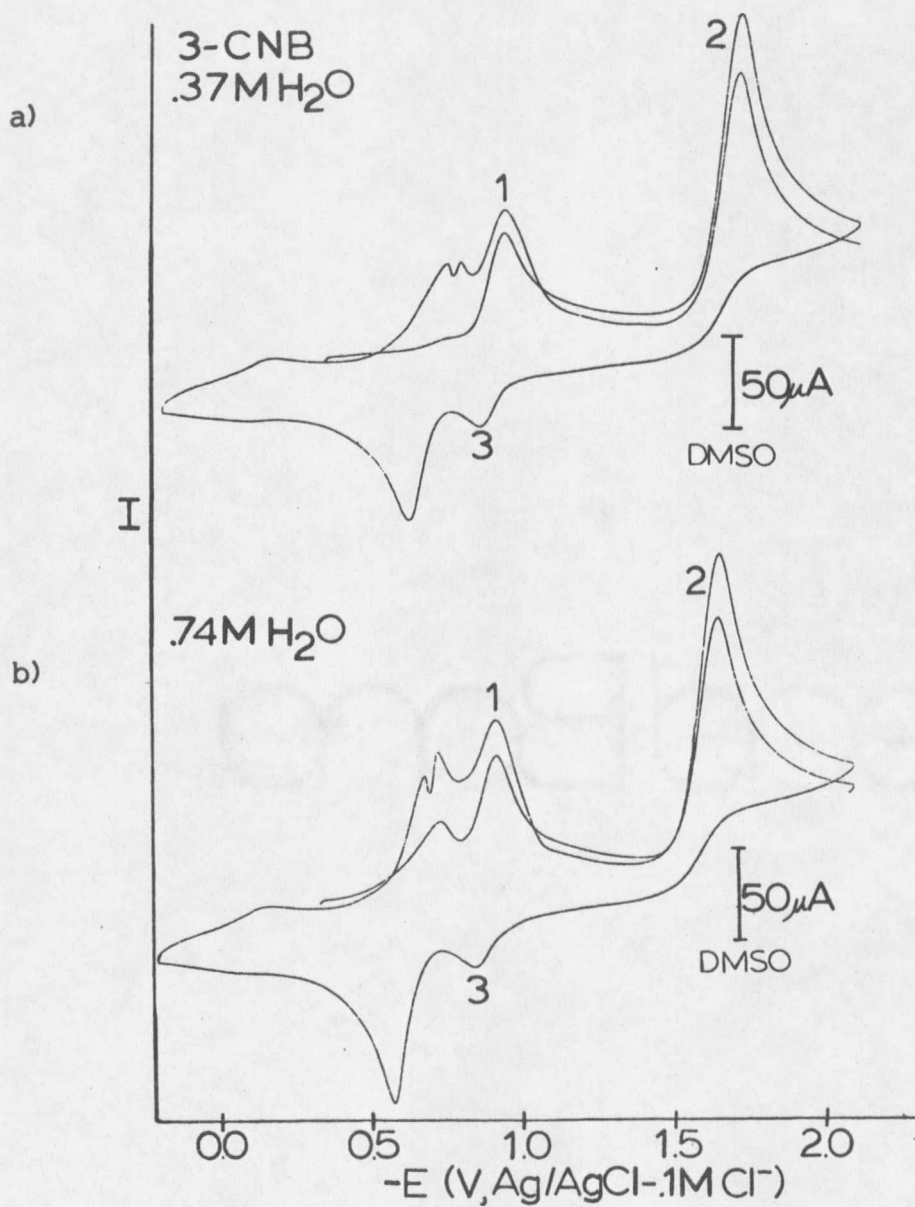


Figure 32. Cyclic voltammograms of 3-chloronitrobenzene in DMSO with a) .37 M H₂O; b) .74 M H₂O.

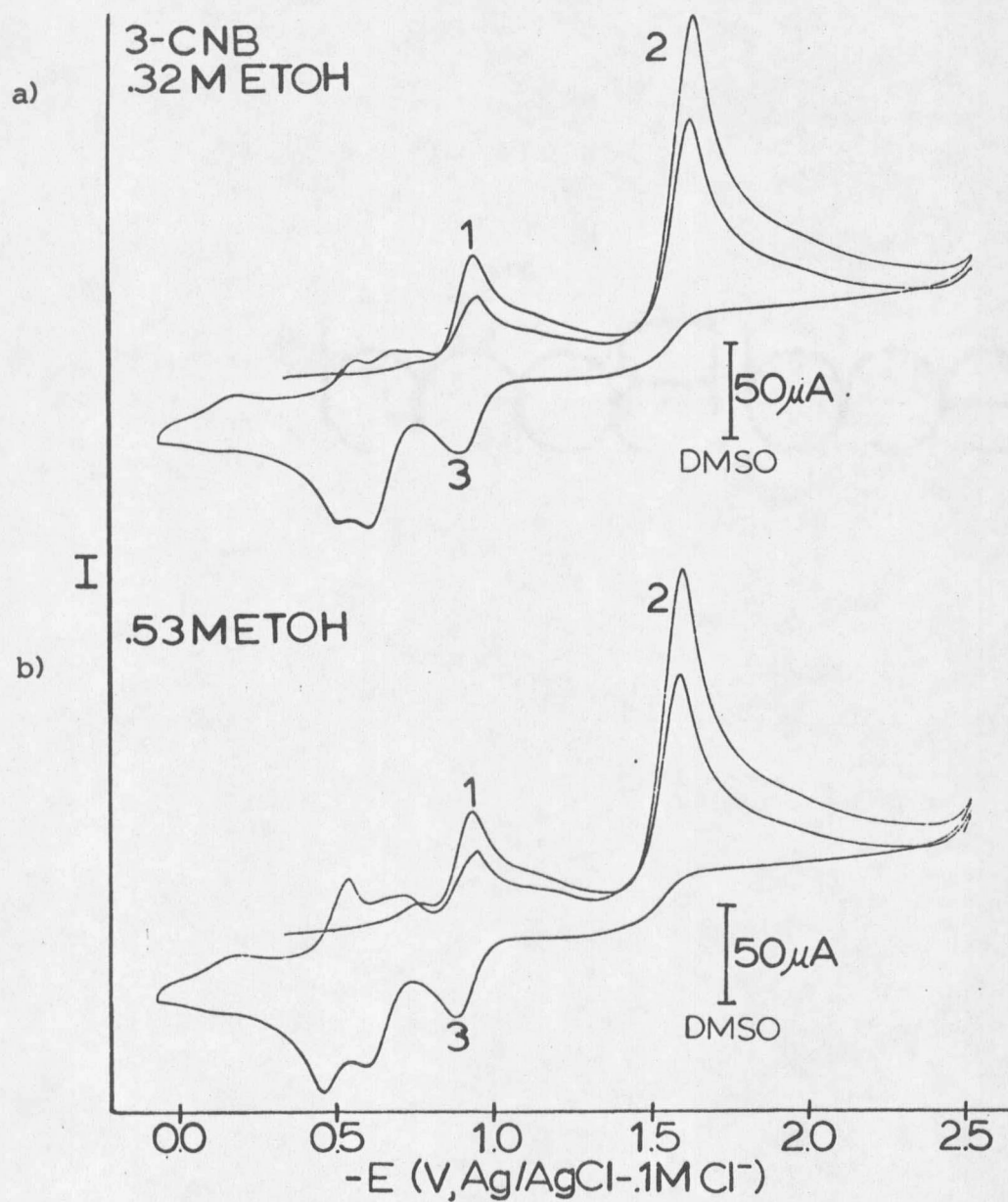


Figure 33. Cyclic voltammograms of 3-chloronitrobenzene in DMSO with a) .32 M EtOH; b) .53 M EtOH.

nitrobenzene. Wave 4 has moved +17mV and a new wave anodic of it has formed, probably a mercury complex due to hydroxide ion. At .53 M, the irreversible wave shifts +78mV. Wave 3 is covered by a shoulder that has shifted +62mV. Wave 4 moves +20mV and a new reversible couple has formed just anodic of wave 4. This could be a surface effect or the oxidation of a protonated species. There are three reductive process for the two oxidative processes. The most cathodic of these is probably the protonated radical anion.

In DMF, the addition of water produces a reversible couple anodic of the nitroso couple, as seen in Figure 34. At .37 M, waves 1 and 3 are steady, but wave 2 shifts +253mV. The prewave on wave 1 due to preprotonation or a surface effect, shifts +67mV. This may be a direct effect of proton availability since the limiting factor in the mechanistic path is the amount of proton source available. The 3-chloronitrosobenzene couple shifts +20mV and increases in size. The reversible couple anodic of the nitroso couple is the mercury complex. It is very broad and faster sweep rates show a more pronounced surface effect. The "hump" cathodic of wave 3 appears to be the protonated dianion oxidation. At .74 M, wave 2 shifts +77mV and the nitroso couple and the new couple grow and shift anodically.

In AN, Figure 35, the shifts in potentials are more pronounced than in DMF or DMSO. At .37 M water, wave 2 moves +312mV. Though

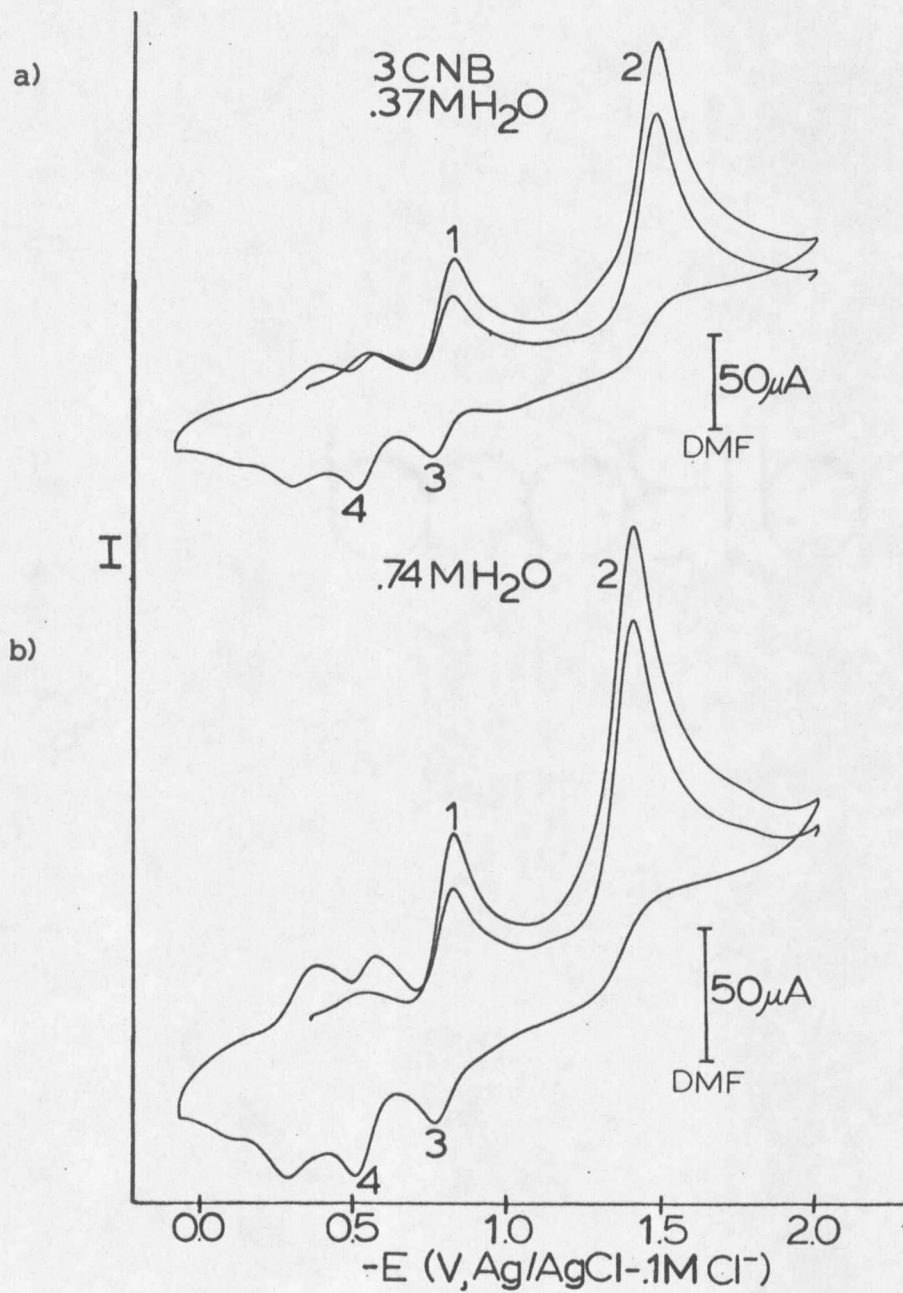


Figure 34. Cyclic voltammograms of 3-chloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

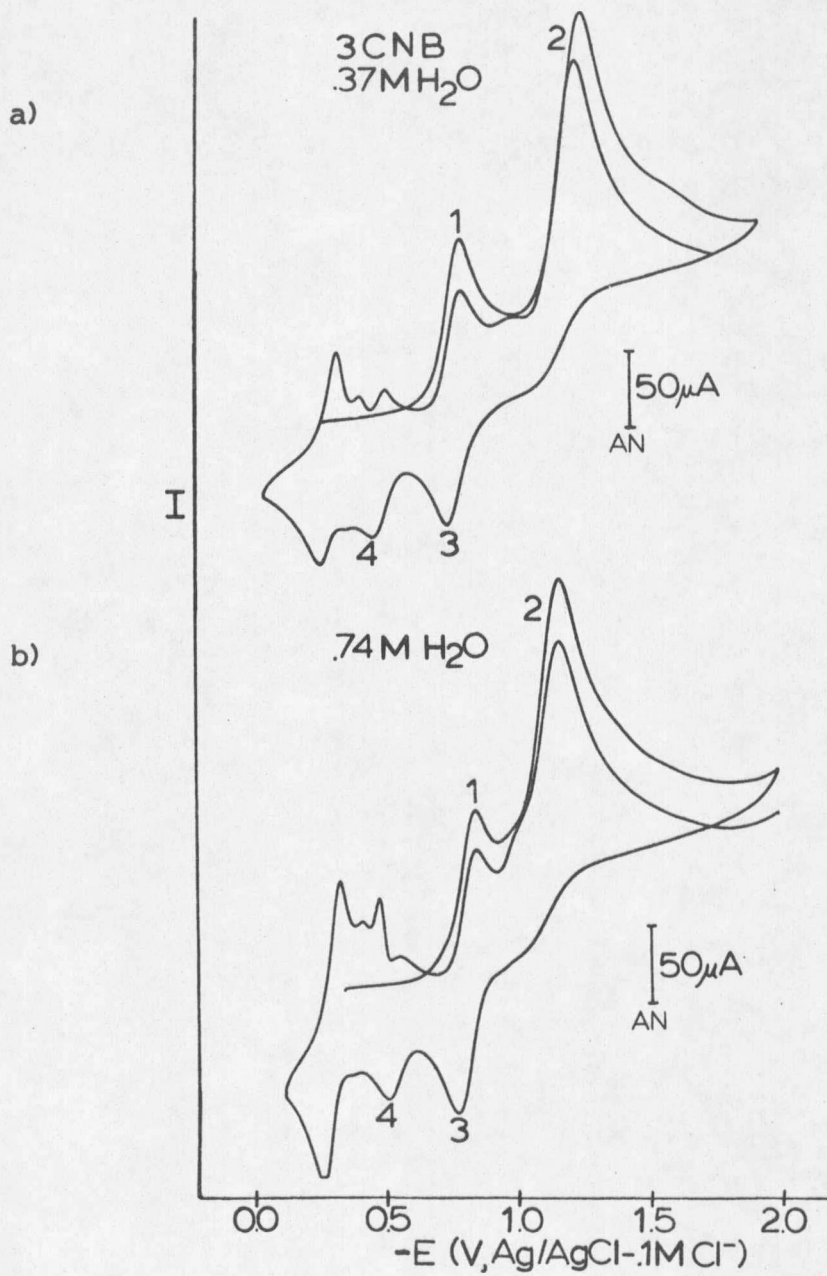


Figure 35. Cyclic voltammograms of 3-chloronitrobenzene in AN with
a) 0.37 M H₂O; b) 0.74 M H₂O.

wave 3 does not move, wave 1 shifts +38mV. It appears that a new wave is forming between 1 and 2 that may cause wave 1 to shift. At .74 M, wave 2 moves +169mV while wave 1 moves +25mV; wave 3 shifts +44mV and wave 4 shifts +24mV. The mercury complex waves appear anodic of wave 4, most likely resulting from the 3-chloronitrosobenzene radical anion oxidation.

4-Chloronitrobenzene. Cyclic voltammograms for experiments having water added to 4-chloronitrobenzene in DMSO appear in Figure 36. Waves 1 and 3 remain relatively steady while wave 2 shifts +119 mV at .37 M H₂O and +50mV more at .74 M H₂O. The cathodic shoulder on wave 3 grew considerably and moves positive with increasing water concentration. The nitroso wave is rounded at the lower water concentration, denoting more than one process; but, this sharpens to the mercury complex wave at the higher water concentration. Note that the mercurous chloride wave decreases with increasing water concentration, indicating a change in the pathway away from chloride loss and probably, towards nitroso formation.

In DMF, Figure 37, the irreversible waves merge at .37 M H₂O and wave 2 shows a shift of +267mV. The nitroso wave increases in size and shifts +38mV. At .74 M, the voltammogram does not appear much different than the previous one. Wave 2 shifts +68mV while the other waves show some slight movements of +10-20mV. Chloride loss

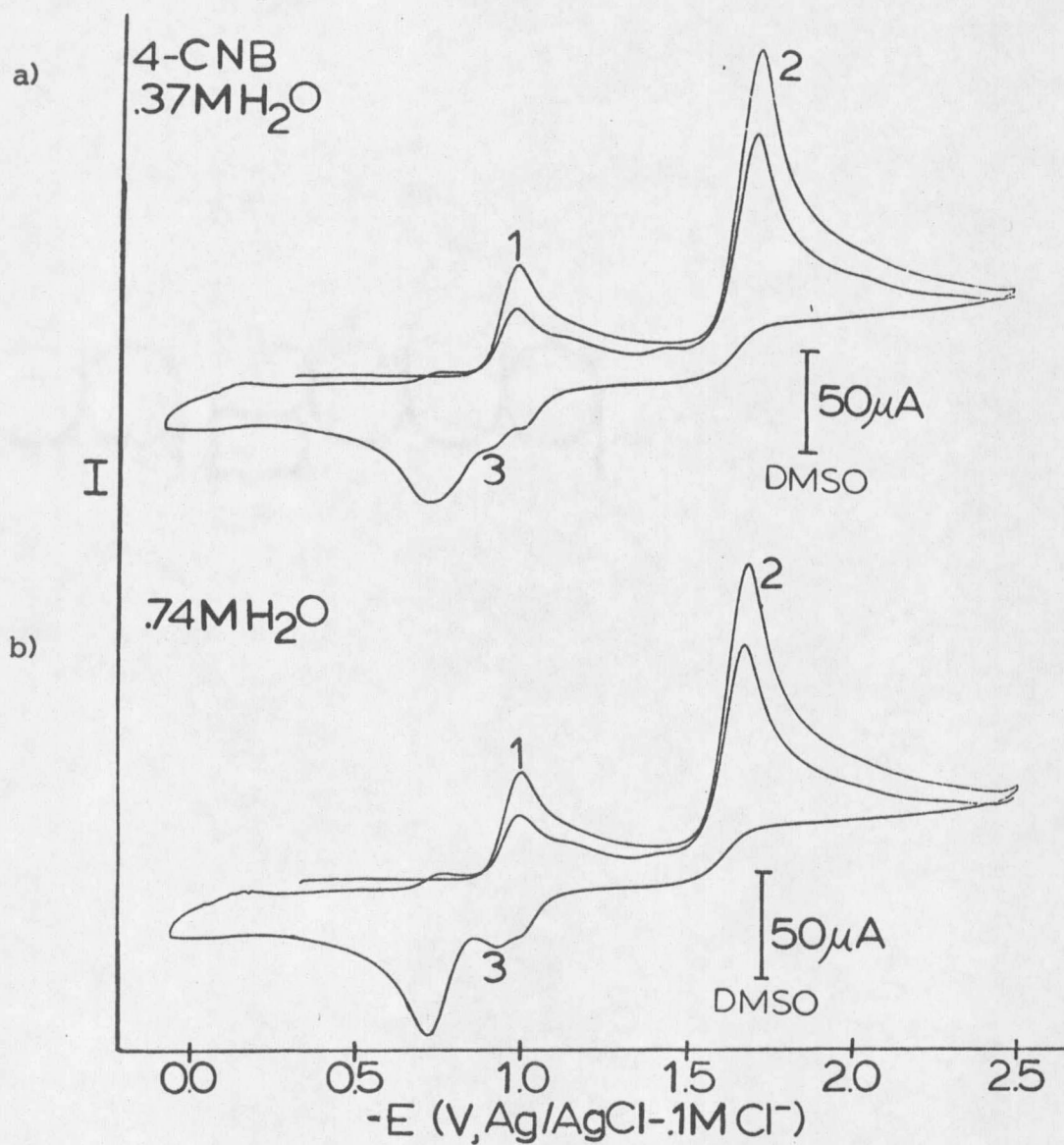


Figure 36. Cyclic voltammograms of 4-chloronitrobenzene in DMSO with a) .37 M H_2O ; b) .74 M H_2O .

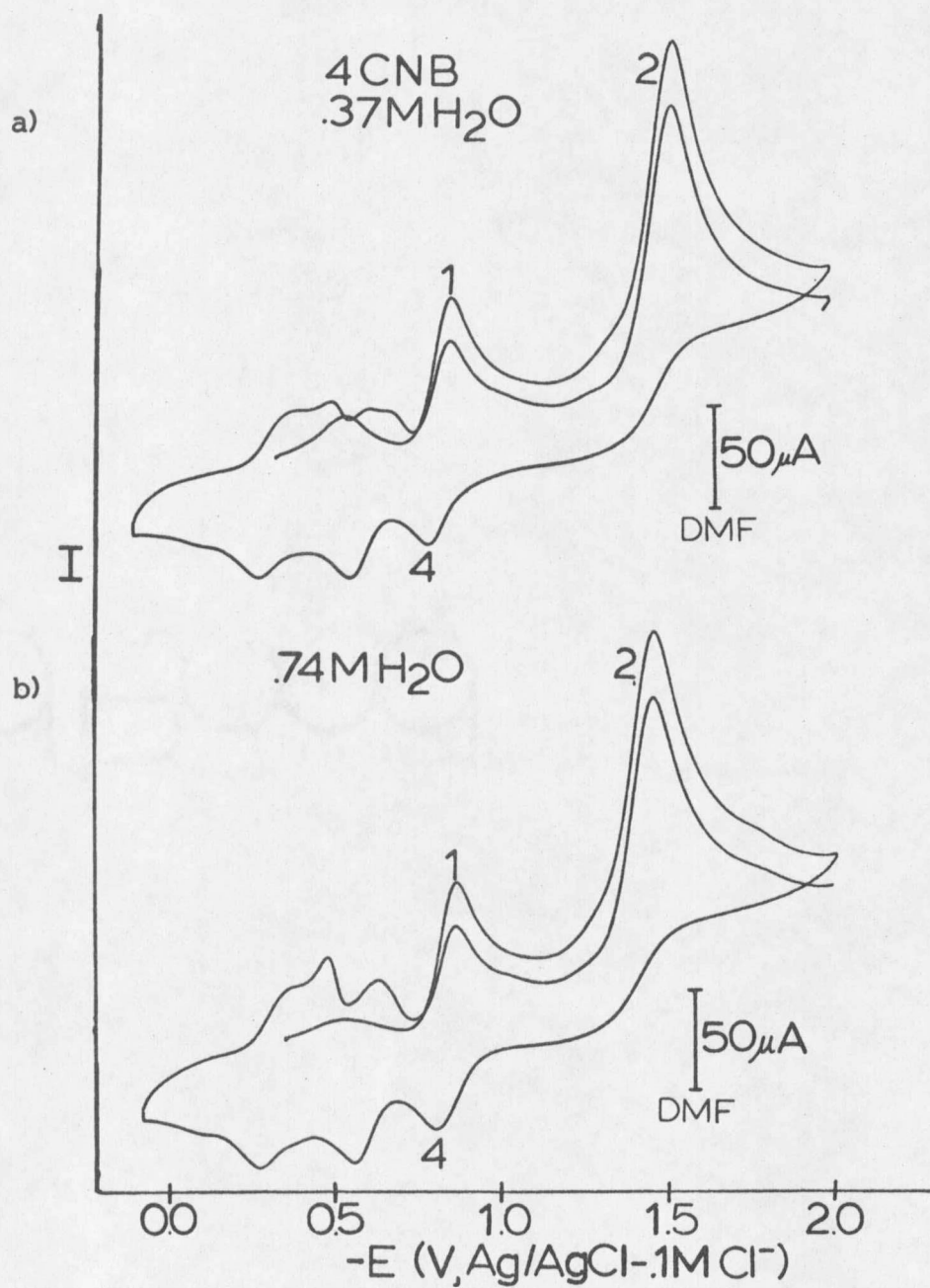


Figure 37. Cyclic voltammograms of 4-chloronitrobenzene in DMF with a) 0.37 M H₂O; b) 0.74 M H₂O.

decreases so that the pathway followed is probably oxidation of a chlorinated nitroso compound.

In AN, Figure 38, wave 2 shifts +365mV while waves 1 and 3 both shift +49mV at a water concentration of .37 M. The wave just anodic of wave 3 is the nitroso wave (4). At .74 M, the only change in the voltammogram is in the potentials. Waves 1, 2, 3 and 4 all shift anodically by +25mV, +118mV, +69mV and +36mV, respectively. The mercury complex waves appear upon the first addition of water and the nitroso formation appears to have increased.

3,4-dichloronitrobenzene. The cyclic voltammograms of 3,4-dichloronitrobenzene (Figure 39) in DMSO yield a change in their appearances upon addition of ethanol. At .35 M, wave 3 shifts +243mV into wave 2 and wave 2 moves +31mV. There appears to be a cathodic shoulder on wave 4, characteristic of the protonated dianion. The new wave, anodic of wave 4, is round and broad denoting two processes. The cathodic end of the wave is probably associated with the nitroso oxidation while the anodic side is the mercury complex. The doubleness of the new wave separates at .70 M and becomes two distinct waves. There is a large preprotonation wave on the anodic shoulder of wave 1. The corresponding oxidation wave would appear under the new waves. The irreversible wave shifts +38mV. Upon extension of the positive limits, the irreproducible reduction waves

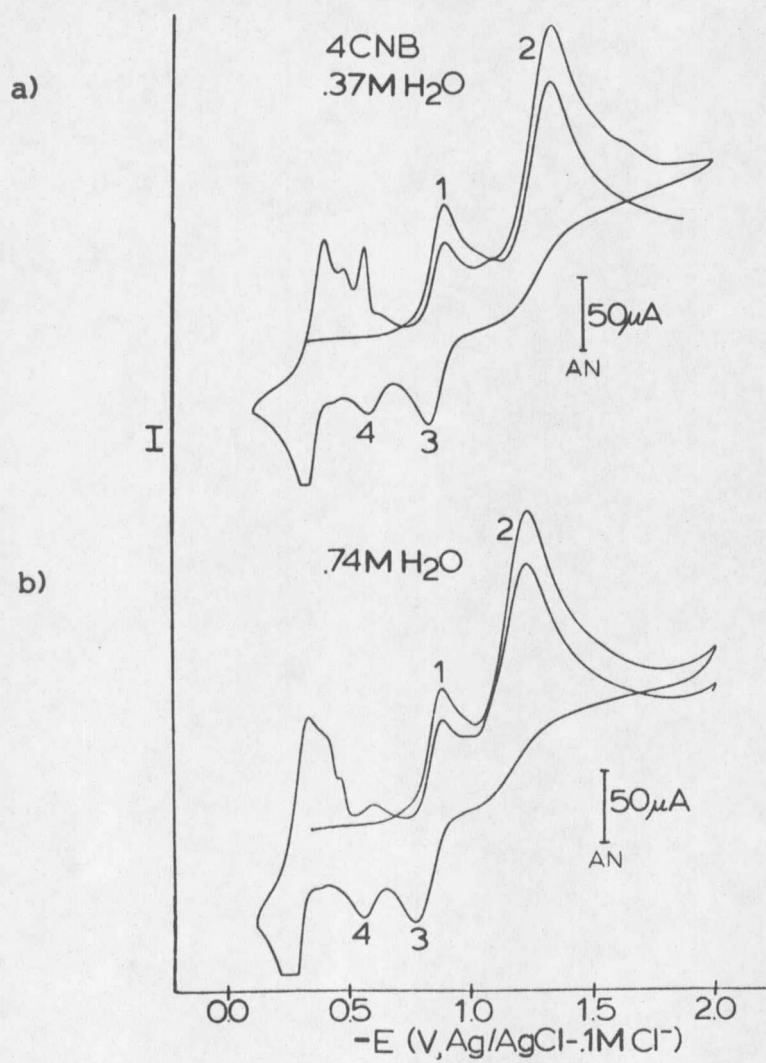


Figure 38. Cyclic voltammograms of 4-chloronitrobenzene in AN with
a) 0.37 M H_2O ; b) 0.74 M H_2O .

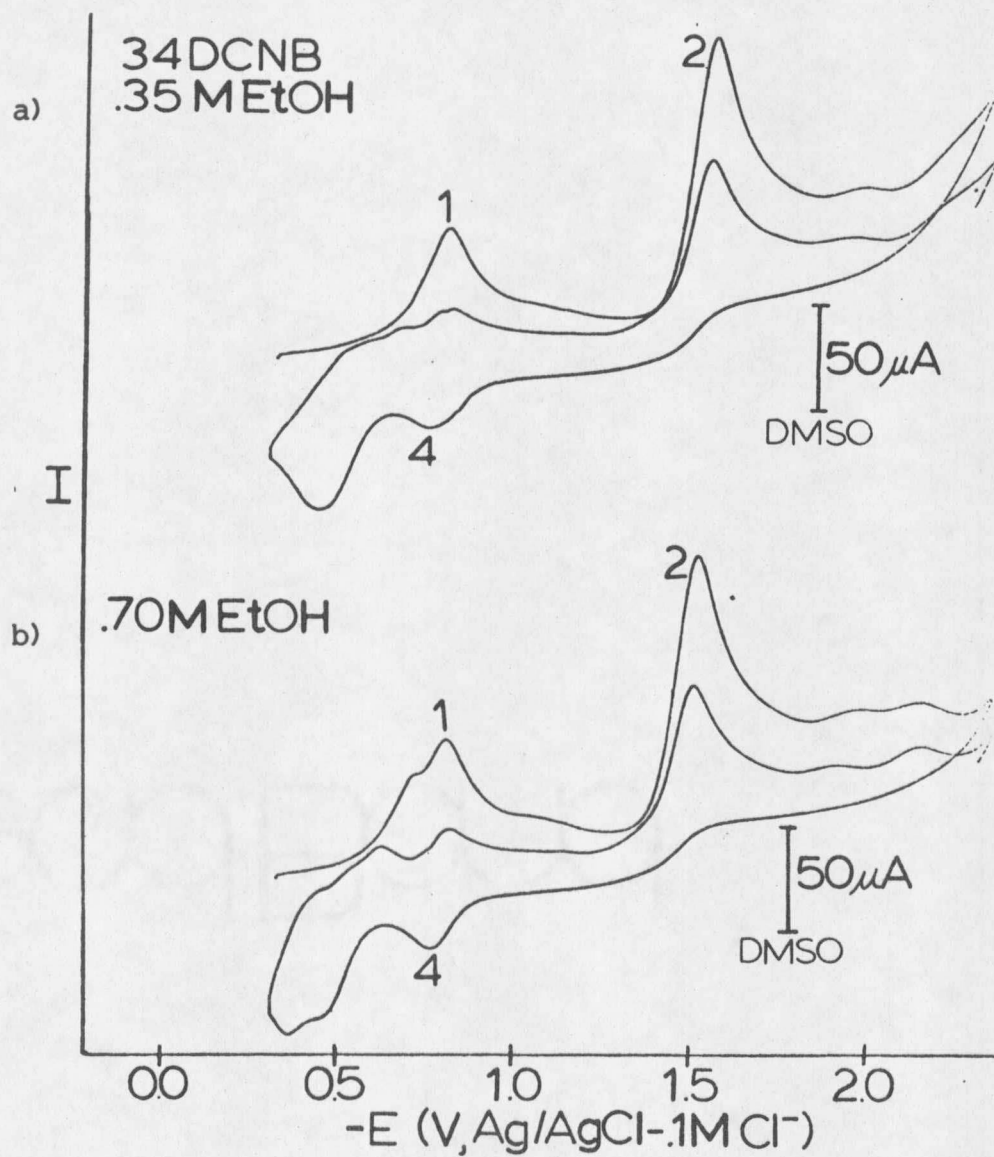


Figure 39. Cyclic voltammograms of 3,4-dichloronitrobenzene in DMSO with a) .35 M EtOH; b) .70 M EtOH.

appear, denoting the surface effects caused by free hydroxide ion-mercury surface. In this case, even though chloride loss still occurs, there is not a separate wave for the less chlorinated dianion. There may be some formation of it under the irreversible wave.

The voltammograms for 3,4-dichloronitrobenzene in DMF with water added are shown in Figure 40. Wave 3 decreases and shifts into wave 2 as this wave moves +125mV. There is more preprotonation and/or adsorption, as is noted by the increase in the prewaves prior to waves 1 and 2. The most cathodic of the new waves appears to be associated with 3-chloronitrosobenzene. The oxidative sweep moves anodically with increasing water concentration. The rate of chloride loss may decrease but chloride loss still occurs.

In AN, the 3,4-dichloronitrobenzene compound shows a +356mV shift in wave 2 with .37 M water (Figure 41). The nitroso wave (4) moves anodically by +72mV. At .74 M, the two waves which were under the one irreversible wave have now moved to the potential of the 3-CNB dianion by shifting +122mV. There is no further loss of chloride.

3,5-dichloronitrobenzene. In DMSO, the cyclic voltammograms of 3,5-DCNB with water added (Figure 42) show large adsorption waves. The two irreversible waves move anodically (not shown) and form one

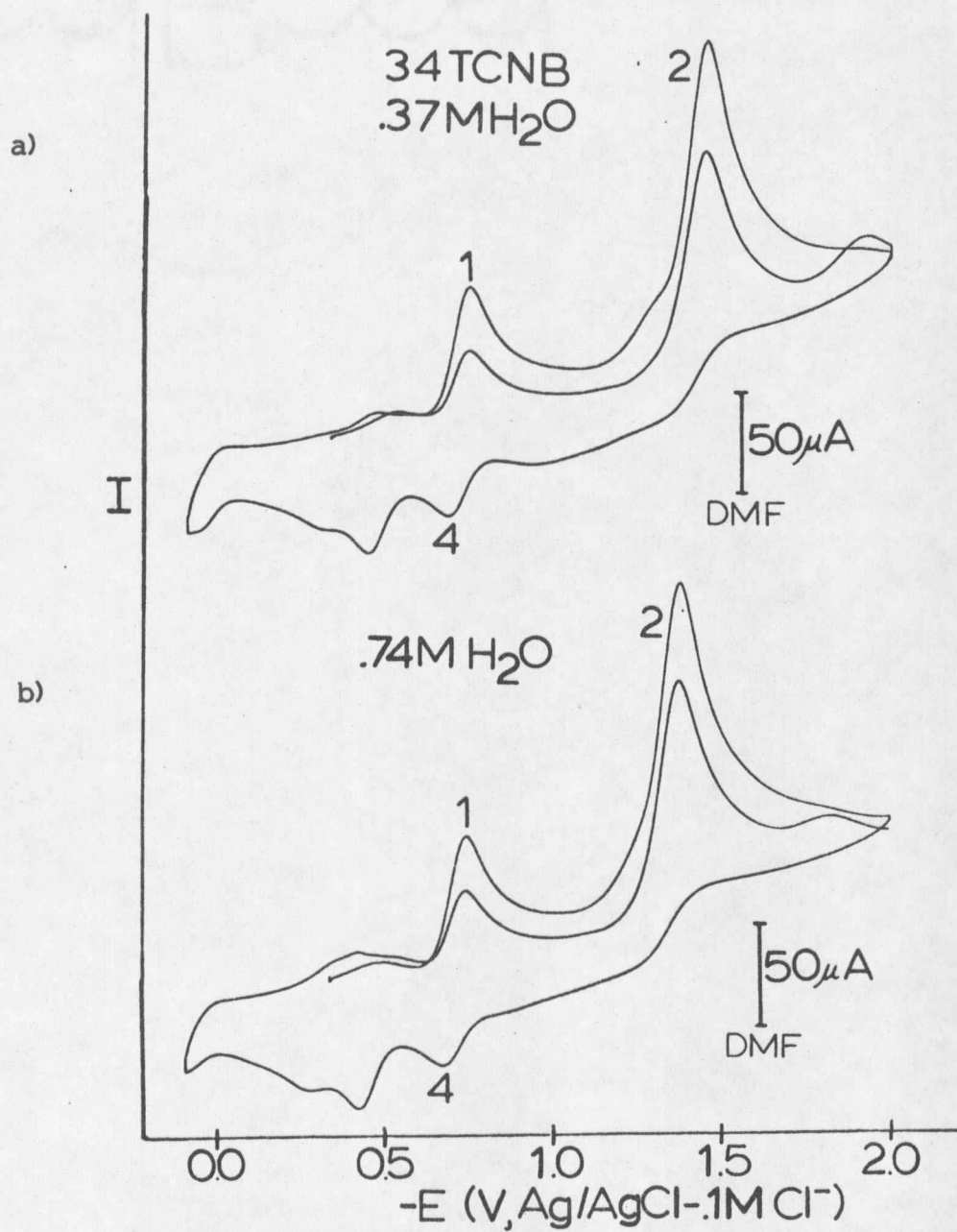


Figure 40. Cyclic voltammograms of 3,4-dichloronitrobenzene in DMF with a) .37 M H_2O ; b) .74 M H_2O .

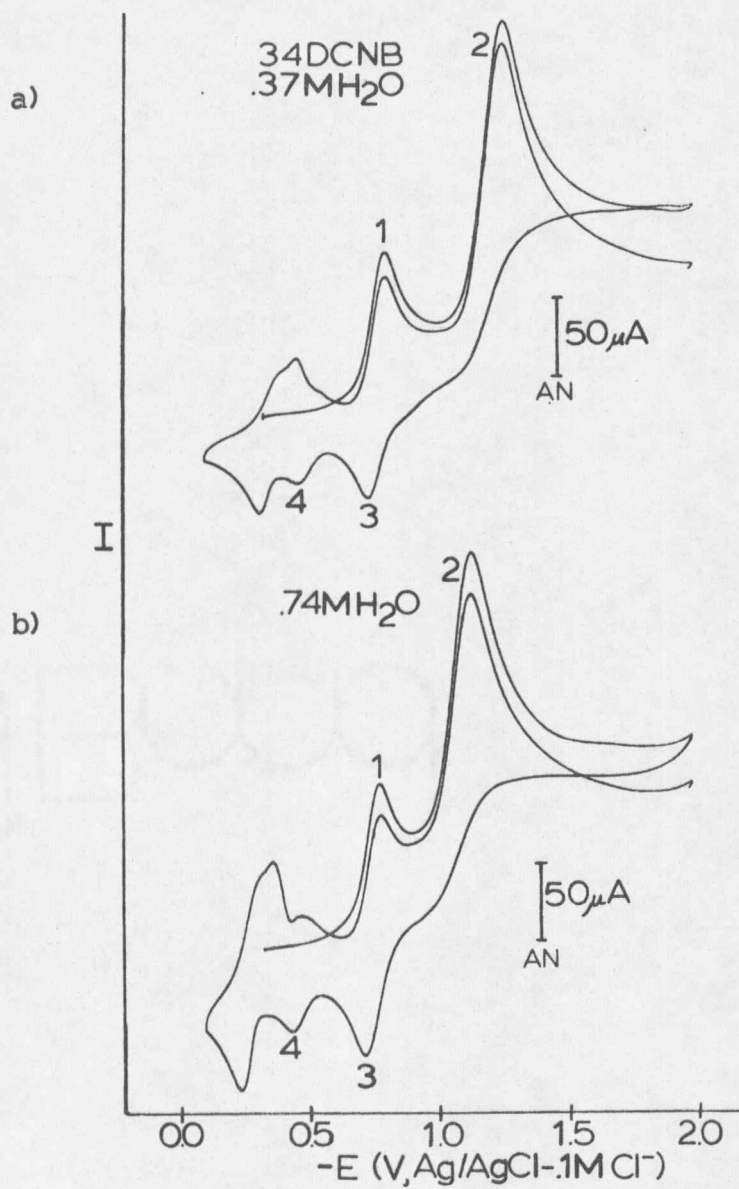


Figure 41. Cyclic voltammograms of 3,4-dichloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

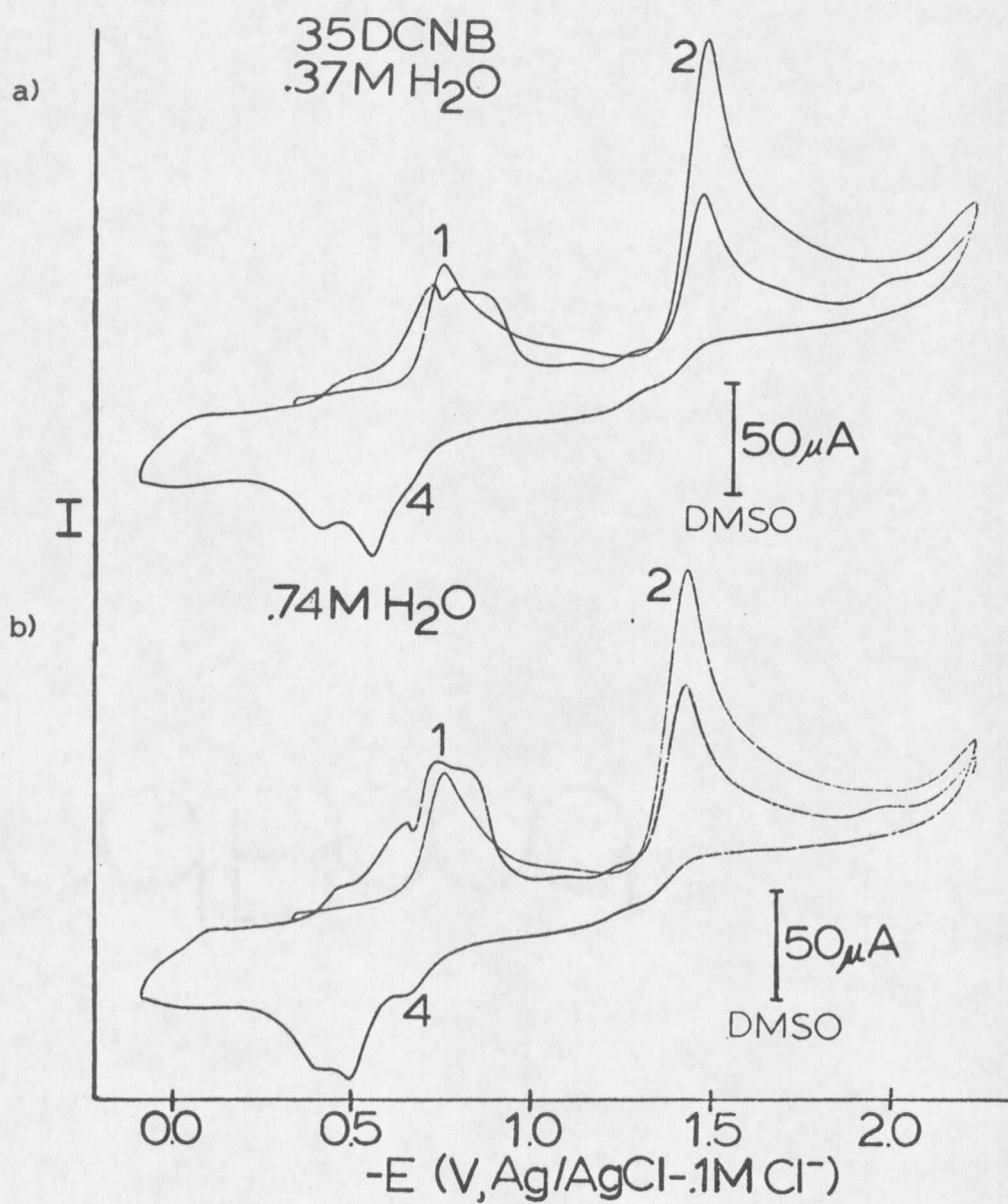


Figure 42. Cyclic voltammograms of 3,5-dichloronitrobenzene in DMSO with a) .37 M H₂O; b) .74 M H₂O.

wave when the water concentration is .37 M. Wave 2 has shifted +104mV. Wave 1 is steady on the first sweep, but the mercury complex and adsorption wave are so large on the second sweep that wave 1 is either obscured or mixed in with the irregular waves. The mercury complex wave is present on the oxidative sweep. There may be some nitroso formation on the cathodic part of the mercury wave. At .74 M water, wave 2 shifts +56mV and the reductive adsorption waves grow. The waves that appear on the second sweep, between waves 1 and 2, may be due to azoxybenzene and azobenzene. The broad cathodic shoulder on wave 1 on the first sweep may be due to adsorption of the reactants or to some 3-CNB radical anion formation if 3-CNB was present as an impurity.

In DMF, Figure 43, addition of water to yield a concentration of .37 M causes a +225mV shift in the potential of wave 2, the dichloro dianion. The wave 4 process decreases but also merges with wave 3. The wave 2 process may increase if it is preprotonation but this wave is obscured by wave 3. The oxidative "hump" grows larger and moves anodically. At higher water concentrations, wave 3 shifts +74mV. Chloride loss decreases rapidly with this shift. The 3,5-DCNB compound has very little chloride loss without water; but, the addition of a proton source pushes the equilibrium towards nitroso formation. The position of the nitroso wave is questionable. It may

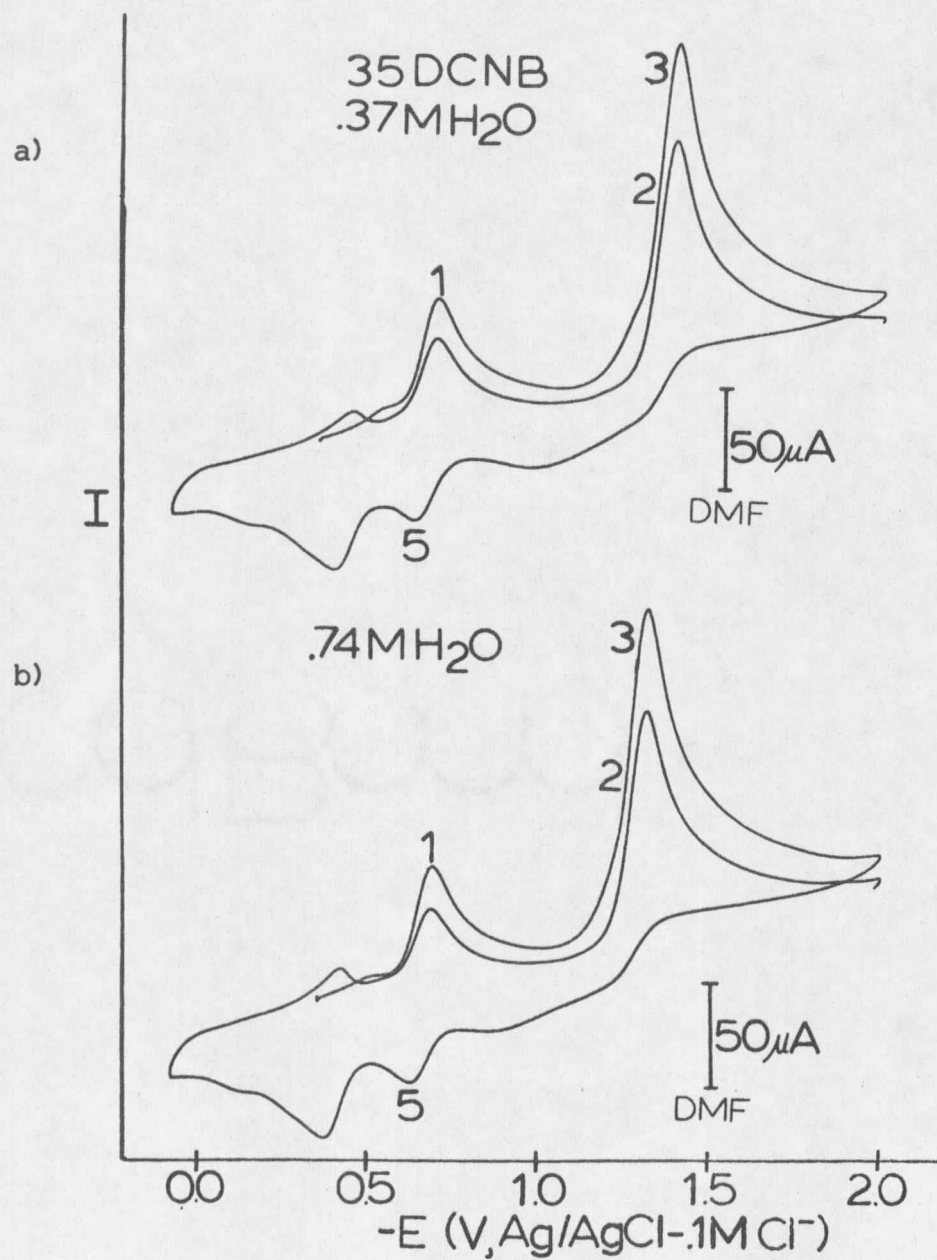


Figure 43. Cyclic voltammograms of 3,5-dichloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

be represented by the new waves or it could be between the new wave and the radical anion wave. The 3,5-dichloronitrosobenzene wave occurs in this area.

In AN, the addition of water to 3,5-dichloronitrobenzene causes quick changes (Figure 44). At .37 M, wave 2 shifted +323mV while waves 1 and 3 shift +30mV and +35mV, respectively. At .74 M, wave 2 continues to shift (+104mV) and there is a cathodic shoulder on waves 1 and 3. These waves are 87mV apart so they cannot represent a reversible couple. The reductive wave may result from surface adsorption and the oxidation wave is associated with the protonated dianion from the E2' process. The cathodic shoulder (wave 4) on the mercury wave may result from nitroso formation.

3,4,5-Trichloronitrobenzene. Cyclic voltammograms for 3,4,5-trichloronitrobenzene with ethanol are shown in Figure 45. Note the shorter positive limit. Waves 3 and 4 merge and move anodically +192mV (from the original wave 3, 3,5-DCNB dianion, potential) and wave 2 becomes a anodic shoulder on wave 3, but it remains steady at .35 M ethanol. At .58 M ethanol, wave 3 shifts +31mV over wave 2. The second sweep yields two waves under wave 3. The first of these waves corresponds to the 3,4,5-TCNB dianion and the second wave represents the 3,5-DCNB dianion formation. Wave 6, the nitroso wave, has grown and is shown as the most anodic wave in the voltammogram.

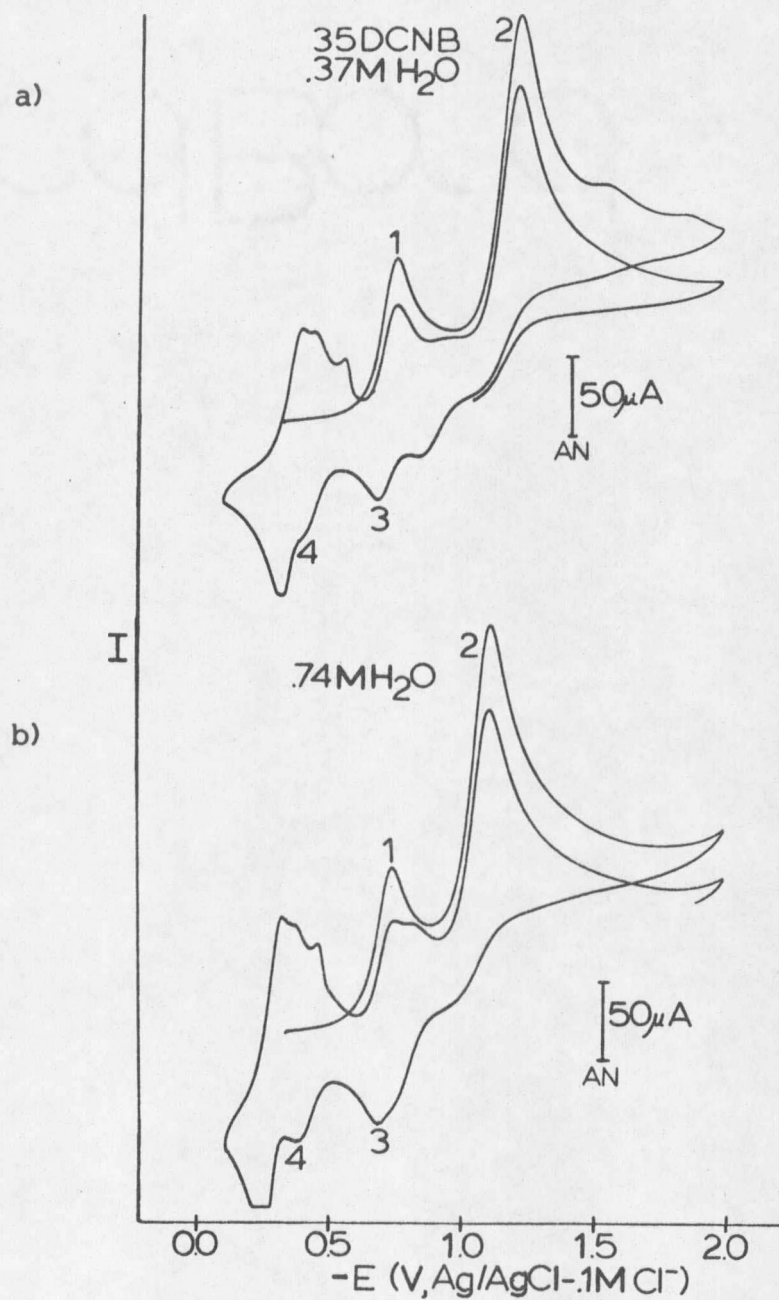


Figure 44. Cyclic voltammograms of 3,5-dichloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

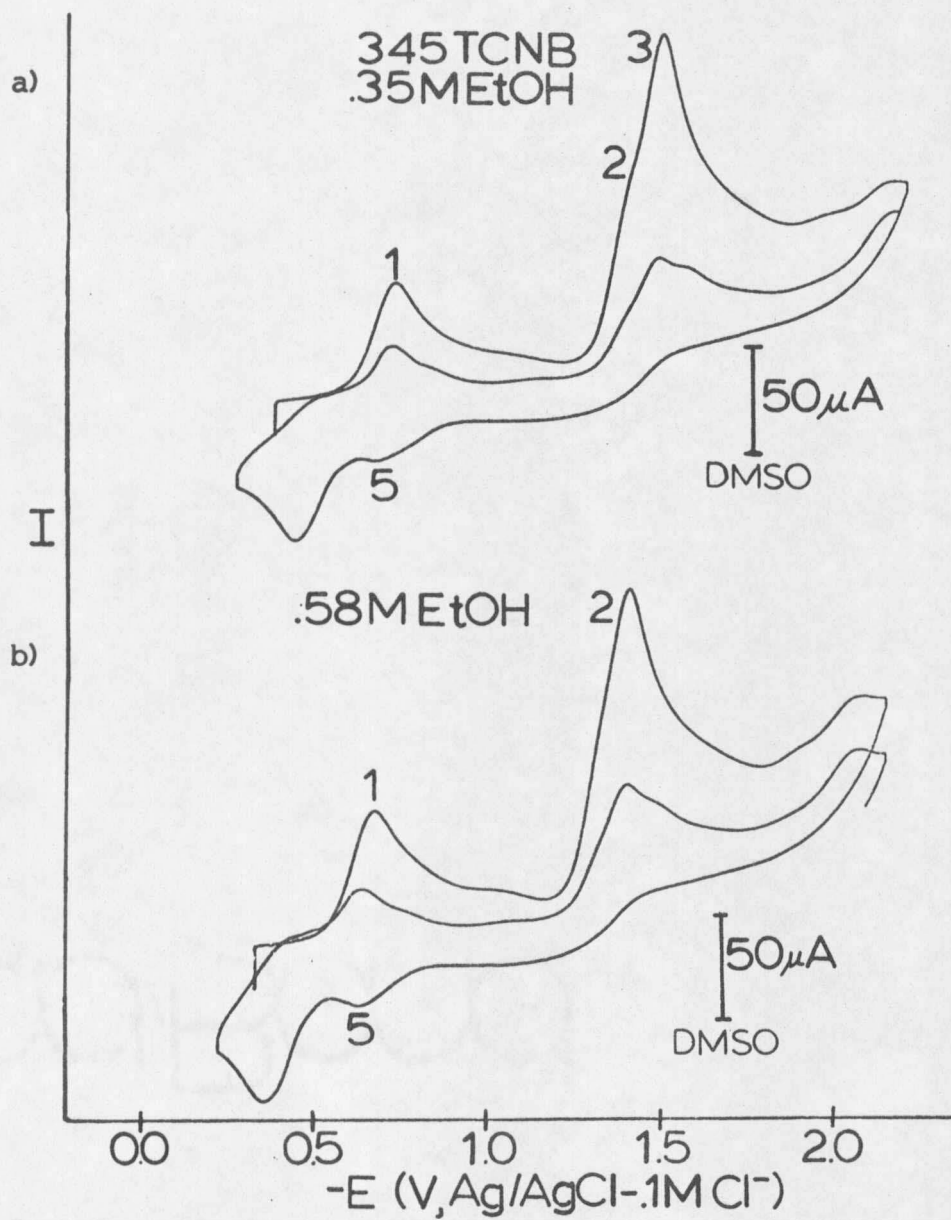


Figure 45. Cyclic voltammograms of 3,4,5-trichloronitrobenzene in DMSO with a) .35 M EtOH; b) .58 M EtOH.

In DMF, Figure 46, the voltammograms of 3,4,5-TCNB with water added to yield a concentration of .37 M, show a decrease in the amount of chloride lost and a +220mV shift in wave 3 while wave 4 merges with it. Wave "a" disappeared or is obscured as wave 3 merges into wave 2. The nitroso wave is quite broad, indicating that both the 3,5-dichloronitroso and 3,4,5-trichloronitrosobenzenes may be present or that the mercury wave may be part of the broad wave. At .74 M, wave 3 shifts +71mV while wave 2 is obscured and apparently does not shift, indicating chloride loss is more rapid than protonation.

In AN, Figure 47, 3,4,5-TCNB with water at .37 M causes waves 2 and 3 to merge and shift +326mV from the initial position of wave 3 or +191mV from wave 2 (original position). Wave 1 shifts +27mV, and wave 5 moves +38mV due to wave 4 pushing on it, as it also shifts +38mV. At .74 M, wave 2 shifts +108mV and wave 4 moved +133mV. The pathway does not change with water addition. The protonated dianion shifts rapidly but there does not appear to be nitroso formation. Here, wave 2 is shifting, indicating a decrease in rate of chloride loss and/or an increase in protonation of the dianion.

Series 2: One Ortho Chlorine

2-Chloronitrobenzene. The addition of water to 2-chloronitrobenzene in DMSO, Figure 48, causes a shift in the potentials of the

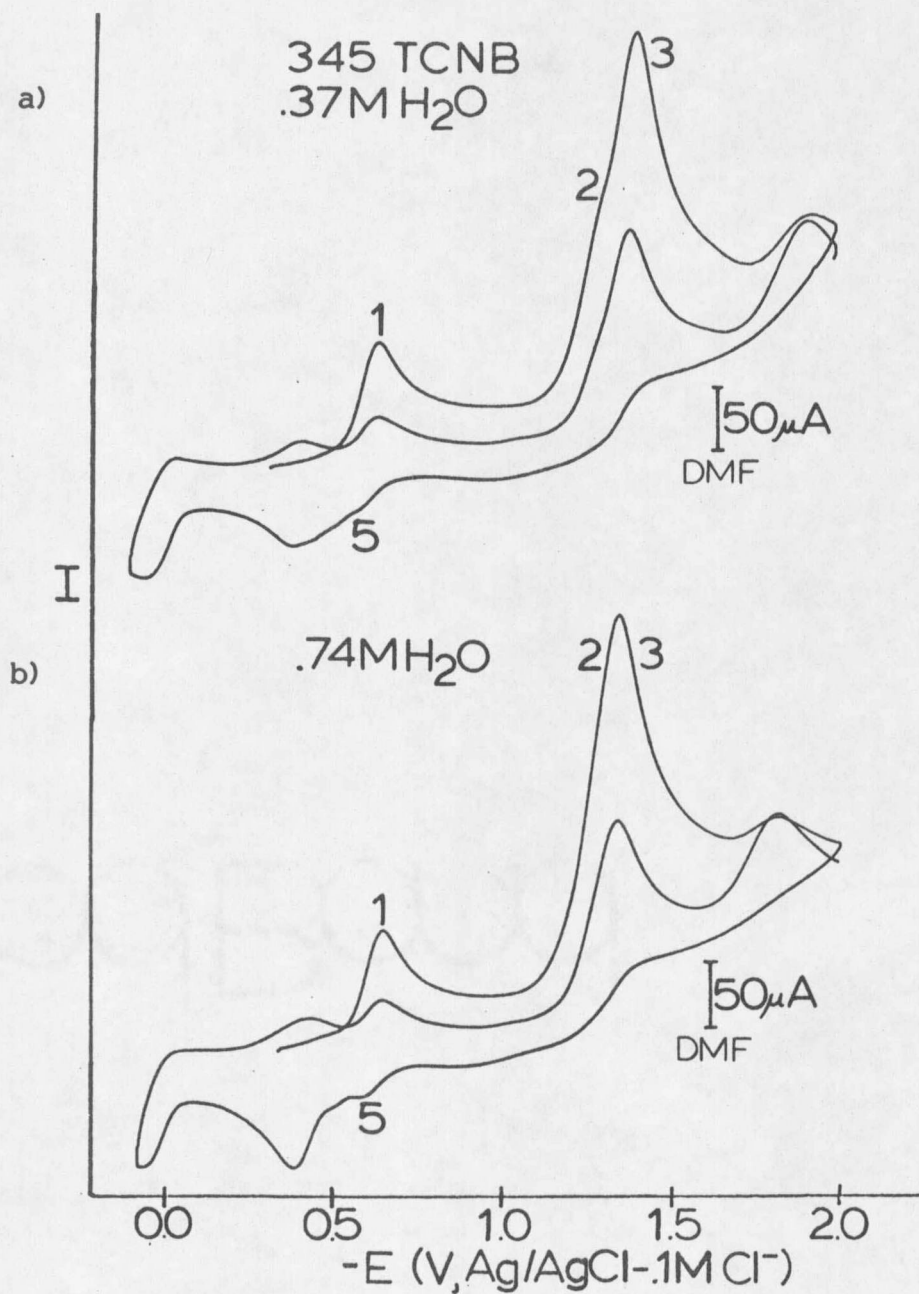


Figure 46. Cyclic voltammograms of 3,4,5-trichloronitrobenzene in DMF with a) 0.37 M H₂O; b) 0.74 M H₂O.

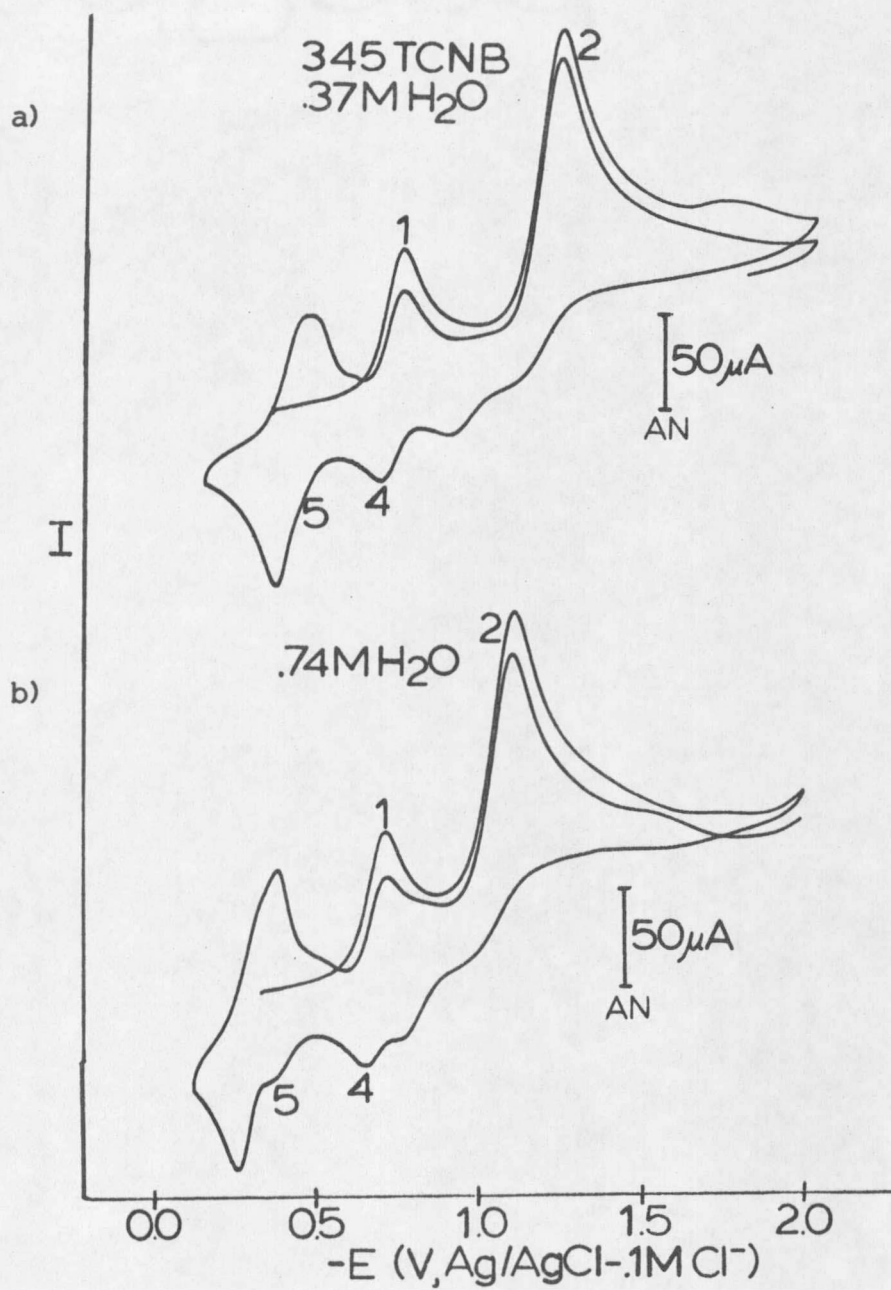


Figure 47. Cyclic voltammograms of 3,4,5-trichloronitrobenzene in AN with a) $0.37 M$ H_2O ; b) $0.74 M$ H_2O .

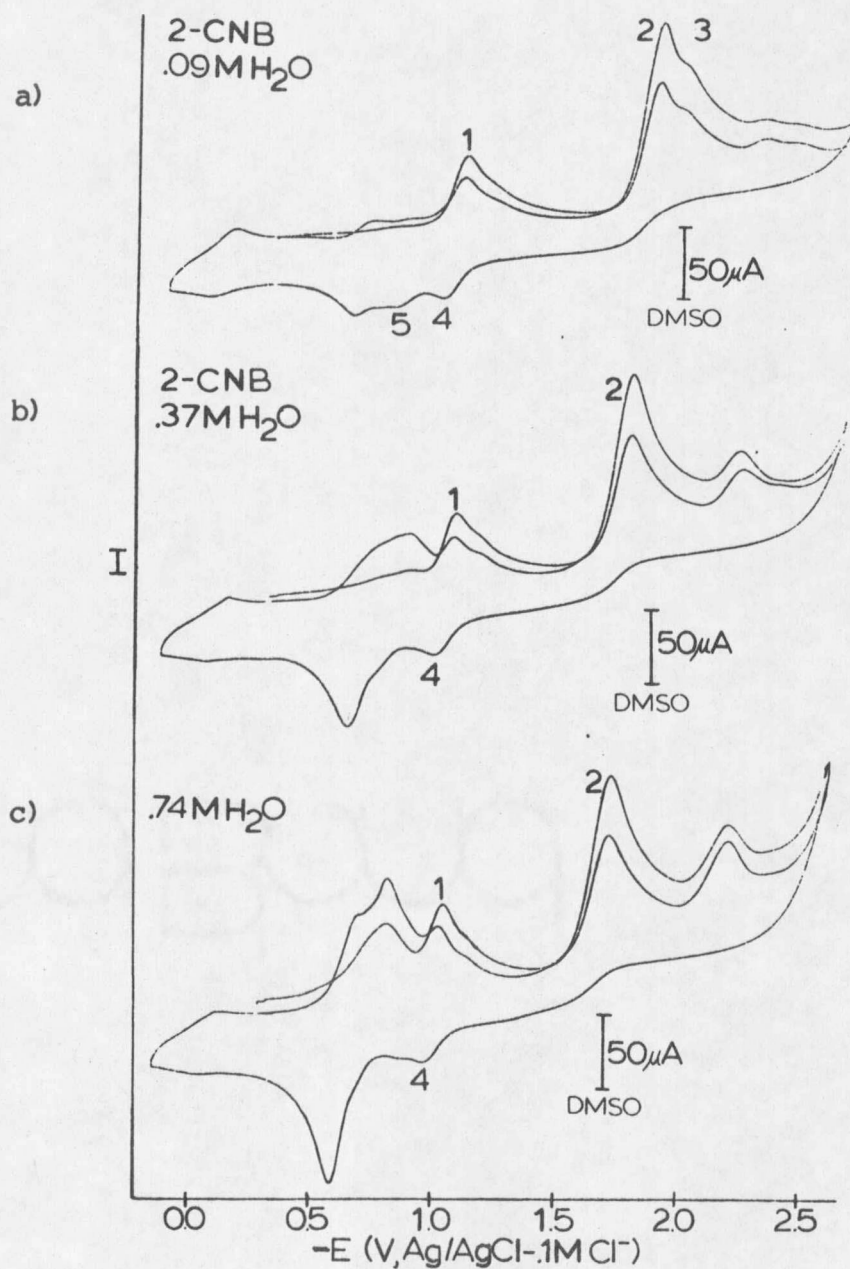


Figure 48. Cyclic voltammogram of 2-chloronitrobenzene in DMSO with
a) .09 M H_2O ; b) .37 M H_2O ; c) .74 M H_2O .

irreversible waves. At .09 M water, the reversible couple remains steady, within experimental error, while both waves 2 and 3 move anodically by +21mV and +73mV, respectively. It is obvious that wave 3 is moving at a faster rate than wave 2. Both processes are now occurring at approximately the same potential. The mercurous chloride wave decreases, marking a shift in the equilibrium between chloride loss and proton addition due to proton availability. The oxidative sweep yields wave 4, the radical anion; wave 5, the nitroso wave; and a new wave that appears to be the mercury complex wave. At .37 M, the mercury complex waves are more noticeable. There appears to be some preprotonation or a residual surface wave prior to wave 1 on the first sweep and the oxidative "hump" is present. Waves 2 and 3 have merged and wave 2 has shifted +99mV. A new wave has formed cathodic of wave 2. This maybe a surface effect. At .74 M, wave 2 shifts +49mV while waves 1 and 4 both shift +20mV, possibly due to changes in liquid junction potential. The total changes in potential for wave 2 from background water (.02 M) to .74 M water is +143mV.

In DMF, the addition of water causes some quick changes in the voltammograms (Figure 49). At .37 M, wave 3 has merged into wave 2 and wave 2 has shifted +196mV. Waves 1 and 4 are steady while wave 5, the nitrosobenzene wave, no longer exists since the rate of chloride loss has decreased and nitrosobenzene does not form. However, the

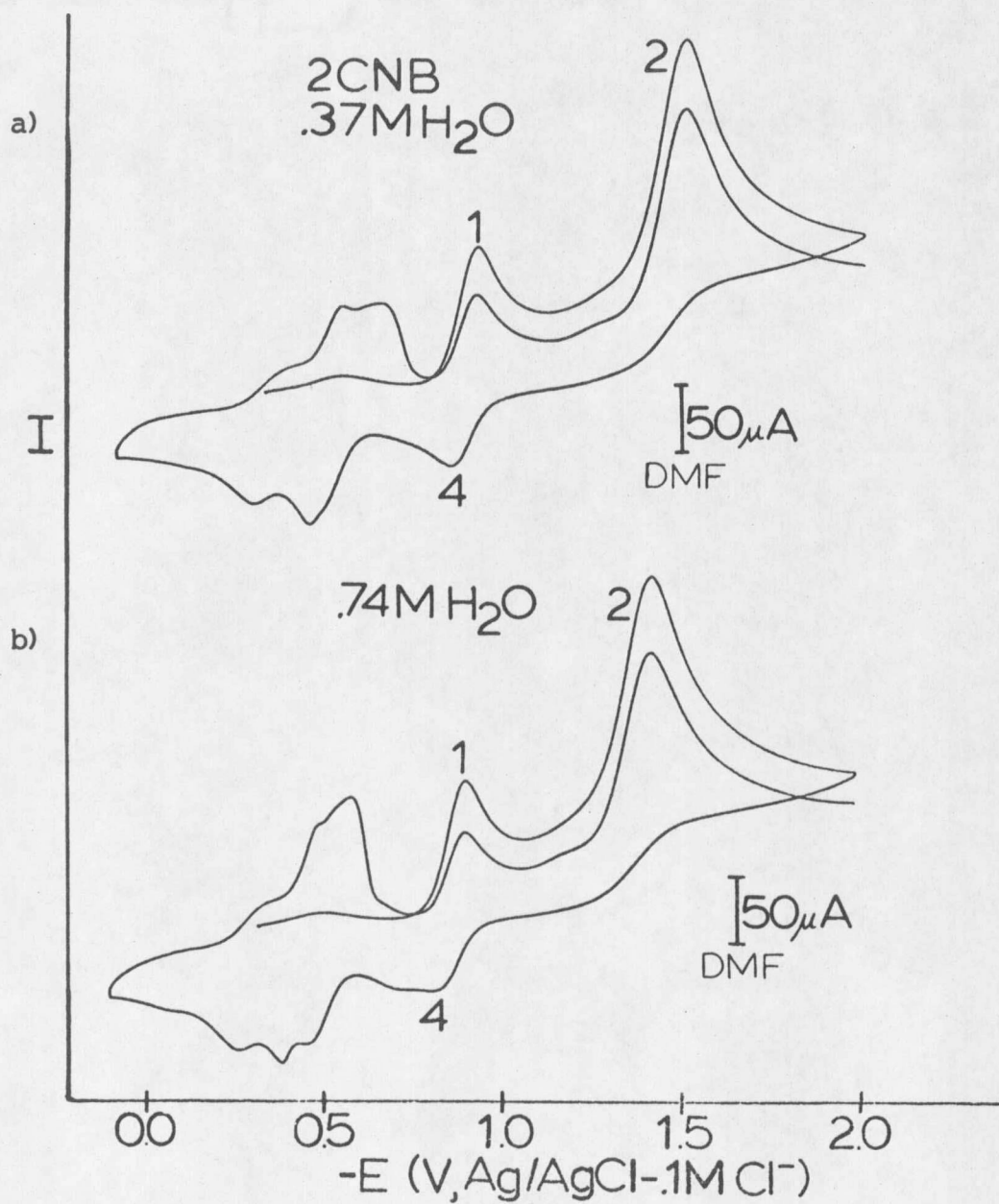


Figure 49. Cyclic voltammograms of 2-chloronitrobenzene in DMF with a) . $37 M H_2O$; b) . $74 M H_2O$.

formation of 2-chloronitrosobenzene is strongly favored. At .37 M, the cathodic shoulder on the new wave (mercury complex) anodic of wave 4 corresponds to the oxidation of the 2-chloronitrosobenzene radical anion. At .74 M, wave 2 shifts +65mV and wave 4 moves +30mV with a new wave appearing just anodic of its peak. This is probably the oxidative "hump" (C3E3 process) which has shifted anodically. The C3E2 process is known, by computer simulating to move rapidly with proton addition.⁹⁷ At .37 M, it is under wave 4; but, with more available protons, it moves anodically and increased in size.

In AN, Figure 50, .37 M water shifts the irreversible wave +370mV. The reversible couple, waves 1 and 3, shift +32mV. There is a new wave just anodic of wave 3 that is probably the oxidative "hump" shifts anodically. Wave 4, the 2-chloronitrosobenzene wave, shifts +69mV, but its reduction wave is covered by the mercury complexation wave or is the wave (4) anodic of the oxidative "hump." At .74 M, waves 1 and 3 shift +76mV and +29mV, respectively, while wave 2 moves +112mV. The shift in wave 1 is most likely due to the approaching wave 2. Wave 2 has shifted a total of +580mV.

2,3-dichloronitrobenzene. The addition of water to 2,3-dichloronitrobenzene in DMSO, Figure 51, demonstrates a change in the mechanistic path. At .37 M, waves 1 and 2 remain steady but wave 3 shifts positive by +88mV while the wave 4 process no longer occurs.

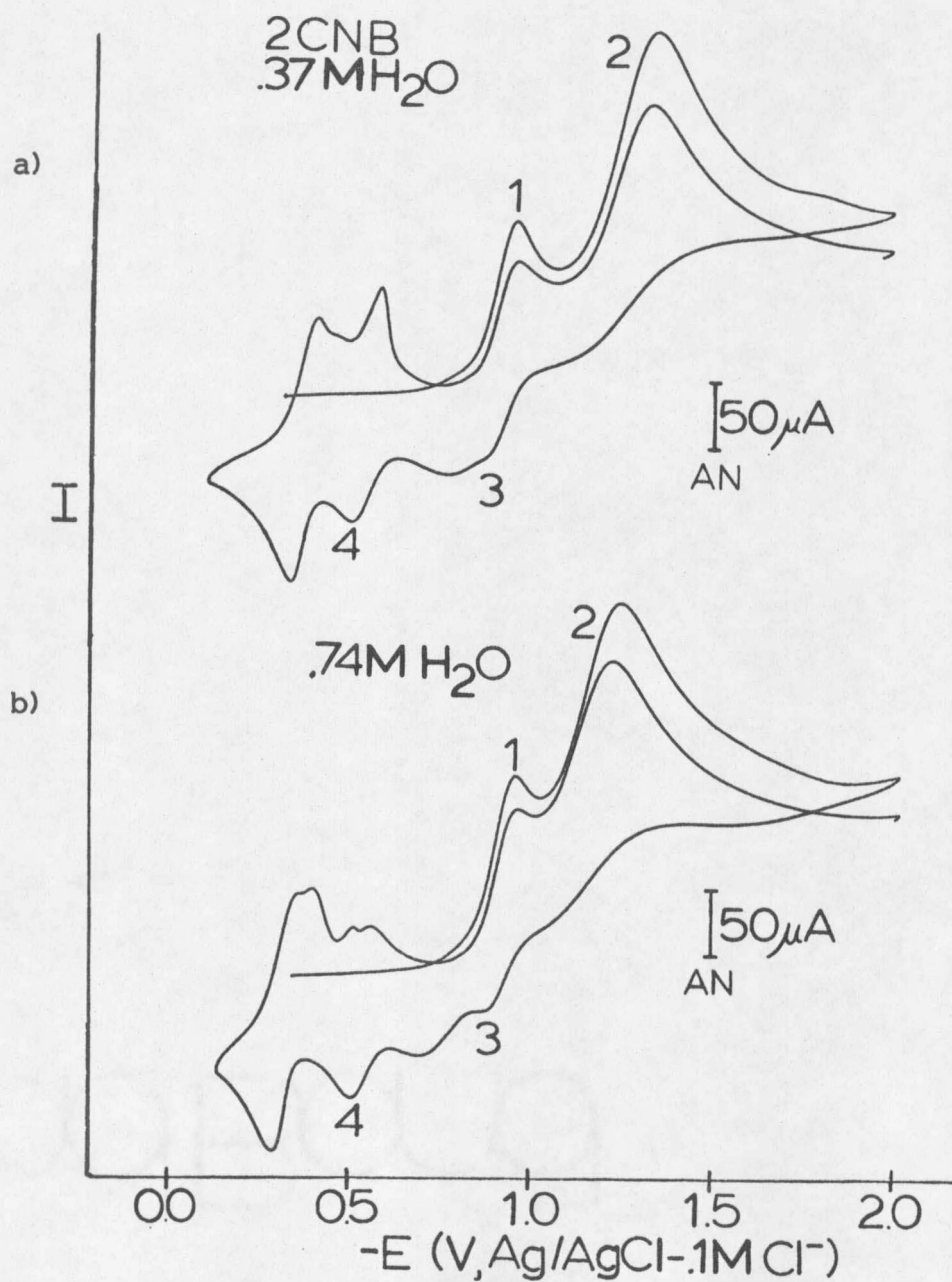


Figure 50. Cyclic voltammograms of 2-chloronitrobenzene in AN with a) 0.37 M H₂O; b) 0.74 M H₂O.

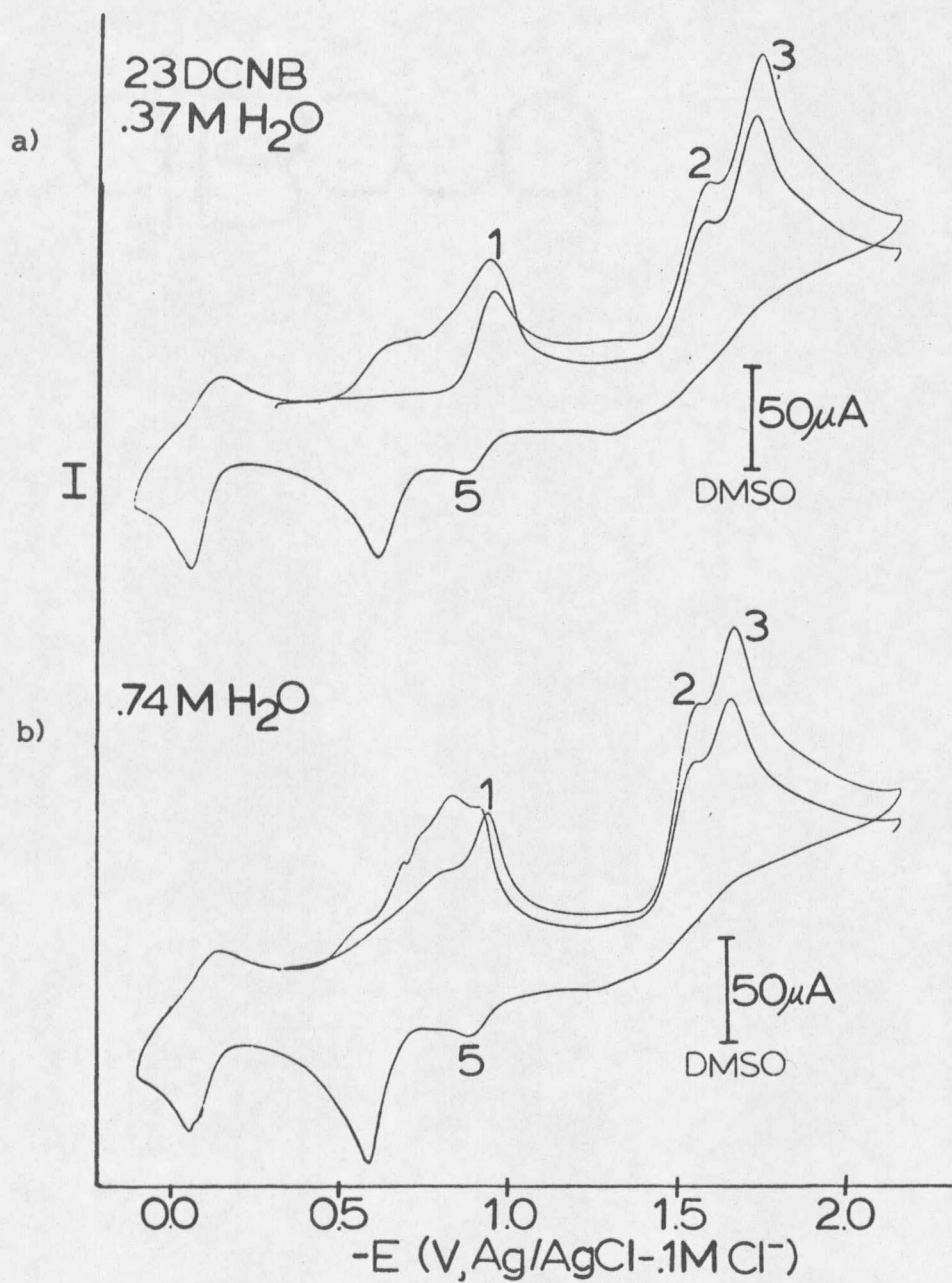


Figure 51. Cyclic voltammograms of 2,3-dichloronitrobenzene in DMSO with a) 0.37 M H₂O; b) 0.74 M H₂O.

This means the mono-chloro compound is formed but not nitrobenzene. There appears to be competition between loss of the ortho and meta chlorines, since at the lower water concentration the 2-CNB dianion formation predominates; but, at .74 M water the 3-CNB dianion formation dominates.

In DMF, Figure 52, waves 1 and 5 remain steady while the wave 4 process no longer occurs at .37 M water and wave 3 shifts +226mV, nearly into wave 2 that has shifted +26mV. At .74 M, wave 2 shifts +90mV and wave 3 merges into it. There is one irreversible wave on the first sweep but the second sweep shows that two processes are actually occurring. The rate of chloride loss may be decreasing. The second irreversible wave is the formation of the 3-CNB dianion. This probably is a slow process at high water concentrations. There is some formation of 2,3-dichloronitrosobenzene.

In AN, Figure 53, all waves shift anodically. Wave 1 moves +31mV at .37 M and wave 4 shifts +48mV. Wave 3 moves into wave 2 while it shifts +257mV. At .74 M, wave 2 shifts +134mV and moves into wave 1. Wave 1 remains steady but wave 4, its reversible counterpart, shifts +110mV, meaning that more than one process is occurring at the potential of wave 4. The wave from the E2' process may be shifting into it. The wave just anodic of wave 4 may be a nitroso wave or part of the mercury complex.

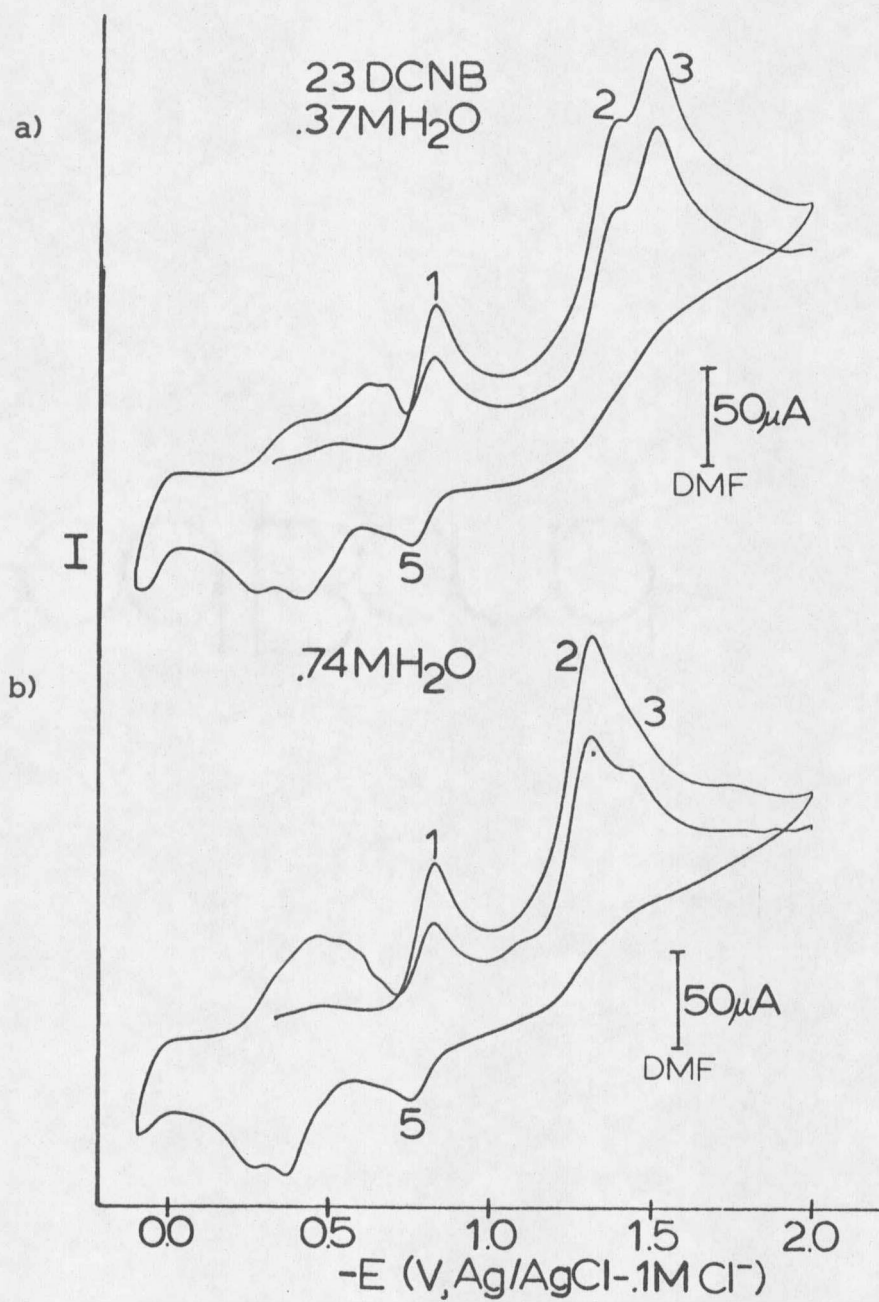


Figure 52. Cyclic voltammograms of 2,3-dichloronitrobenzene in DMF with a) .37 M H_2O ; b) .74 M H_2O .

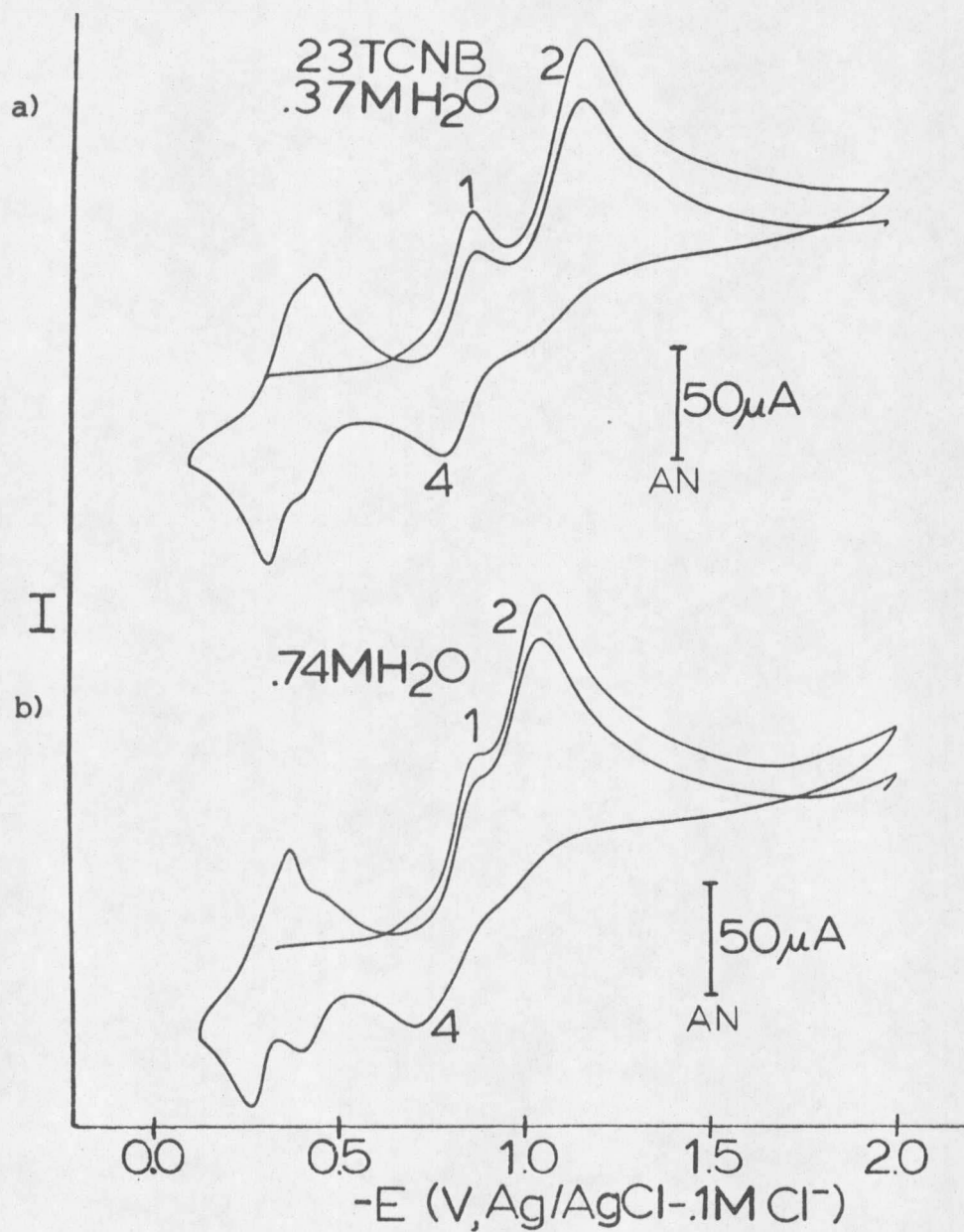


Figure 53. Cyclic voltammograms of 2,3-dichloronitrobenzene in AN with a) $0.37 M H_2O$; b) $0.74 M H_2O$.

2,4-Dichloronitrobenzene. In DMSO, Figure 54, the addition of water to 2,4-dichloronitrobenzene at a concentration of .37 M causes waves 2 and 3 to shift by +42mV and +146mV, respectively. Wave 4 is no longer a competing process and disappears, since chloride loss decreases and nitrobenzene is probably not formed. Wave 5 appears to shift +81mV but wave 5 is actually the shoulder on a new wave and it's the new wave (mercury complex) which is +81mV from the position of wave 5 prior to water addition. As more water is added, to yield a concentration of .74 M, wave 1 remains steady while wave 2 shifts +40mV and wave 3 becomes a cathodic shoulder on wave 2. The oxidative sweep shows the real wave 5, now uncovered, as the mercury wave shifts +80mV. There may be competition between positions of chloride loss since the potentials are not too far apart but it appears that the 2-CNB dianion (-6mV at .37 M, -12mV at .74 M) is closer than the 4-CNB dianion (-24mV at .37 M, -25mV at .74 M). This is a different result from the voltammogram without water.

Figure 55 shows the voltammograms for water addition to 2,4-DCNB in DMF. This is a good case for observing the increase in peak height as wave 4 shifts +80mV. The cathodic shoulder on the mercury wave appears to result from 4-chloronitrosobenzene radical anion oxidation. The 2,4-dichloronitrosobenzene wave may be part of the mercury wave, if it is present. Increasing the water concentration

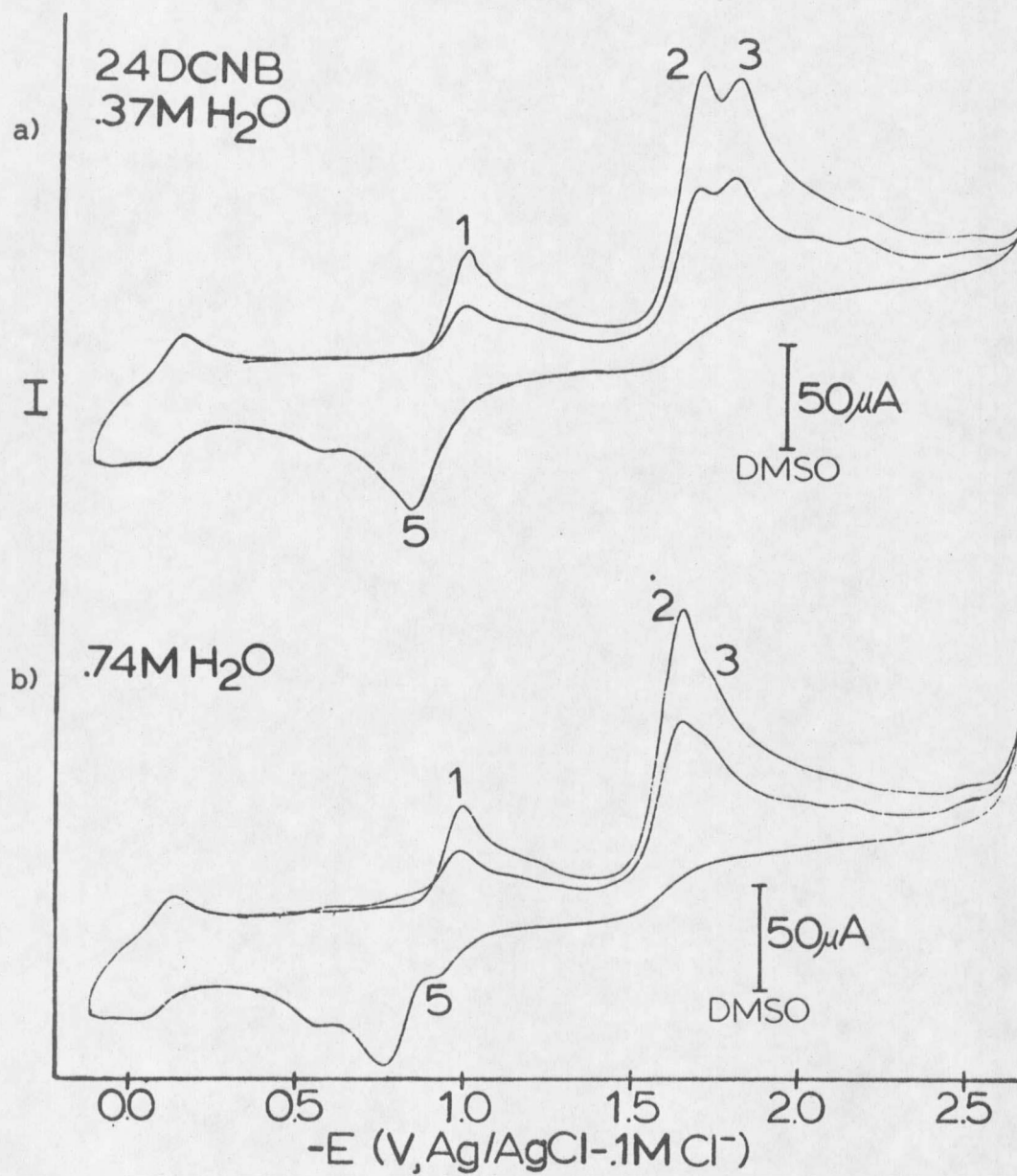


Figure 54. Cyclic voltammograms of 2,4-dichloronitrobenzene in DMSO with a) 0.37 M H₂O; b) 0.74 M H₂O.

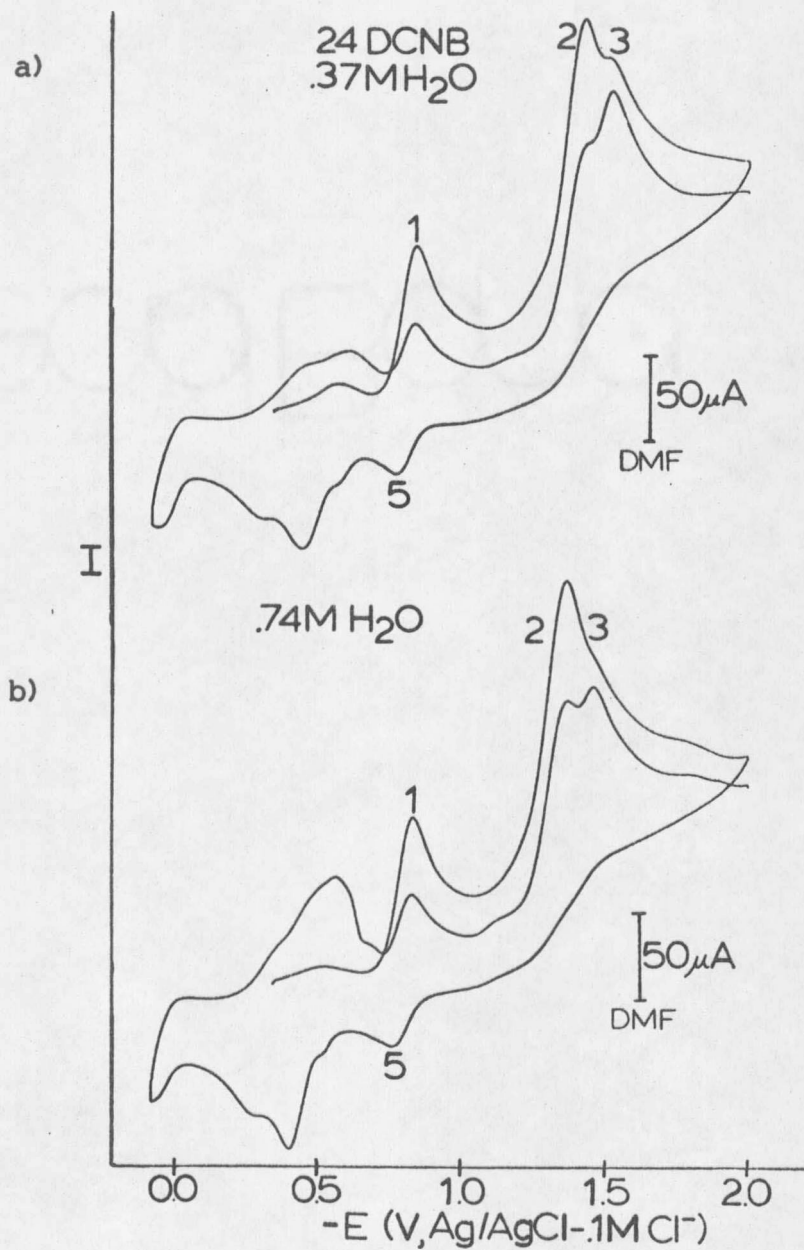


Figure 55. Cyclic voltammograms of 2,4-dichloronitrobenzene in DMF with a) .37 M H_2O ; b) .74 M H_2O .

to .74 M, wave 3 shifts +50mV into wave 2, becoming only a shoulder on the first sweep. Wave 2 shifts +58mV. Chloride loss appears to remain rapid, so that protonation may be controlling whether dechlorination or hydroxide loss occurs.

In AN, Figure 56, .37 M water causes waves 1 and 5 to shift by +30mV and +50mV, respectively. Wave 3 decreases and shifts +324mV into wave 2, itself moving +298mV; but, both processes are still occurring. There is a wave for the NB dianion on the second sweep (wave 4). At .74 M, the irreversible waves both shift +109mV while the reversible couple shifts less than +20mV. The potential corresponds to the reduction of 2,4-DCNB to 4-CNB. The oxidative sweep shows a rounded wave moving through wave 5 at the higher water concentration that is probably due to the $E2^1$ or $E2C3$ process. The nitroso wave (6) is probably the cathodic shoulder on the mercury complex.

2,5-Dichloronitrobenzene. The voltammograms of 2,5-dichloronitrobenzene in DMSO after the addition of ethanol are shown in Figure 57. At a concentration of .35 M, wave 3 has merged with wave 2, causing wave 2 to increase in height and shift +102mV. The reversible couple remains steady but a new set of waves appear anodic of the couple. These appear to be the mercury complex waves. There appears to be some preprotonation at both .35 M and .47 M ethanol.

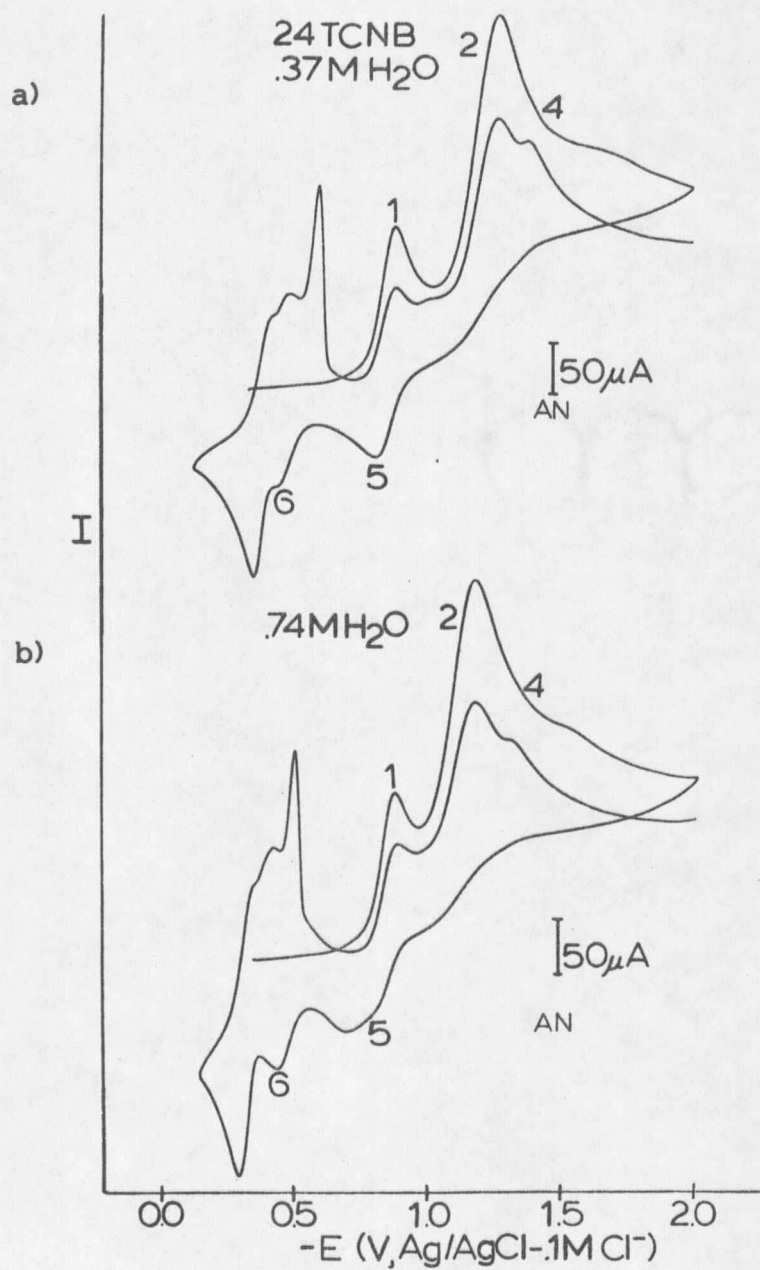


Figure 56. Cyclic voltammograms of 2,4-dichloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

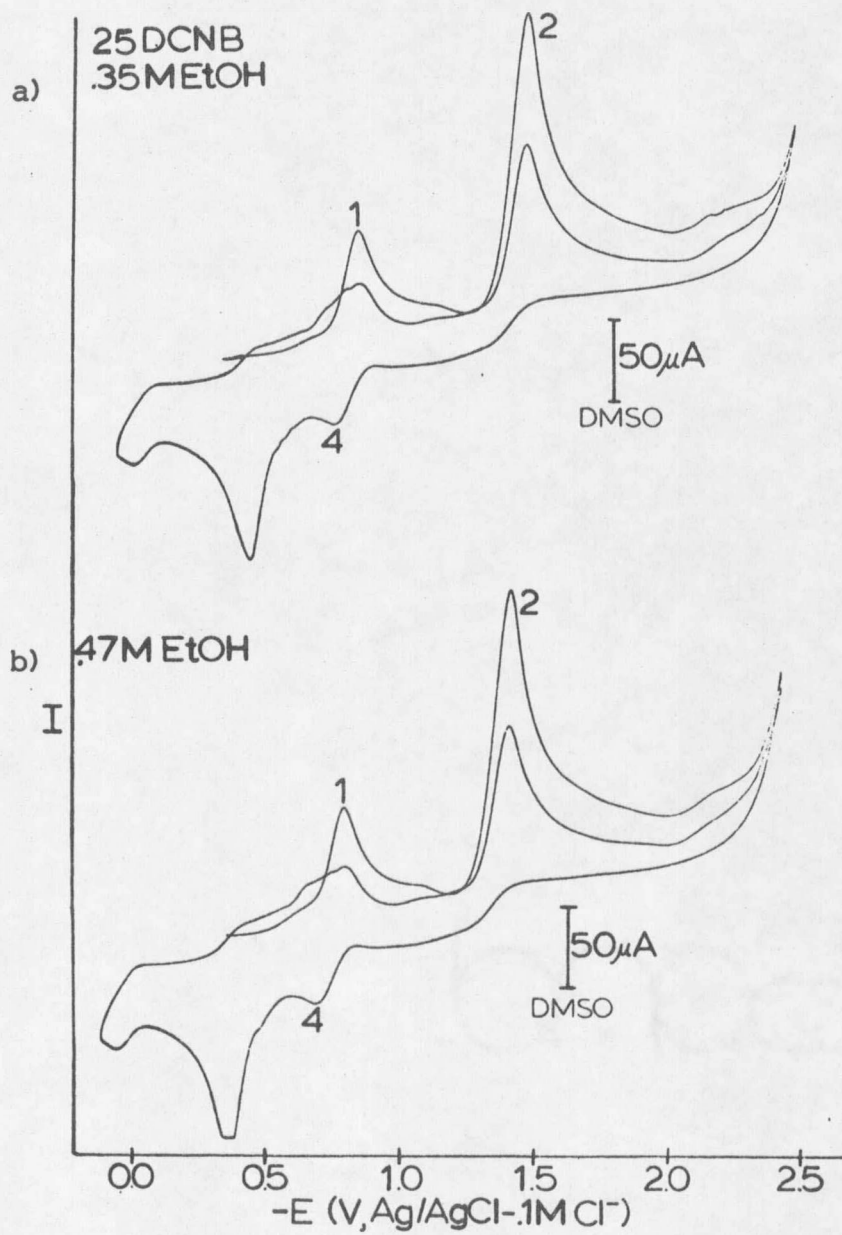


Figure 57. Cyclic voltammograms of 2,5-dichloronitrobenzene in DMSO with a) .35 M EtOH; b) .47 M EtOH.

There is also a +22mV shift in wave 2 at the higher concentration. Dianion formation of the less chlorinated compound occurs under the tail of the irreversible wave. This process is not predominant.

In DMF, Figure 58, a water addition (.37 M) causes wave 3 to join wave 2, which shifts +125 mV. Waves 1 and 4 are reasonably stable. The oxidative "hump" due to the C3E2 process moves positive and increases as proton availability increases. There is small oxidative wave prior to the mercury wave that appears to relate to the E2' process at .74 M water or it may be the 3-chloronitrosobenzene radical anion oxidation. The amount of chloride loss may have decreased due to increased protonation. Part of the mercury wave may also represent a nitroso compound.

In AN, addition of water to yield a .37 M solution causes wave 2 to shift +320mV (Figure 59). There is a very small bump, cathodic of wave 2, labeled "b" that may result from the 3-CNB dianion formation. At higher water concentrations (.74 M), the mercury wave shifts anodically revealing another wave on the oxidative sweep that may represent oxidation of a nitroso radical anion.

2,3,4-Trichloronitrobenzene. The compound 2,3,4-trichloronitrobenzene in DMSO is represented in Figure 60 at various ethanol concentrations. At .35 M, wave 3 shifts into wave 2 as it moves +71mV while wave 2 moves +38mV. Wave 6 moves anodically, increases

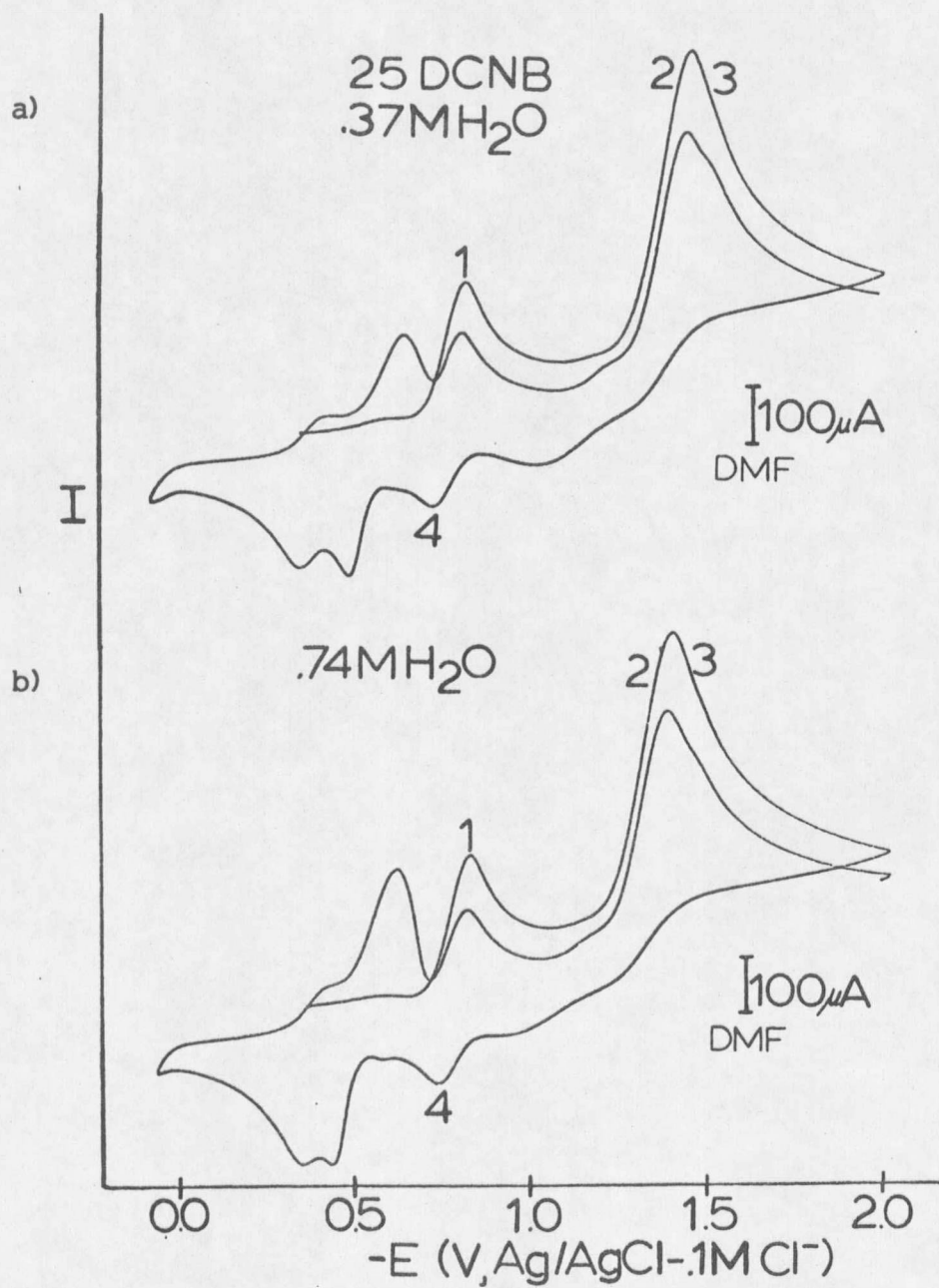


Figure 58. Cyclic voltammograms of 2,5-dichloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

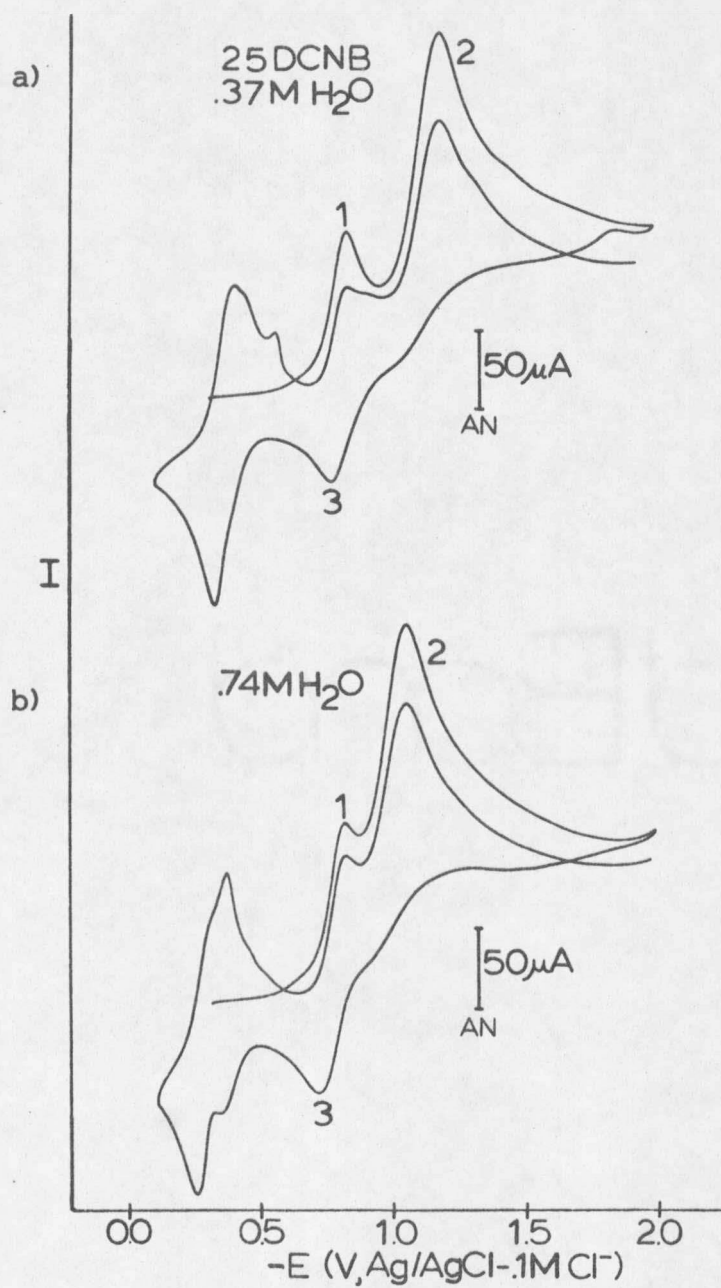


Figure 59. Cyclic voltammograms of 2,5-dichloronitrobenzene in AN with a) .37 M H_2O ; b) .74 M H_2O .

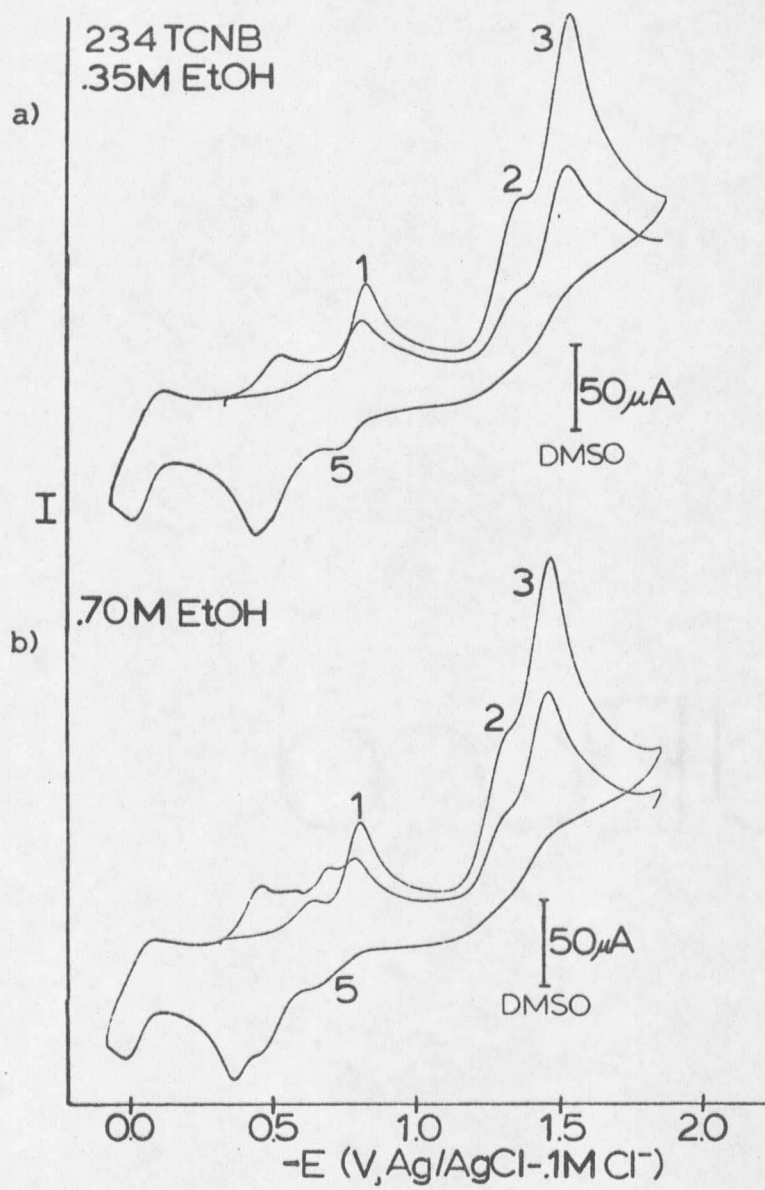


Figure 60. Cyclic voltammograms of 2,3,4,-trichloronitrobenzene in DMSO with a) .35 M EtOH; b) .70 M EtOH.

in size and appears on the cathodic shoulder of a new wave. Preprotonation occurs on the first sweep prior to wave 1. At .70 M, wave 3 shifts at a greater rate than wave 2, moving +46mV and causing wave 2 to be a small shoulder on wave 3. Wave 5 has become a broad wave but looking closely, the bottom of wave 5 is actually another wave that is sliding off of wave 5 on its anodic trek. At higher ethanol concentrations (not shown), wave 5 reappears as the other wave shifts. The mercury complex wave is present as the most anodic wave. Chloride loss continues in significant amounts throughout this series. The 2,3-DCNB dianion or the 3,4-dichloro dianion appears to form quite readily.

The voltammograms of 2,3,4-trichloronitrobenzene in DMF with water are shown in Figure 61. Waves 3 and 4 merge and shift +115mV at .37 M while wave 2 only shifts +20mV, due to changes in liquid junction potential. The C3E2 process yields the oxidative "hump." Anodic of wave 5, the new wave appears. It is broad and may represent more than one process. Either the 2,3- or the 3,4-dichloronitrosobenzene wave occurs on the cathodic shoulder of the new wave or at the peak itself. The 3-chloronitrosobenzene wave may form but it is obscured by the new wave. The rate of chloride loss does not appear to decrease. At .74 M wave 3 shifts +60mV but the wave 4 process, 3-CNB formation, is still apparent on the second

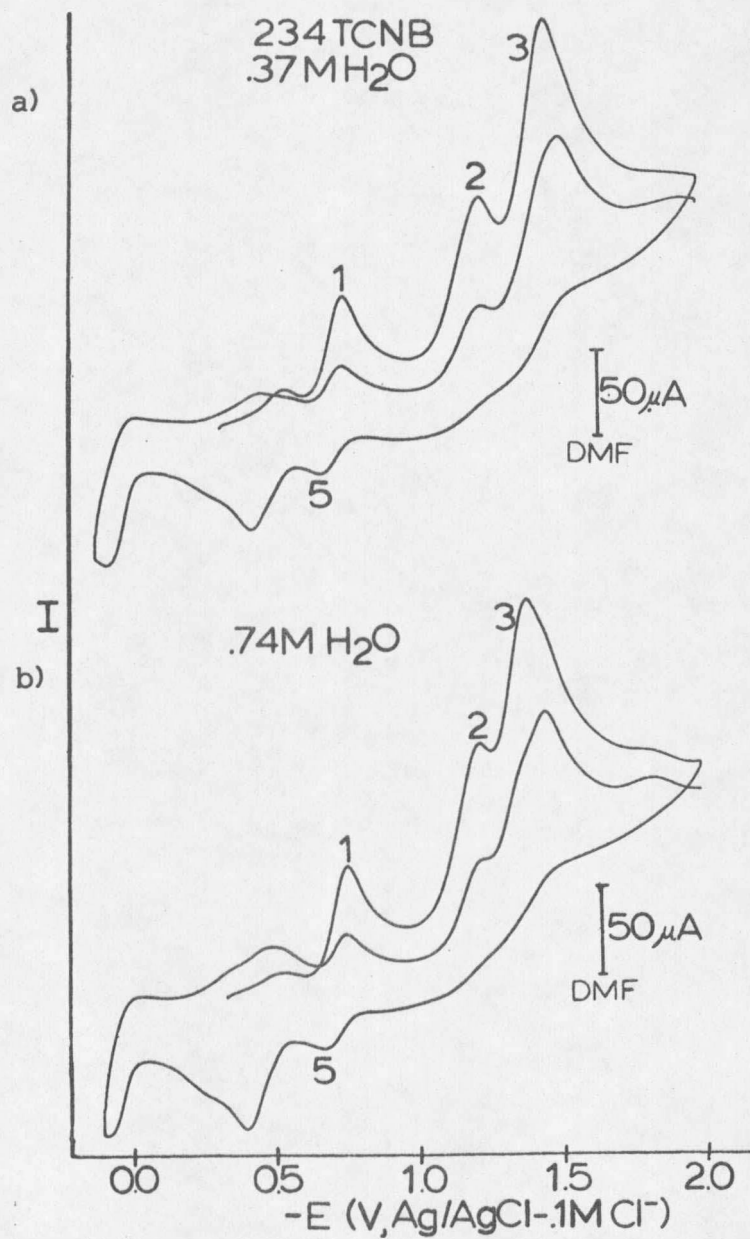


Figure 61. Cyclic voltammograms of 2,3,4-trichloronitrobenzene in DMF with a) .37 M H_2O ; b) .74 M H_2O .

sweep as the amount of it increases.

In AN, Figure 62, 2,3,4-TCNB undergoes the same reduction pathway with water added. Wave 2 shifts +152mV in a .37 M solution of water/AN and the anodic part of wave 3 (see Figure 19c) shifts approximately +455mV into wave 2 and wave 2 increases in height. The cathodic part of wave 3 shifts +288mV and becomes the smaller of the two irreversible waves. Wave 2 consists of loss of the ortho chlorine after formation of the 2,3,4-TCNB dianion with subsequent reduction to the 3,4-DCNB dianion. Wave 3 (cathodic) corresponds to the 3-chloro or 4-chloro dianion which has probably not shifted as much because the process is decreasing due to a reduction in chloride loss. At .74 M water, wave 2 shifts +106mV while wave 3 (cathodic) shifts +86mV. The mercury complex wave is sharp and the cathodic shoulder (wave 5), that is uncovered at the higher water concentration as the mercury wave shifts anodically, may be due to nitroso oxidation.

2,3,5-Trichloronitrobenzene. The cyclic voltammograms of 2,3,5-trichloronitrobenzene in DMSO yield a decrease in the chloride wave, merging of two processes and positive movement in the irreversible waves upon addition of ethanol (Figure 63). The reversible couple remains steady but waves 3 and 4 merge and shift +134mV while wave 2 moves +36mV. This corresponds to loss of the ortho chlorine and

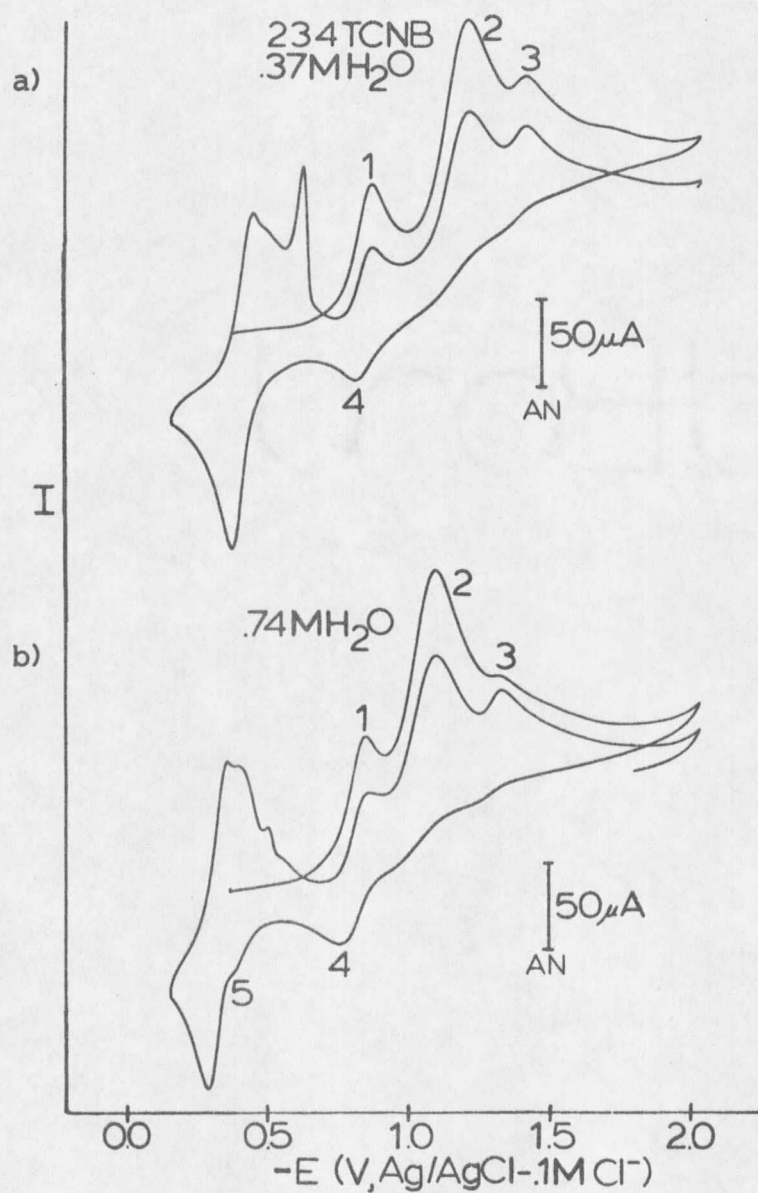


Figure 62. Cyclic voltammograms of 2,3,4-trichloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

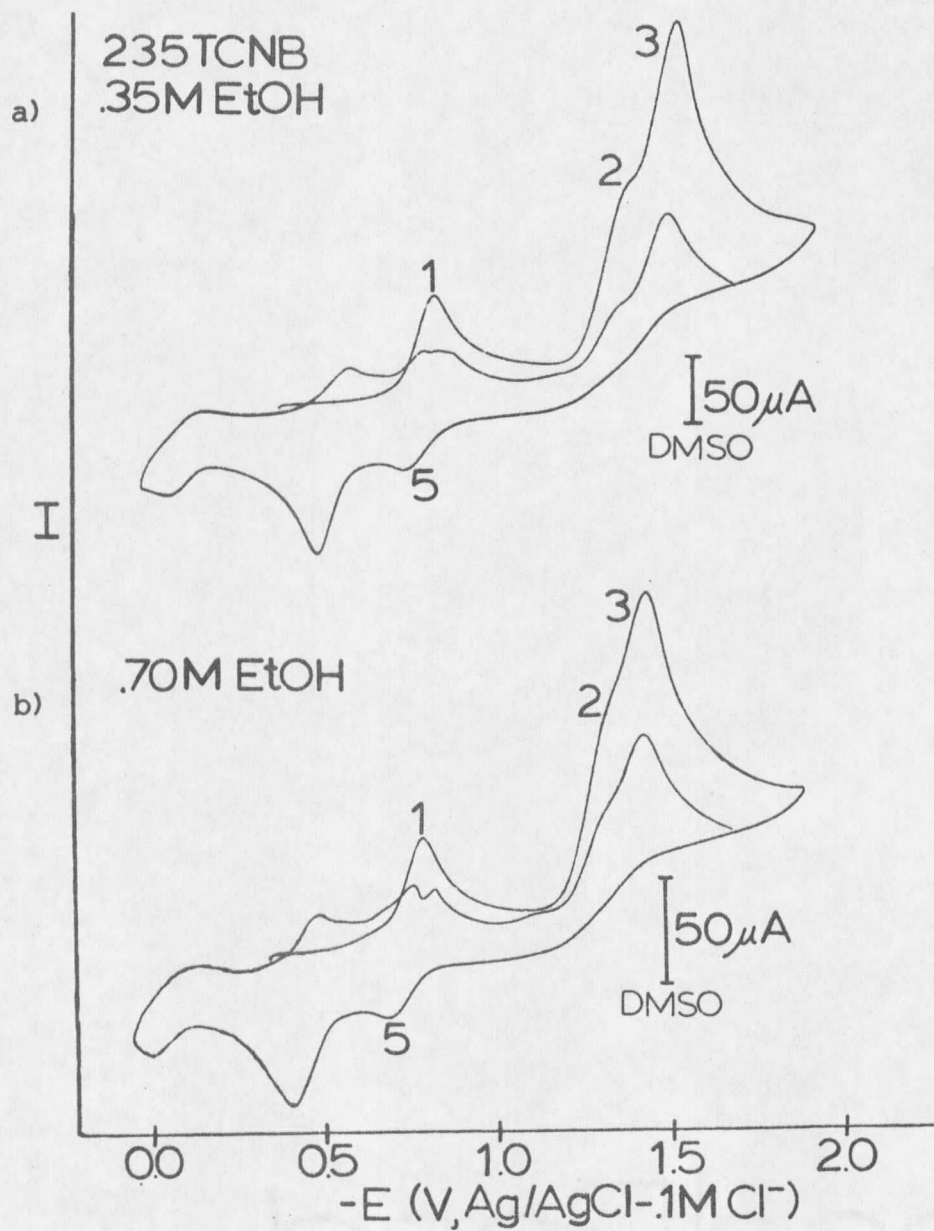


Figure 63. Cyclic voltammograms of 2,3,5-trichloronitrobenzene in DMSO with a) .35 M EtOH; b) .70 M EtOH.

formation of the 3,5-dichloro dianion. At .70 M, wave 3 shifts +56mV showing continued movement. The double peaks on the second sweep at wave 2 appear to be surface effects but there may also be competition due to preprotonation.

In DMF, Figure 64, water addition to 2,3,5-TCNB causes waves 3 and 4 to merge shifting wave 3 +199mV. Wave 2 is steady, as is the reversible couple. Chloride loss continues but the formation of 3,5-dichloronitrosobenzene increases. The oxidative "hump" is large and broad. At .74 M, wave 3 shifts into wave 2 causing wave 2 to increase and wave 3 to decrease. The second sweep reveals the wave 4 process is still present. Wave 2 shifts +39mV and wave 3 moves +133mV as chloride loss decreases.

Using AN as the solvent, the 2,3,5-TCNB compound changes its pathway with water addition (Figure 65). Wave 3 has moved into wave 2 and wave 2 has grown and shifted +198mV. There is a small cathodic shoulder on wave 2. This may be some formation of the 3-CNB dianion. Wave 2 is the formation of the 2,3,5-TCNB dianion and the 3,5-DCNB dianion. There is a protonated dianion cathodic of wave 4 which has grown larger and moved anodically. There is no nitroso formation.

2,4,5-trichloronitrobenzene. In DMSO, cyclic voltammograms of 2,4,5-trichloronitrobenzene with ethanol added show a decrease in the chloride wave and merging of the irreversible waves (Figure 66).

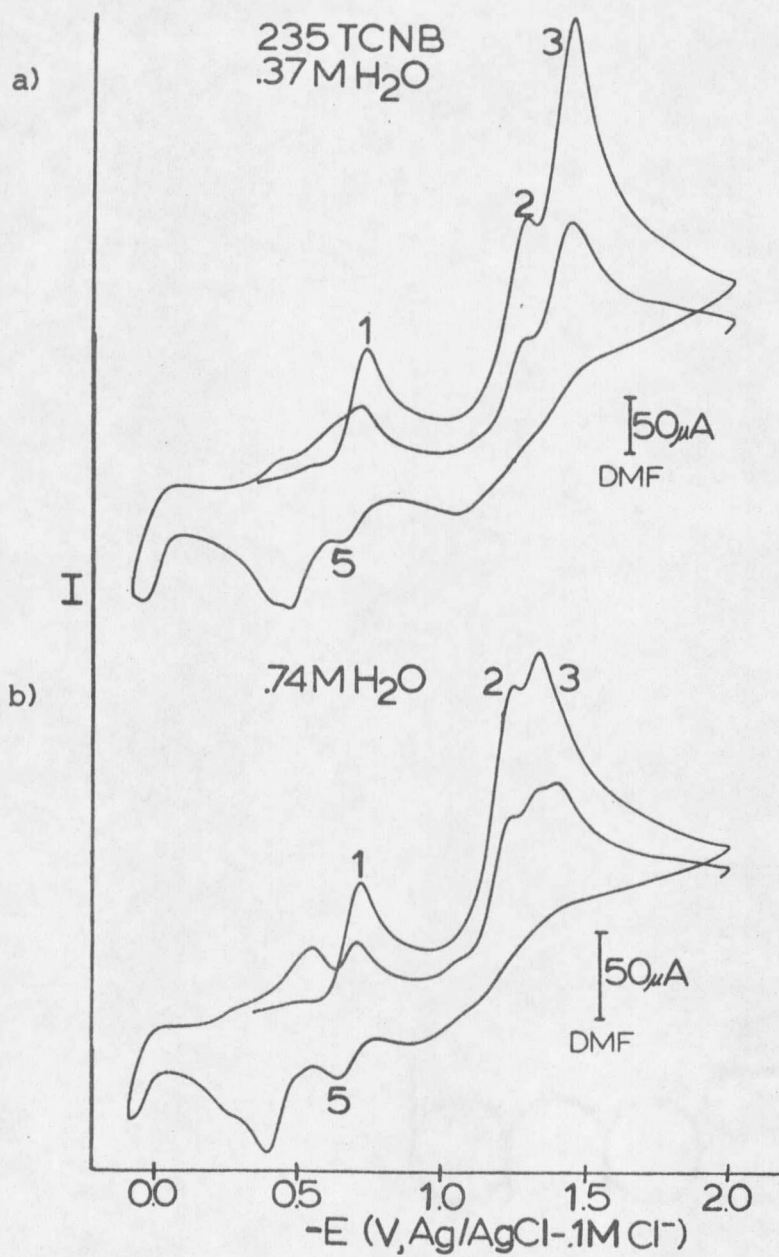


Figure 64. Cyclic voltammogram of 2,3,5-trichloronitrobenzene in DMF with a) 0.37 M H₂O; b) 0.74 M H₂O.

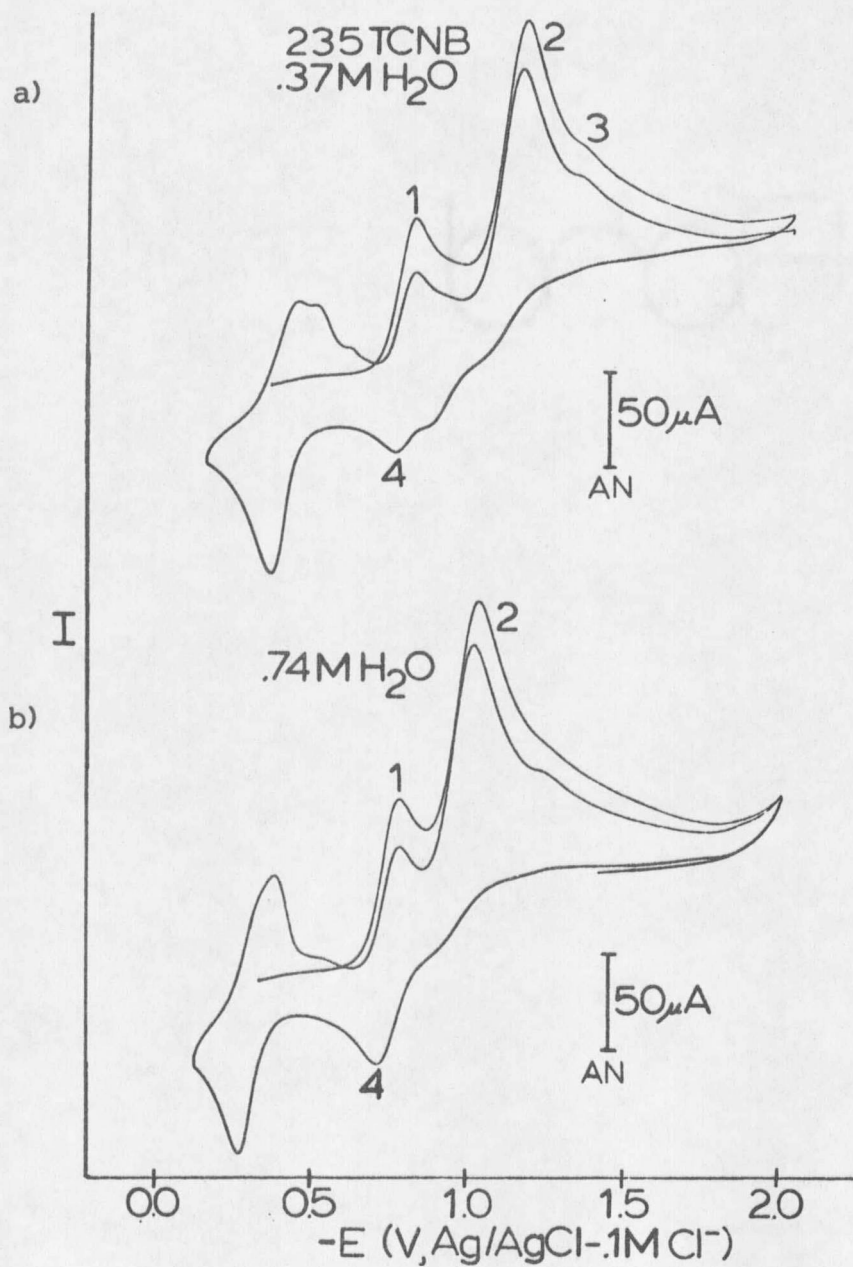


Figure 65. Cyclic voltammograms of 2,3,5-trichloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

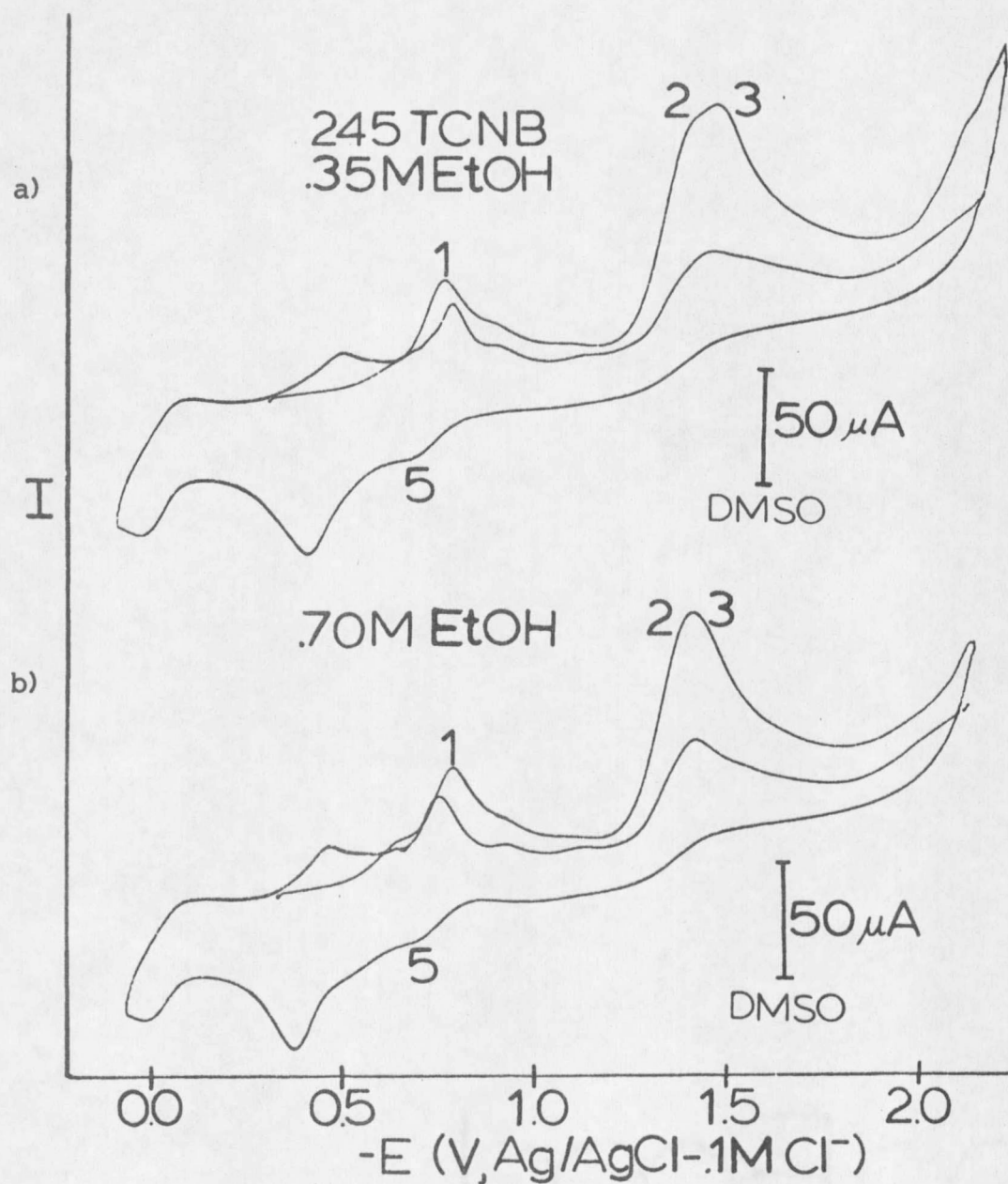


Figure 66. Cyclic voltammograms of 2,4,5-trichloronitrobenzene in DMSO with a) .35 M EtOH; b) .70 M EtOH.

Voltammograms with less ethanol added show waves 3 and 4 merging and moving towards wave 2, thus producing the rounded wave seen at .35 M. Wave 2 remains steady and wave 3 shifts +75mV. The new oxidative wave is broad and denotes more than one process. The nitroso wave and the mercury complex wave may both be present in this area. There is some preprotonation of the radical anion and a reverse wave for this process may occur near the radical anion oxidation. Changing to .70 M ethanol, the irreversible waves form one peak, though it is still broad. Both formation of the 2,4,5-trichloro dianion and the 2,5-dichloro dianion occur at the potential of this wave. It has shifted +35mV from the potential of wave 2 at .35 M.

Cyclic voltammograms of 2,4,5-TCNB in DMF with water additions are shown in Figure 67. The preprotonation or adsorption wave prior to wave 1 increases at .34 M as does preprotonation of the dianion that appears as a anodic shoulder on wave 2. Wave 4 no longer exists and wave 3 merges with wave 2; but, the merged wave is round and broad denoting both processes occur at equilibrium rates. Chloride loss is still rapid but some nitroso formation occurs. The first wave anodic of wave 5 results from either the oxidation of the protonated radical anion ($E2''$) or the 3,4-dichloronitrosobenzene radical anion. The potential of the irreversible wave gives no clue as to which dianion is being formed. Both the 3,4-DCNB and the 2,5-

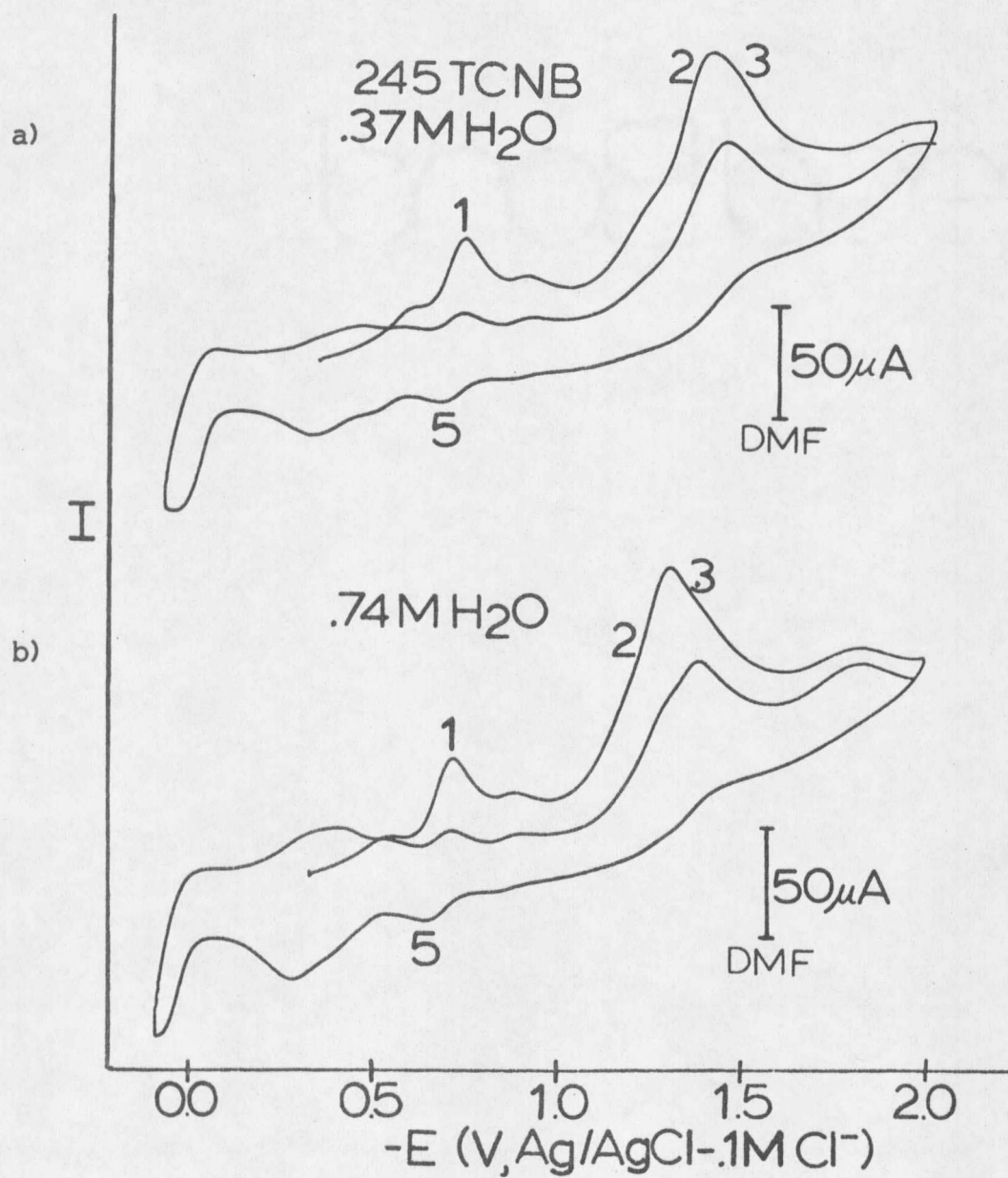


Figure 67. Cyclic voltammograms of 2,4,5-trichloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

DCNB dianions occur at the same potential. There may be a competitive process for position of chloride loss or both may be occurring in equal amounts. At higher water concentrations the nitroso waves are smeared and chloride loss does not significantly decrease.

In AN, Figure 68, the potentials of the waves for 2,4,5-TCNB shift rapidly. Waves 2 and 3 merge and shift +306mV at a water concentration of .37 M while wave 4 decreases and becomes a small bump on the cathodic shoulder of wave 2. It corresponds with the potential for the 3-CNB dianion under the same conditions. Wave 1 shifts +25mV but wave 6, its reversible couple, shifts +34mV due to wave 5 shifting into it. At .74 M, wave 2 moves +114mV, uncovering more of the mono-chloro wave. Wave 2 is due to more than one process, including both the 2,4,5-TCNB dianion and the 2,5-DCNB dianion, and the cathodic shoulder results from 3-CNB dianion formation that occurs at a low rate. There does not appear to be any nitroso formation.

2,3,4,5-Tetrachloronitrobenzene. Cyclic voltammograms of 2,3,4,5-tetrachloronitrobenzene in DMSO with ethanol are shown in Figure 69. At an ethanol concentration of .35 M, waves 4 and 5 merge, both moving anodically, then move into wave 3 to form a single peak. This wave is large and broad, denoting more than one process.

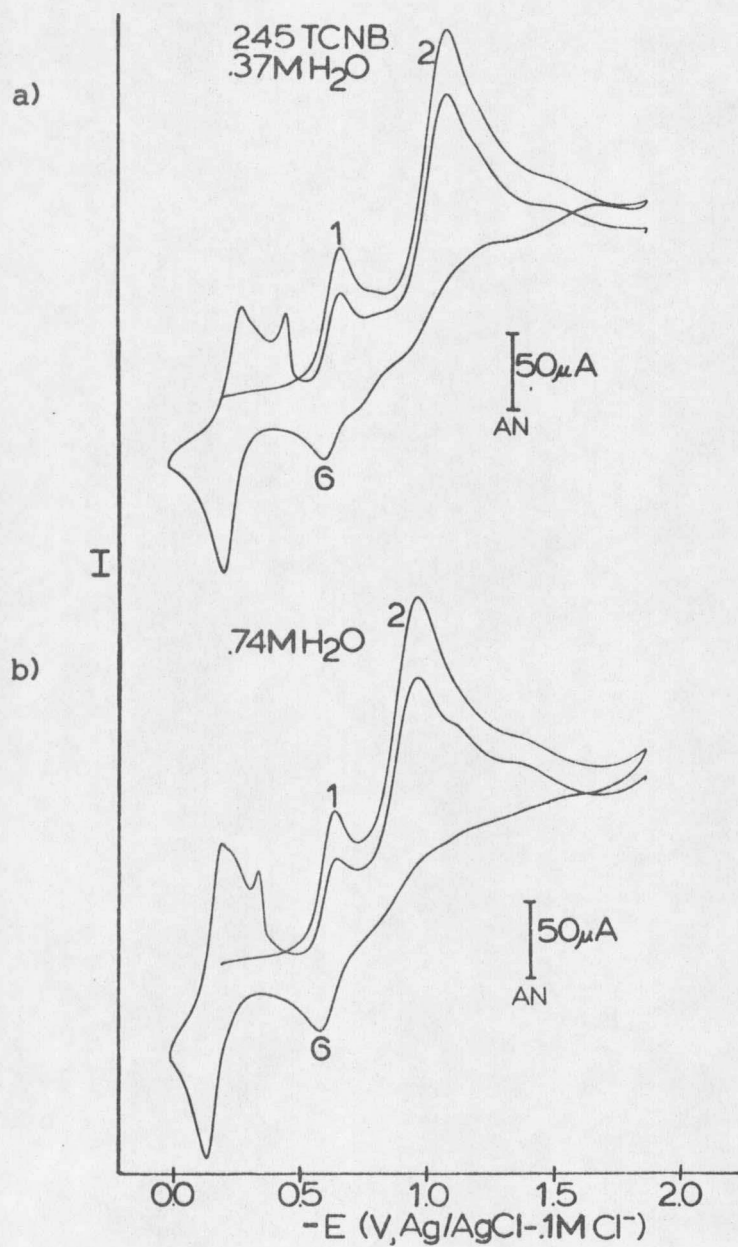


Figure 68. Cyclic voltammograms of 2,4,5-trichloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

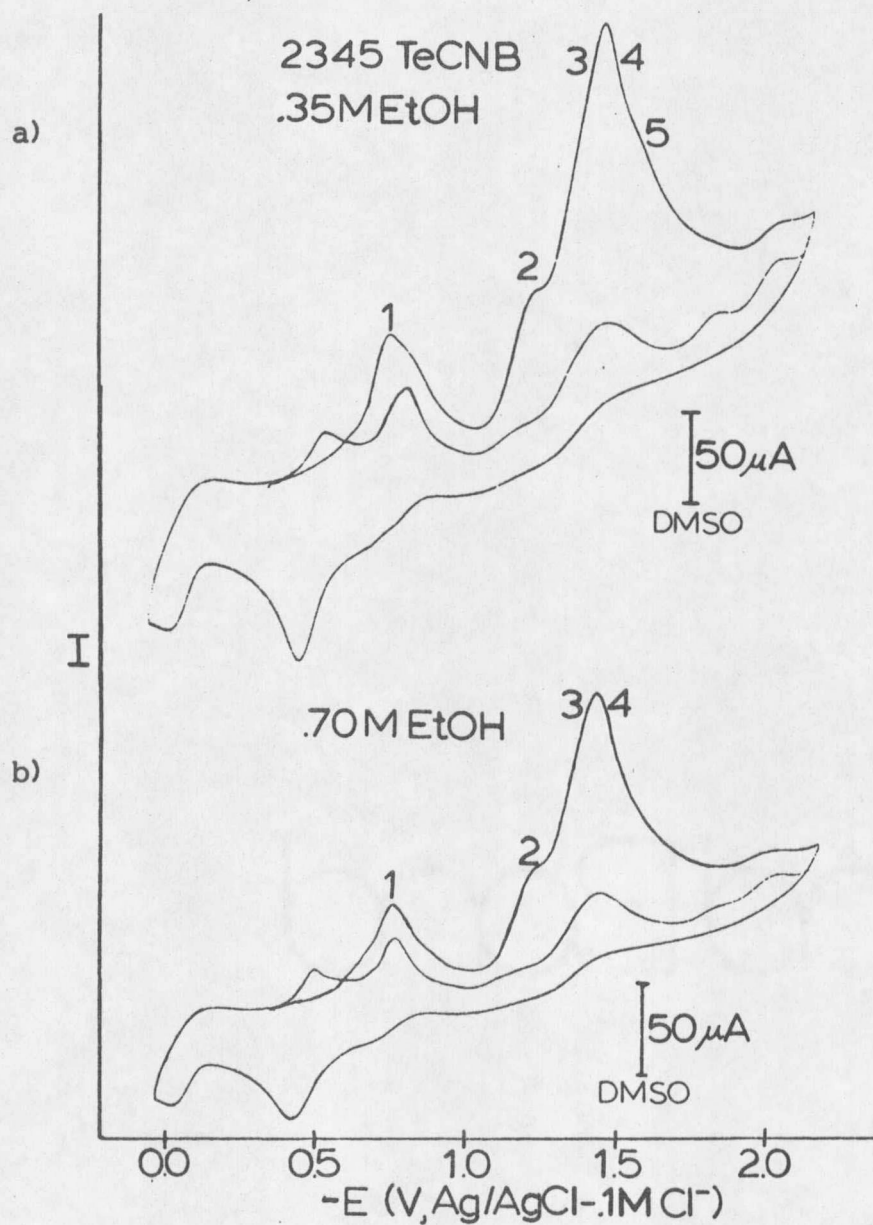


Figure 69. Cyclic voltammograms of 2,3,4,5-tetrachloronitrobenzene in DMSO with a) .35 M EtOH; b) .70 M EtOH.

The potential of the peak does not correspond to any particular compound. Looking at the second sweep, the wave appears to have shoulders on both sides of the peak. The multiple processes that appear to be occurring at the shoulder potential and the peak potentials are formation of the 3,4,5-TCNB dianion, the 2,4,5-TCNB dianion, the 3,5-DCNB dianion and the 2,5-DCNB dianion. Chloride loss is apparently occurring rapidly with competition between loss from the meta and para positions. The second sweep shows the process on the cathodic shoulder on wave 1 is now dominate which may correspond to the 3,4,5-TCNB radical anion. At .70 M ethanol, competition still exists. The pathway has not changes except for a more normal appearance of wave 1.

Cyclic voltammograms of 2,3,4,5-tetrachloronitrobenzene in DMF with water additions are shown in Figure 70. In a .37 M water/DMF solution, wave 3 becomes a shoulder on wave 4 as it shifts +136mV. The amount of chloride loss decreases and the nitroso formation increases. At .74 M, wave 4 shifts +67mV to merge completely with a stable wave 3. Waves 3 and 4 are due to the 3,4,5-TCNB and 3,5-DCNB dianions, respectively. The wave just anodic of wave 5, that appears as a shoulder on the new wave, is probably due to the 3,5-dichloro-nitrosobenzene radical anion oxidation while the new wave, which is round and broad, may represent both the 3,4,5- trichloronitroso-

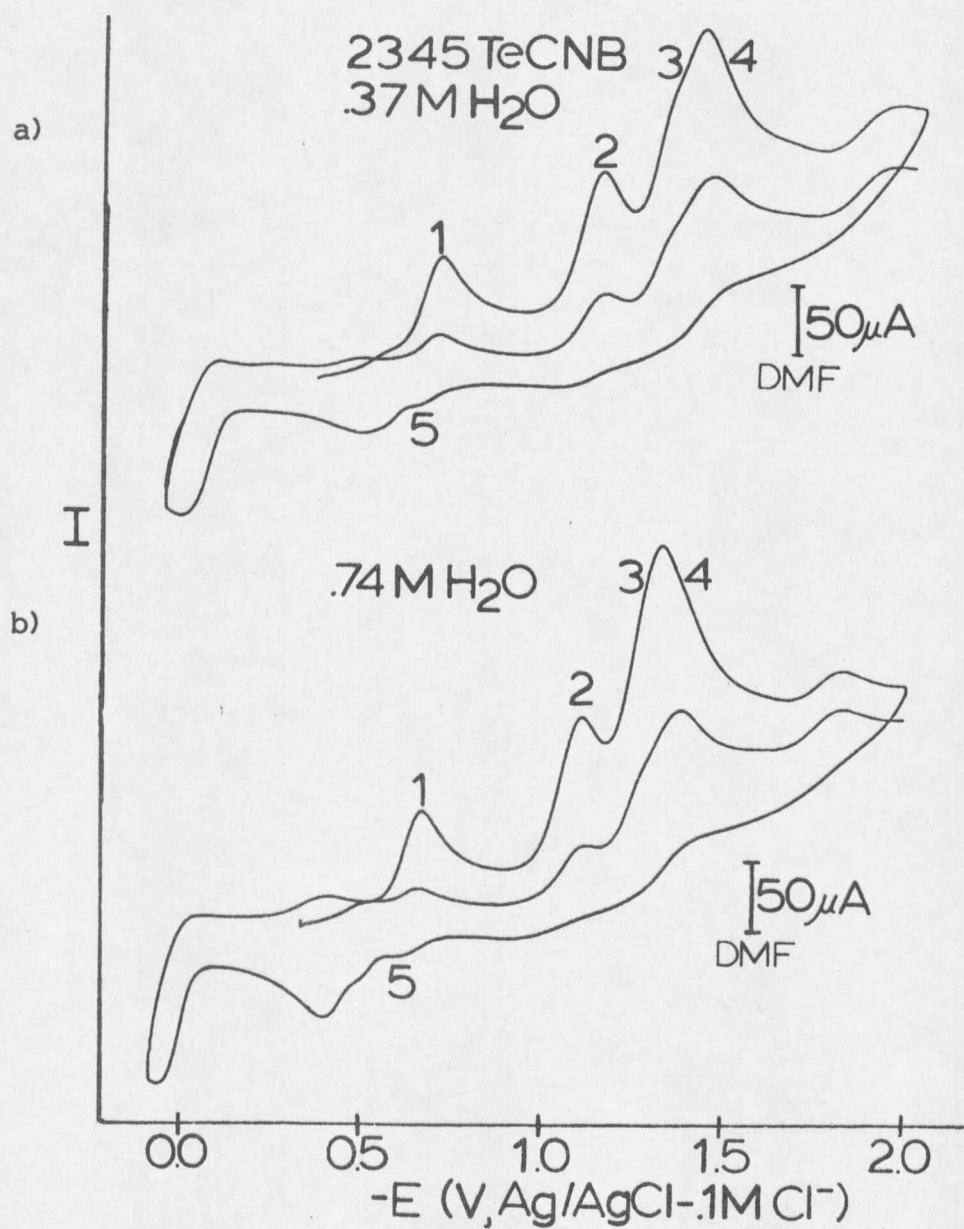


Figure 70. Cyclic voltammograms of 2,3,4,5-tetrachloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

benzene radical (cathodic side) and the mercury complex (anodic side).

In AN, Figure 71, the addition of water to 2,3,4,5-TeCNB causes wave 2 to shift +61mV while waves 3 and 4 merge and shift into it, causing a increase in the peak height of wave 2. The second irreversible wave at .37 M is due to the 3,4,5-TCNB dianion with some 3,5-dichloro dianion formation following it. At .74 M, wave 2 shifts +114mV and wave 3 merges with it. There are two waves on the reductive sweep cathodic of wave 2, arising from an unknown source. The most cathodic of these corresponds to the wave which appears as a small peak at the negative end of most of AN voltammograms. There does not appear to be nitroso formation; but, note how the wave cathodic of wave 5 in .37 M water shifts into wave 5 in .74 M H₂O. This is a good example of the shifting of the E2' (or C3E2) process.

Series 3: Two Ortho Chlorines.

2,6-Dichloronitrobenzene. In DMSO, Figure 72, the addition of water to 2,6-dichloronitrobenzene causes wave 4 to shift into wave 3 and wave 2 remains steady somewhere under wave 3, that itself has shifted +100mV. The reversible radical anion couple is steady and a new oxidative wave forms. This is due to the mercury complex wave, but it also could be the nitroso wave. The wave is rounded on the anodic side and gives the appearance of two processes. At .74 M,

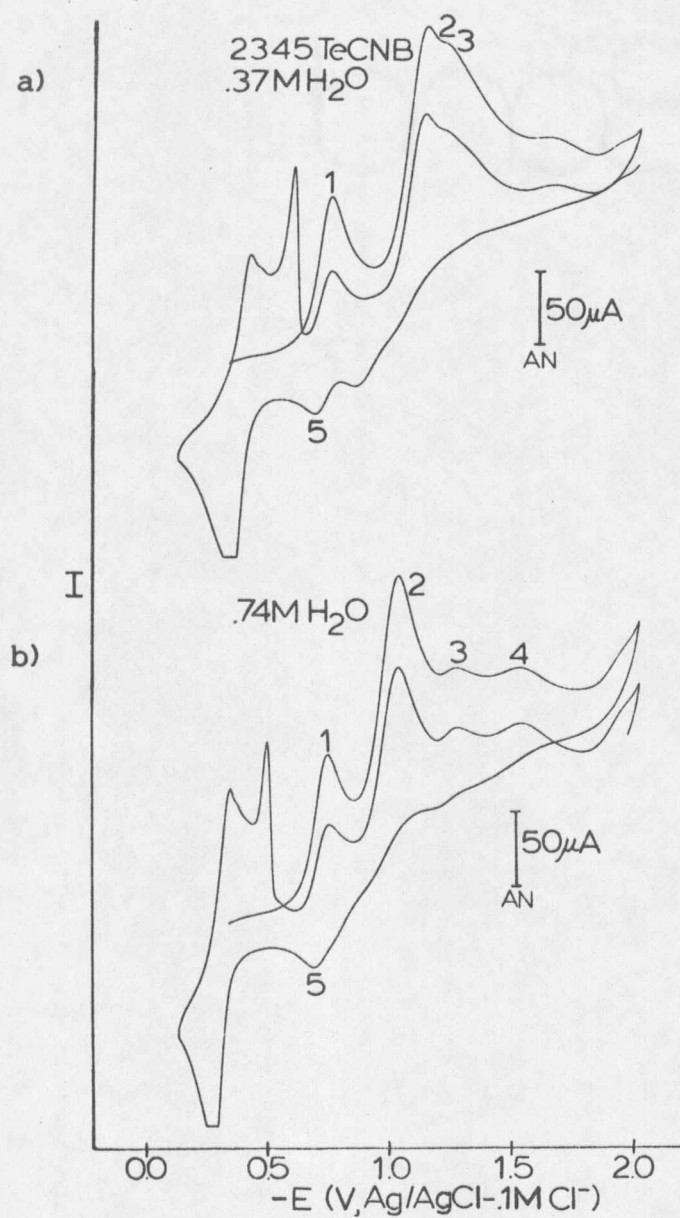


Figure 71. Cyclic voltammograms of 2,3,4,5-tetrachloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

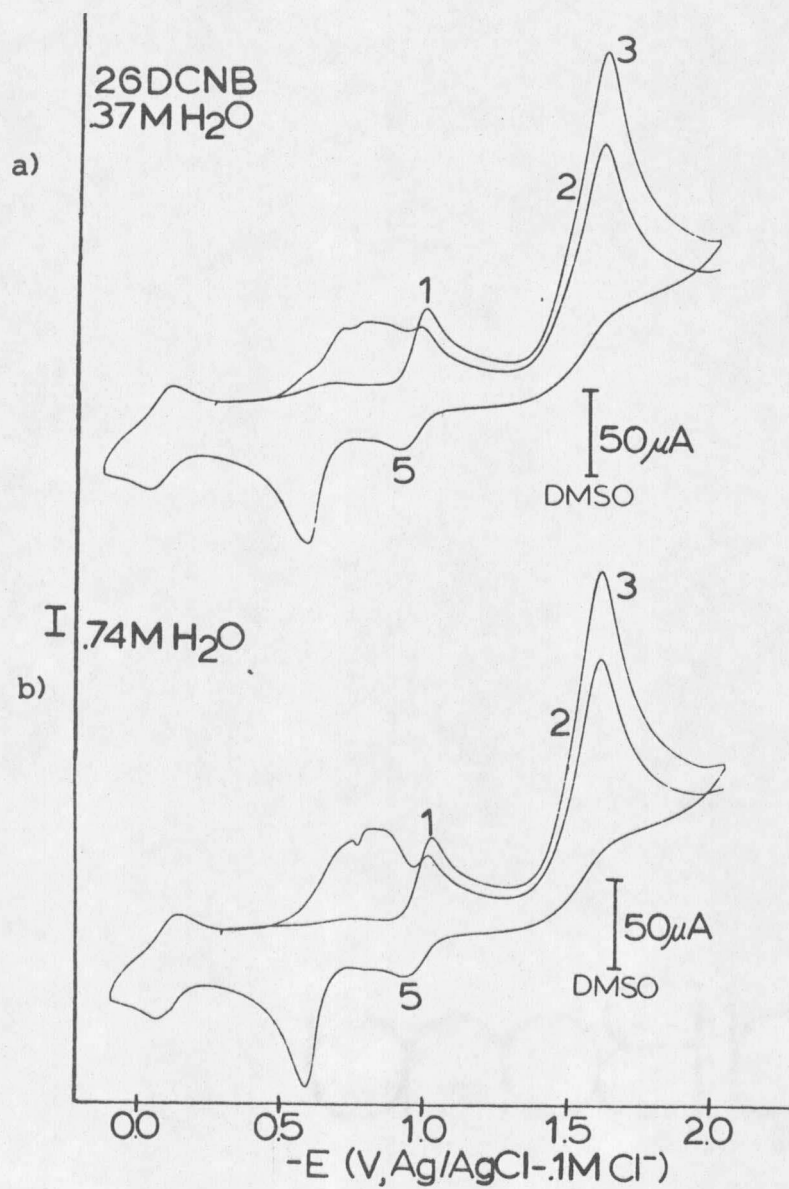


Figure 72. Cyclic voltammograms of 2,6-dichloronitrobenzene in DMSO with a) .37 M H₂O; b) .74 M H₂O.

this wave is a sharp peak. The nitroso wave is probably between wave 5 and the mercury complex wave. The irreversible wave has shifted +43mV from the position of wave 3. Chloride loss is occurring very rapidly and the nitroso formation is probably secondary. The irreversible wave represents both the formation of the 2,6-dichloro and the 2-chloro dianions.

In DMF, Figure 73, the pathway of reduction of 2,6-DCNB with water present has changed towards chloride loss. Wave 2 remains steady, but wave 3 shifts +186mV and moves on top of it. Wave 4, the formation of the NB dianion, decreases and can't be seen. Wave 1 shifts about +10mV, probably due to liquid junction potential changes. The mercury complex and surface adsorption waves form. The nitroso wave appears as a small wave between wave 5 and the mercury complex. At .74 M, wave 1 shifts another +10mV while wave 2 apparently remains steady, since the irreversible wave has not moved positive of the wave 2 potential and wave 3 shifts +68mV.

In AN, Figure 74, wave 2 shifts +168mV while wave 3 shifts +301mV and moves over the top of wave 2. Wave 1 is relatively stable but has a prewave which is probably due to preprotonation. The height of the irreversible wave decreases, indicating less chloride loss. The nitroso wave has shifted anodically and may be the small "belly" prior to the first of the mercury waves or the first actual

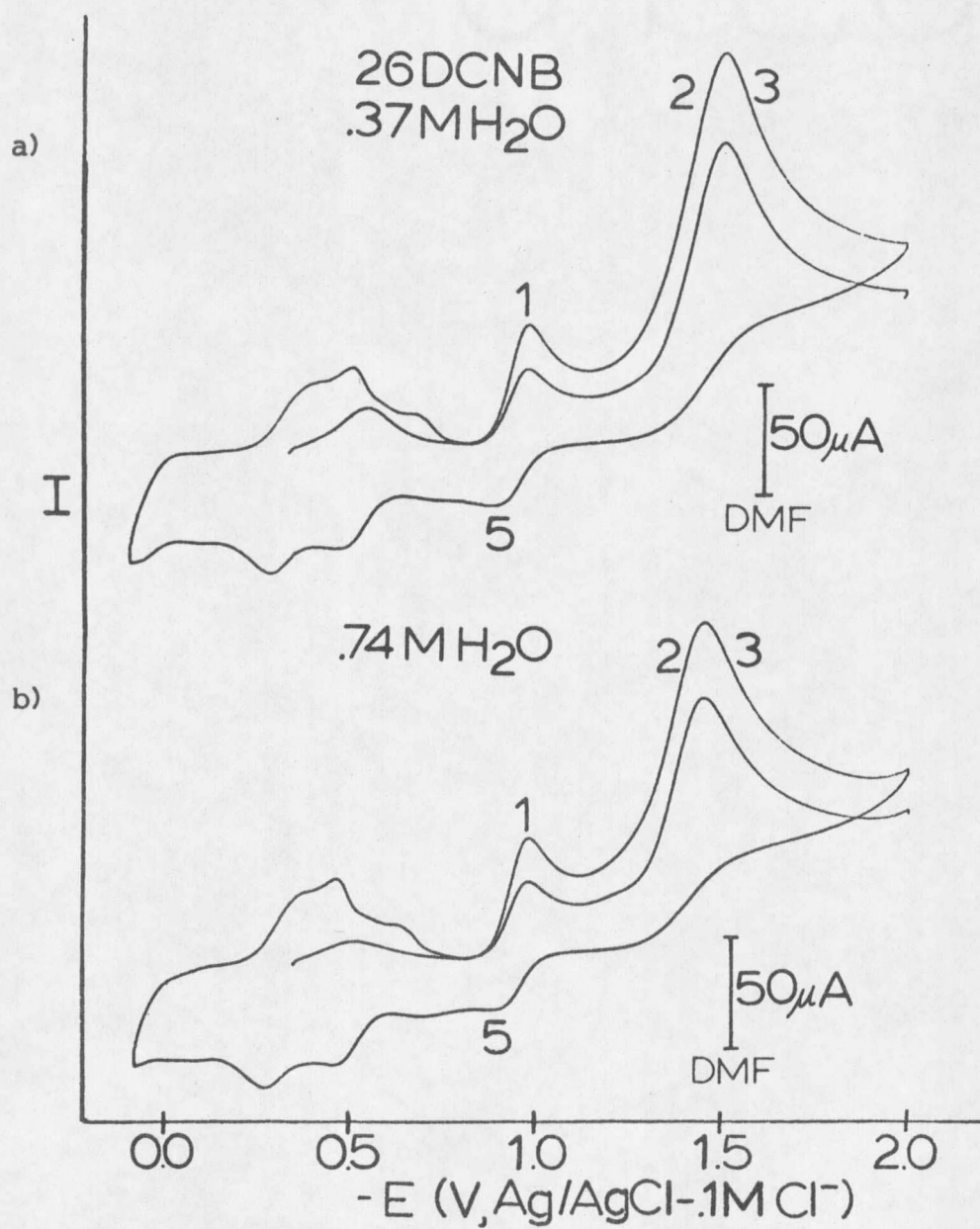


Figure 73. Cyclic voltammograms of 2,6-dichloronitrobenzene in DMF with a) $.37\text{ M H}_2\text{O}$; b) $.74\text{ M H}_2\text{O}$.

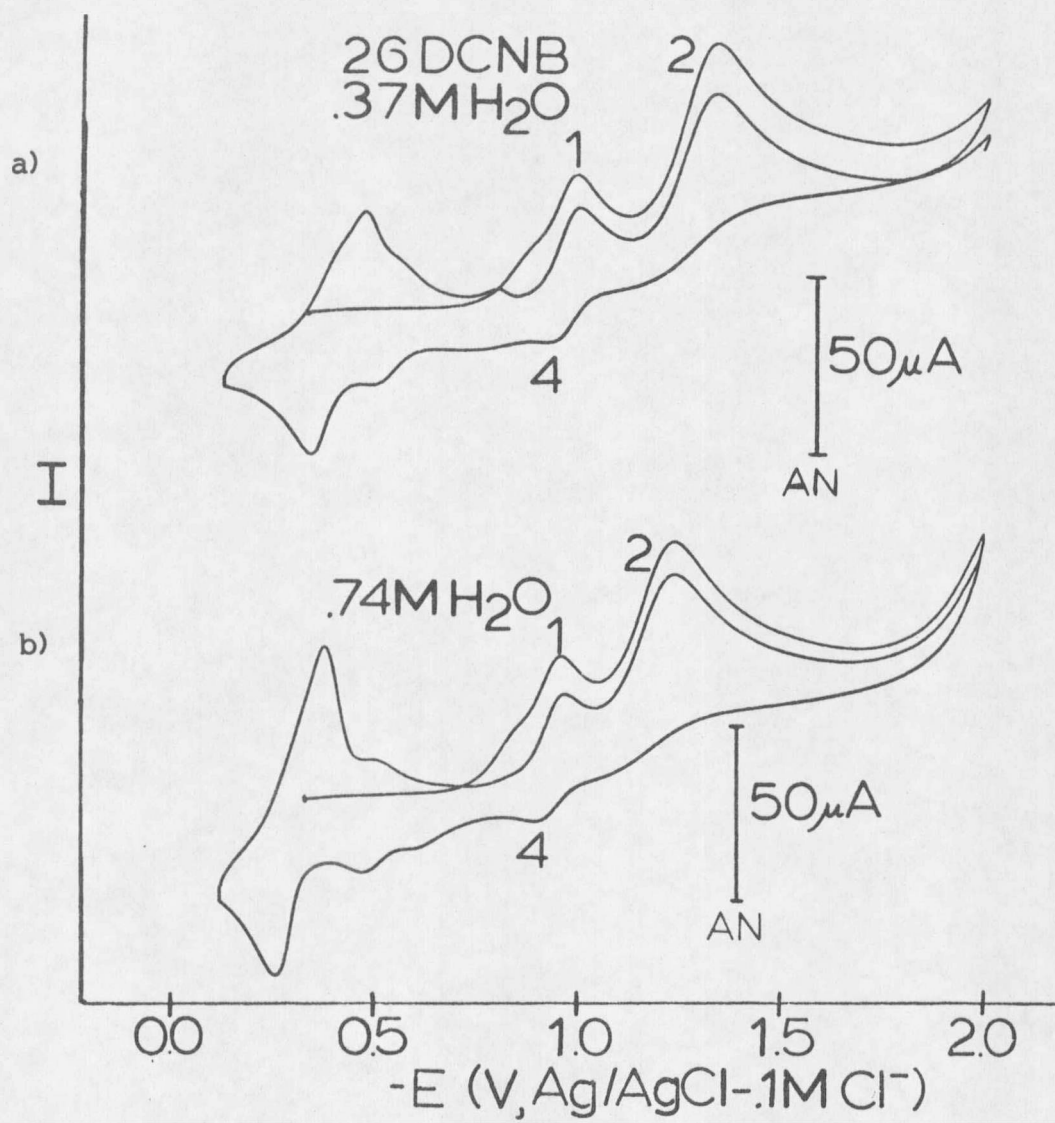


Figure 74. Cyclic voltammograms of 2,6-dichloronitrobenzene in AN with a) 0.37 M H₂O; b) 0.74 M H₂O.

wave anodic of wave 4. At .74 M, the irreversible wave shifts +97mV while wave 1 shifts +33mV. Wave 4 shifts +22mV and the nitroso waves appears as one of the small peaks anodic of wave 4 and on the shoulder of the mercury complex wave.

2,3,6-Trichloronitrobenzene. Cyclic voltammograms of 2,3,6-trichloronitrobenzene appear at different water concentrations in Figure 75. When the water concentration is .35 M, wave 5 disappears and wave 3 shifts +47mV as wave 4 merges with it. Wave 4 most likely has also decreased. Wave 2 is steady and appears as a anodic shoulder on wave 3. When the cathodic limit is set just past wave 2, a double wave appears on the oxidative sweep under wave 1. This is related to the radical anion of the trichloro compound and the radical anion of 2,5-DCNB. Apparently, chloride is lost as soon as the dianion starts to form. If the sweep is stopped prior to the 2,5-DCNB dianion formation, the 2,5-DCNB radical is oxidized and correspondingly reduced. There are two other oxidative waves. The most cathodic of these forms when the potential is held at the base of wave 2, and the other wave forms when the potential is held at the base of wave 3. The wave associated with wave 3 appears to be the surface effect and the second wave may be another surface phenomena.

In a solution of .34 M water and DMF (Figure 76), reduction of 2,3,6-trichloronitrobenzene yields a anodic shift of +162mV as waves

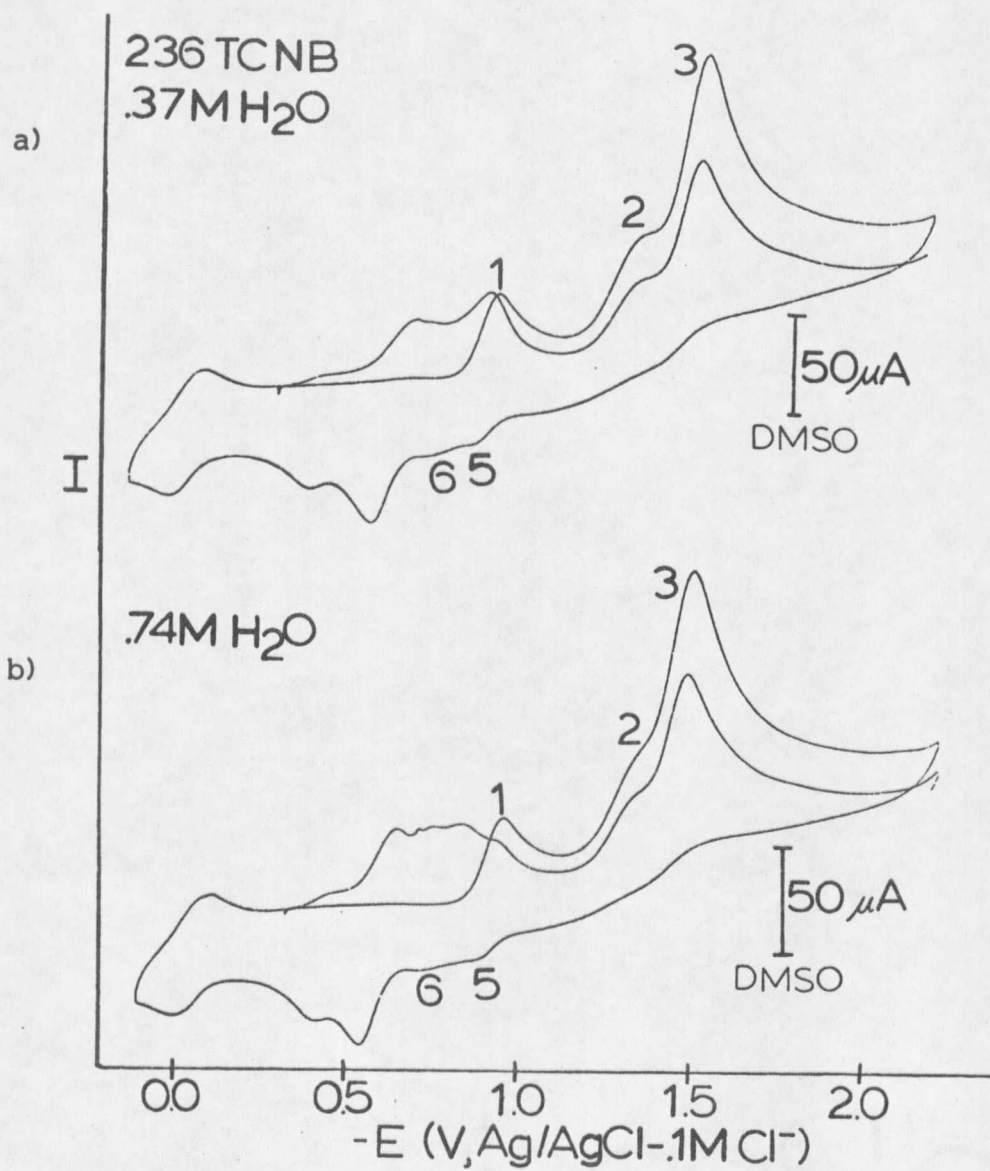


Figure 75. Cyclic voltammogram of 2,3,6-trichloronitrobenzene in DMSO with a) .35 M H₂O; b) .74 M H₂O.

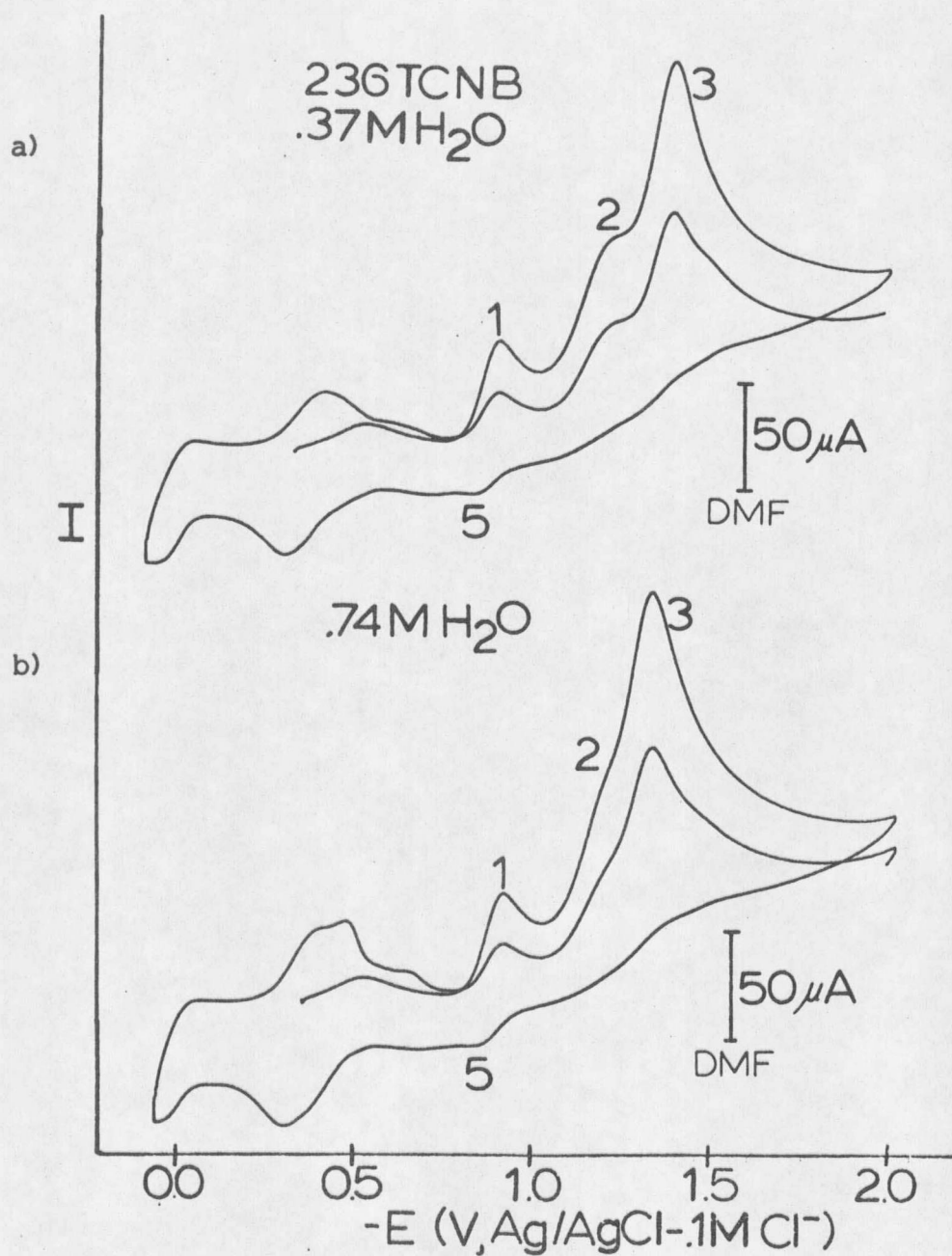


Figure 76. Cyclic voltammograms of 2,3,6-trichloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

3 and 4 merge and move positively. The other waves remain relatively steady, with only minor fluctuations. The potential of wave 3 corresponds to the dianion of authentic 2,3-DCNB in .34 M water. This is a change in the pathway from the compound without water. The 2,3-DCNB dianion (-9mV) is much closer to the potential of wave 3 than the 2,5-DCNB dianion (-58mV). There is a bump just anodic of wave 5 that may be the protonated dianion by the E2' process or the oxidative "hump" that shifts anodically. Just positive of this, there is a shoulder on a new wave. This may represent the 2,3-dichloronitrosobenzene radical anion oxidation. At higher water concentrations, wave 3 continues to correspond to the 2,3-DCNB dianion. Wave 3 shifts +69mV to overtake wave 2 which results in a decrease in the rate of chloride loss. The mercury complex waves have grown.

Figure 77 shows the series of voltammograms for water addition to 2,3,6-TCNB in AN. Wave 3 moves quickly over wave 2 by shifting +322mV. Wave 2 moves +90mV while waves 1 and 4 shift +41mV and +36mV, respectively. In a .37 M solution, the irreversible wave is broad and may correspond to the 2,5-DCNB dianion (+69mV), the 2,6-DCNB dianion (-59mV) or the 2,3-DCNB dianion (+89mV), as well as the 2-CNB dianion (-75mV) or the 3-CNB dianion (-61mV) and the 2,3,6-TCNB dianion. When the anodic limit is moved more positive, it is

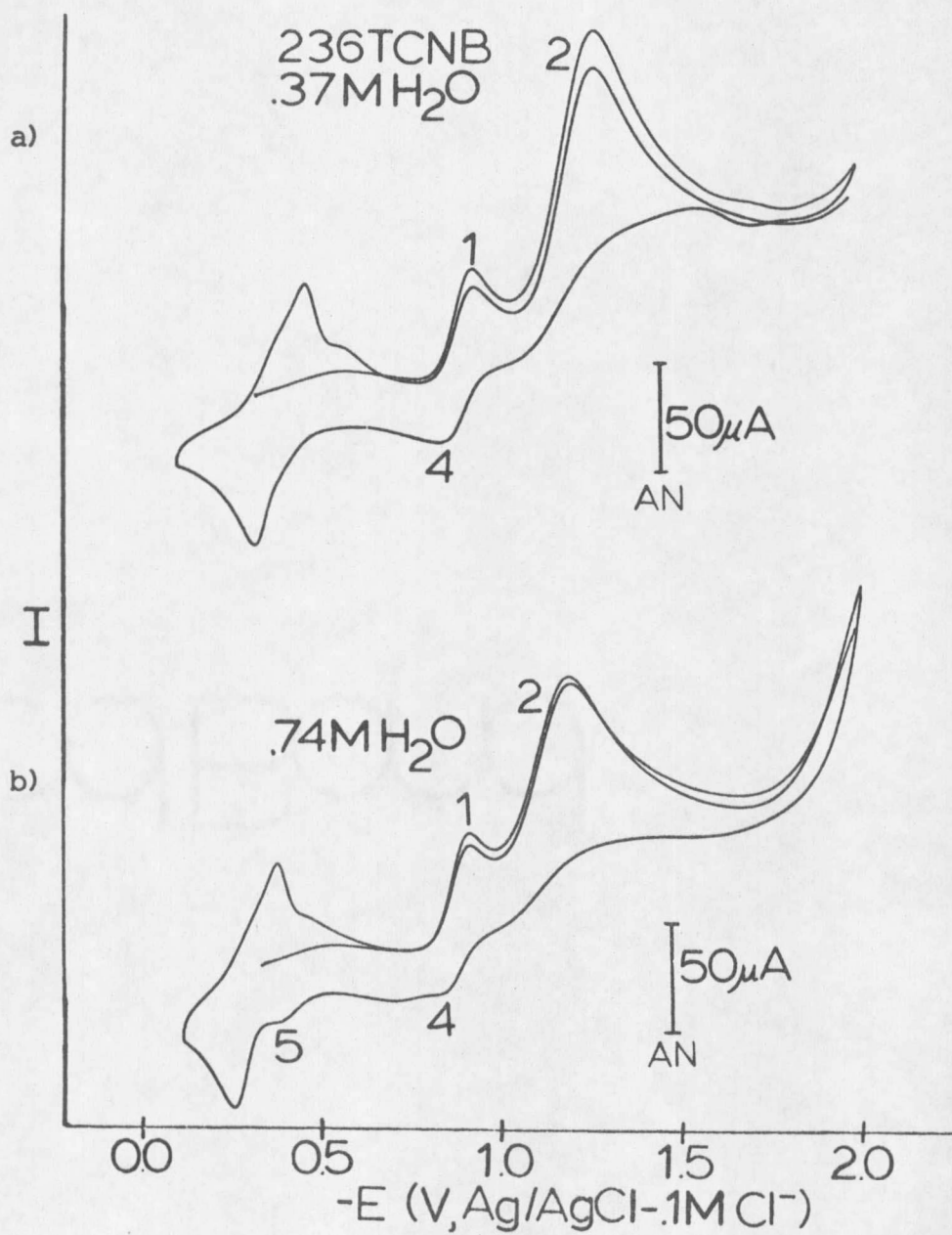


Figure 77. Cyclic voltammograms of 2,3,6-trichloronitrobenzene in AN with a) 0.37 M H₂O; b) 0.74 M H₂O.

difficult to distinguish a chloride wave. There appears to be no nitroso formation at the low water concentration. At .74 M water, the possible dianions are the 2,5-DCNB dianion (-129mV), the 2,6-DCNB dianion (-48mV) or the 2,3-DCNB dianion (-137mv). It is apparent that the 2,6-DCNB dianion is formed. This is a change in the mechanistic pathway. There is a cathodic shoulder (wave 5) on the mercury waves that was uncovered when the mercury waves shift anodically due to increased hydroxide concentration, since proton addition will cause an increase in nitrosobenzene formation. This wave is probably due to a nitroso compound.

2,4,6-Trichloronitrobenzene. Cyclic voltammograms of 2,4,6-trichloronitrobenzene with water added in DMSO are shown in Figure 78. The potential for the formation of the 2,4,6-TCNB dianion remains steady at both concentrations, as does the reversible couple. The formation of nitrobenzene (wave 5) no longer occurs as wave 4 moves +146mV into wave 3, that also shifts +39mV at .37 M water. Increased nitroso formation is represented by a cathodic shoulder on the new mercury complex wave. At .93 M, wave 4 moves +51mV and becomes a shoulder on wave 3, that correspondingly shifts +13mV. Wave 3 corresponds to the reduction of the 2,4-DCNB dianion and wave 4 to either the 2-CNB or 4-CNB dianion.

In DMF, Figure 79, the potentials of waves 3 and 4 in 2,4,6-

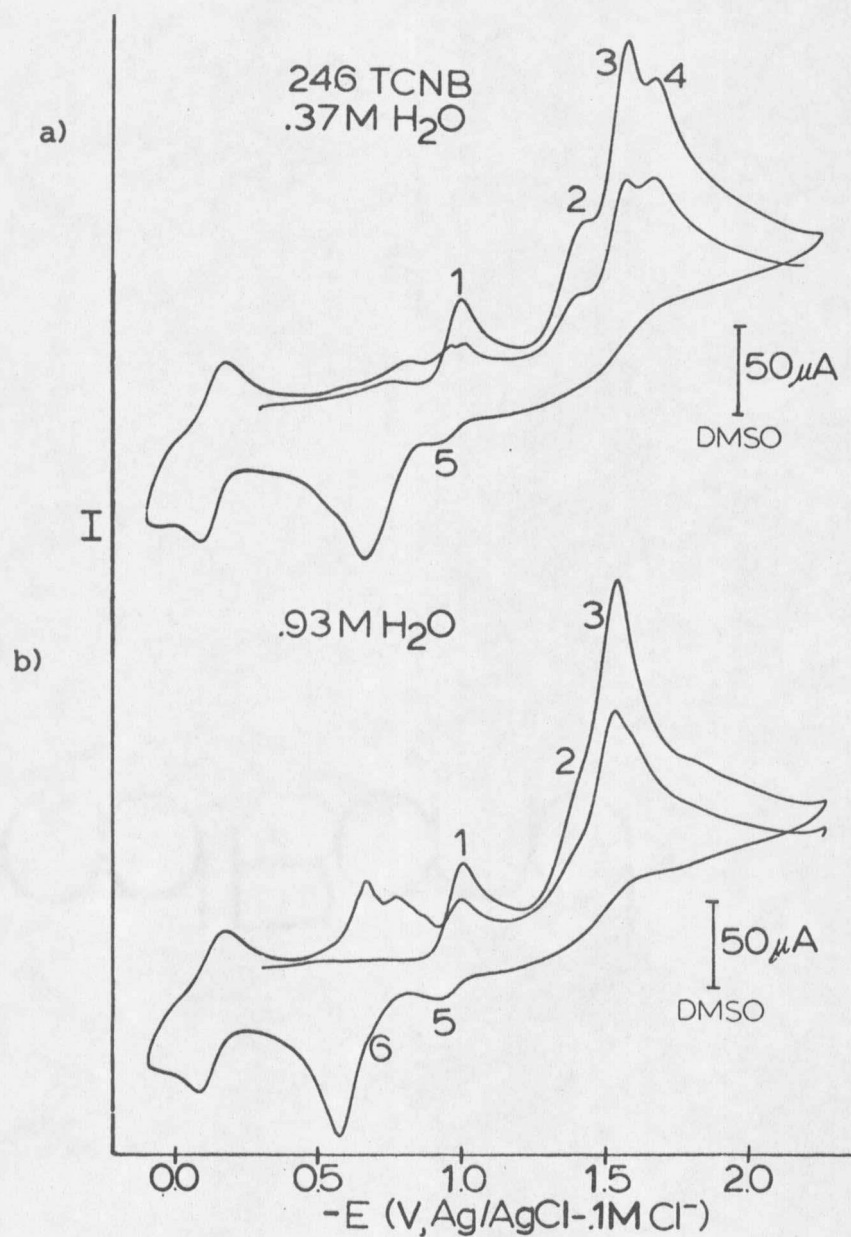


Figure 78. Cyclic voltammograms of 2,4,6-trichloronitrobenzene in DMSO with a) .37 M H₂O; b) .93 M H₂O.

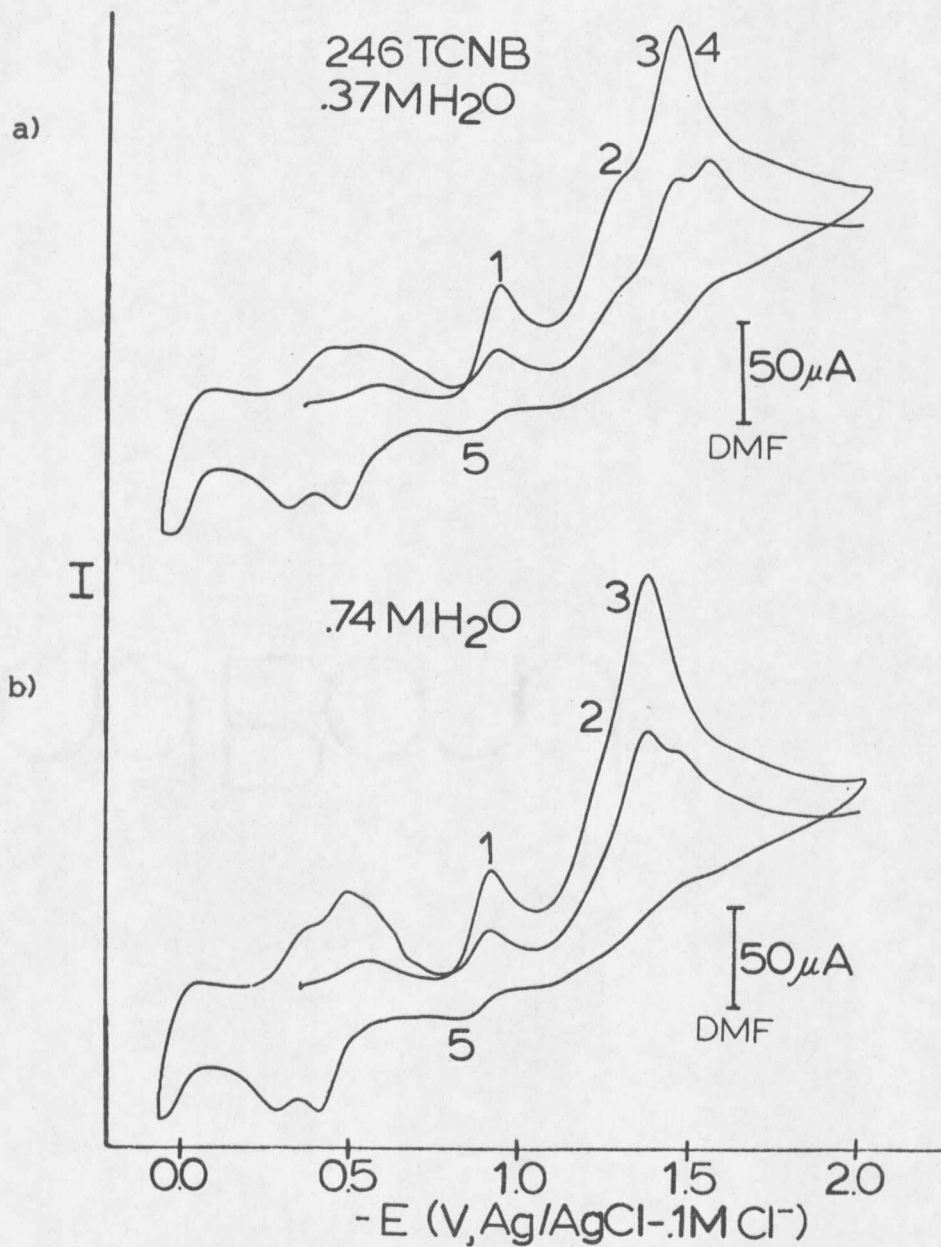


Figure 79. Cyclic voltammograms of 2,4,6-trichloronitrobenzene in DMF with a) 0.37 M H₂O; b) 0.74 M H₂O.

trichloronitrobenzene with .37 M water merge and shift anodically +100mV until wave 2 is an anodic shoulder on wave 3. Wave 2 does not shift. Wave 3 corresponds to the 2,4-DCNB dianion while wave 4, appearing on the second sweep, is probably the 4-CNB dianion wave. The oxidative sweep yields two new waves. The wave just anodic of wave 5 corresponds to 2,4-dichloronitrosobenzene while the cathodic shoulder on this is the 4-chloronitrosobenzene wave. The other new wave is due to the mercury complex. At .74 M, wave 3 merges and obscures wave 2.

In AN, Figure 80, the addition of water causes all waves to shift anodically. It is difficult to distinguish which compounds are formed. The irreversible wave is broad, denoting more than one process. There is probably competition between loss of the ortho and para chlorines yielding either the 2,4-DCNB dianion (+52mV) or the 2,6-DCNB dianion (-1mv). Loss of another chloride ion will yield either the 2-CNB dianion (-16mv) or the 4-CNB dianion (-23mV) at the same potential. It appears that the 2,6-DCNB dianion is formed, again a change in pathways. At a higher water concentration, a small wave occurs just anodic of wave 5, corresponding to either a nitroso compound or a protonated species. The wave just anodic of this, a shoulder on the mercury wave, may also be due to a nitroso compound.

2,3,4,6-tetrachloronitrobenzene. The cyclic voltammograms of

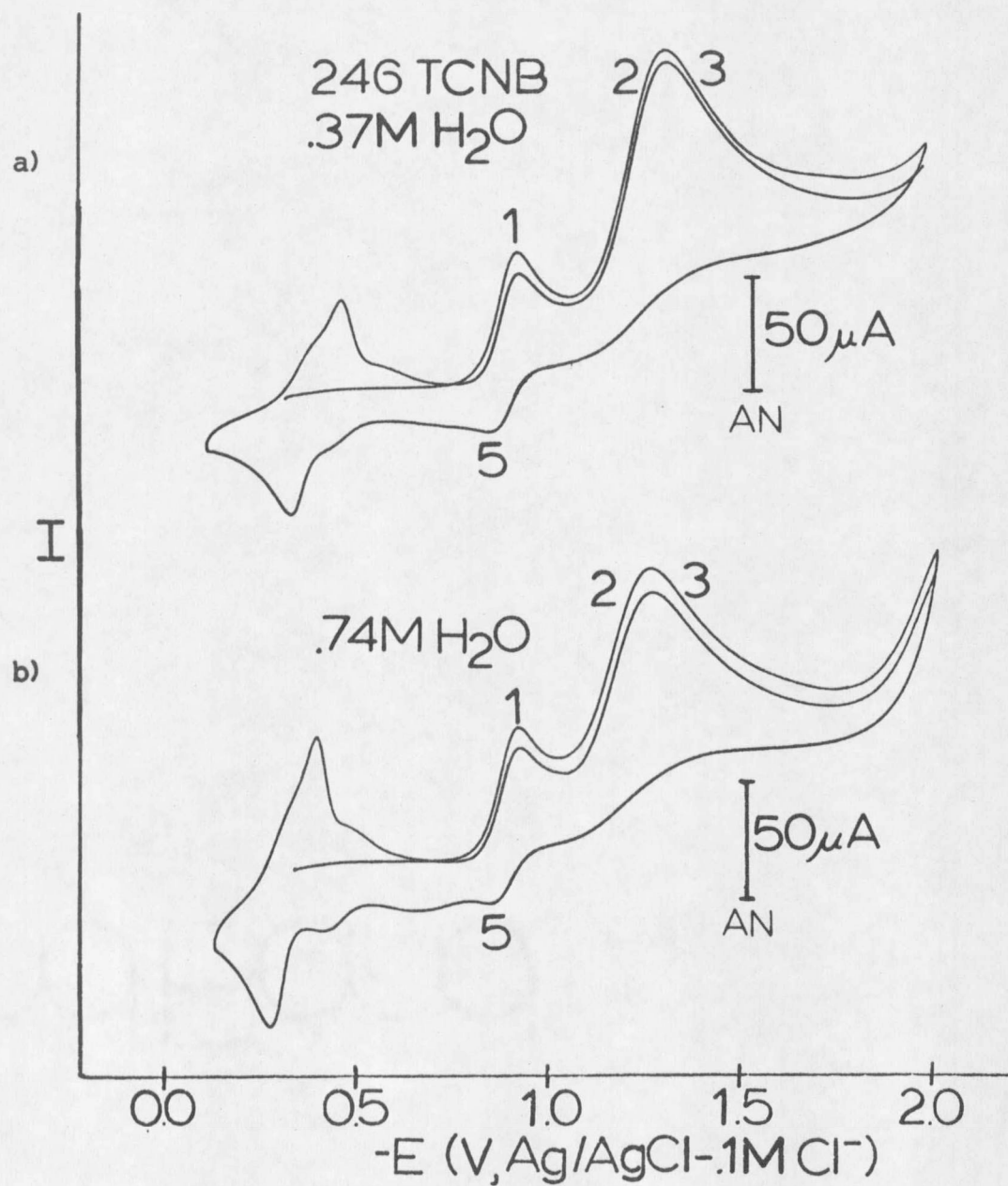


Figure 80. Cyclic voltammograms of 2,4,6-trichloronitrobenzene in AN with a) 0.37 M H_2O ; b) 0.74 M H_2O .

2,3,4,6-tetrachloronitrobenzene with water in DMSO are shown in Figure 81. Wave 5 merges into wave 4 at .37 M by shifting +152mV. Wave 2 moves -25mV (cathodically) while the other waves are steady. The mercury complex is sharp but other waves may be present on the anodic and cathodic tails of it. At .74 M, wave 4 no longer is present and wave 3 decreases and shifts +73mV. Wave 2 moves +36mV. Wave 3 appears to be the 2,4,5-trichloro dianion, wave 4 the 2,5-dichloro dianion and wave 5, while it exists, the 3-chloro dianion. Wave 2 may be broad due to loss of both the ortho and para chlorines with formation of both 2,3,6- and 2,4,5-TCNB.

Cyclic voltammograms of 2,3,4,6-tetrachloronitrobenzene in DMF with water additions are shown in Figure 82. The wave 5 process has decreased and wave 4 shifts into wave 3 and wave 3 moves +71mV. At .34 M, there appears to be competition between the position of chlorine loss. The potential of the irreversible waves are not consistent throughout a pathway. The potential of wave 3 does not correspond to a particular compound, so the potential is due to competing processes. There is a increase in nitroso formation and an increase in the size of the mercury complex.

The 2,3,4,6-tetrachloronitrobenzene voltammograms in AN with water added are shown in Figure 83. Wave 3 shifts +285mV and wave 2 is obscured by it. There is some formation of 3,4-DCNB dianion on

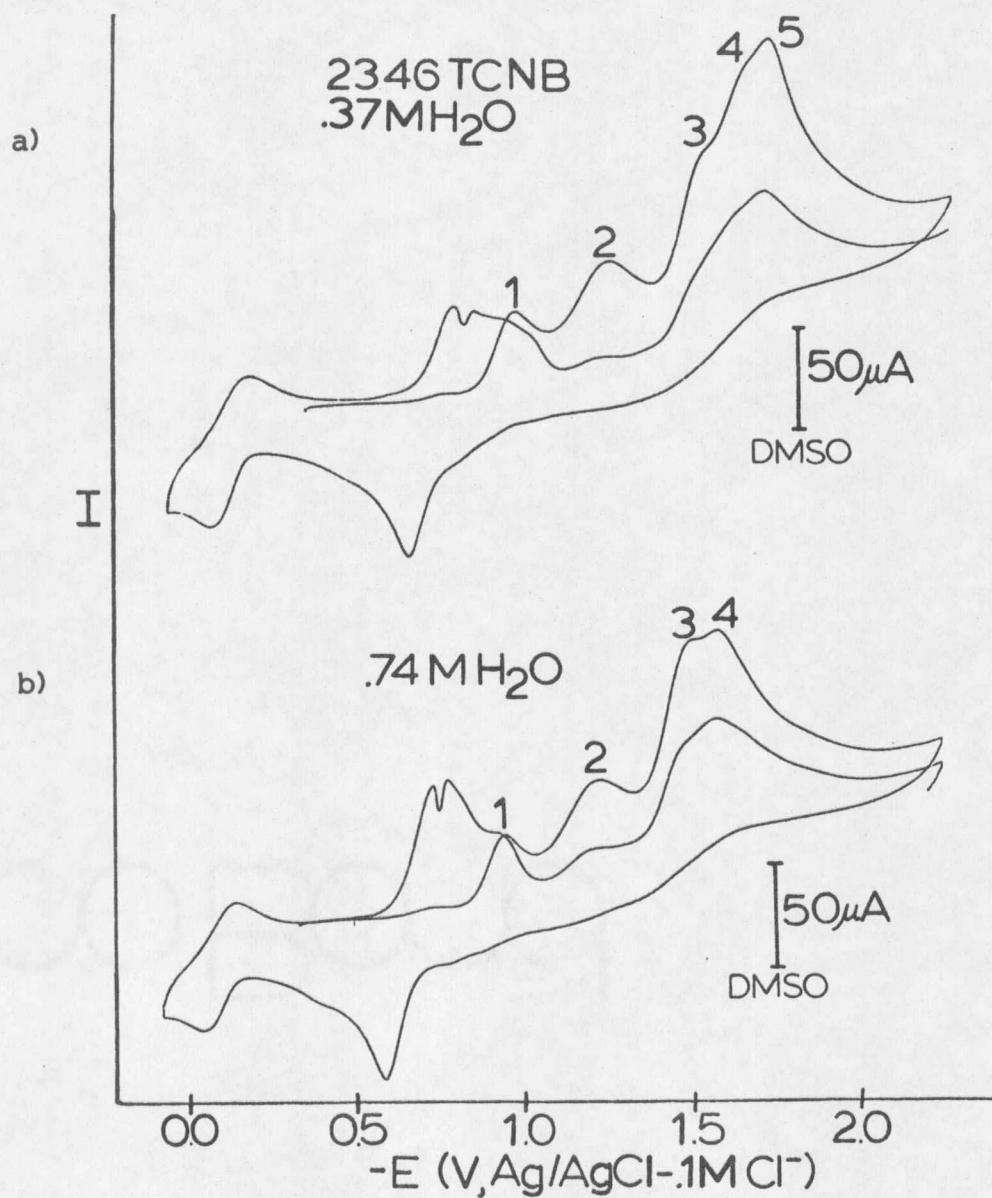


Figure 81. Cyclic voltammograms of 2,3,4,6-tetrachloronitrobenzene in DMSO with a) .37 M H₂O; b) .74 M H₂O.

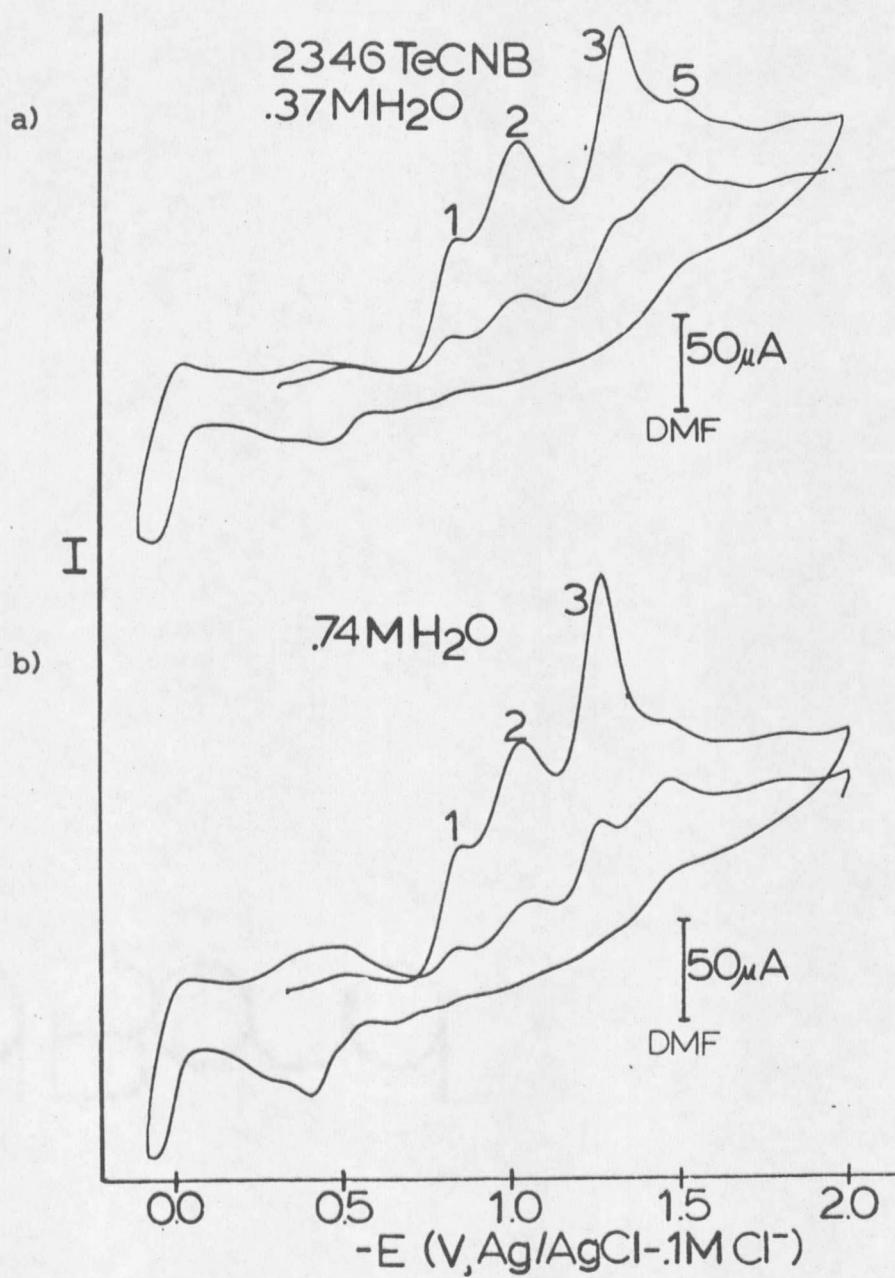


Figure 82. Cyclic voltammograms of 2,3,4,6-tetrachloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

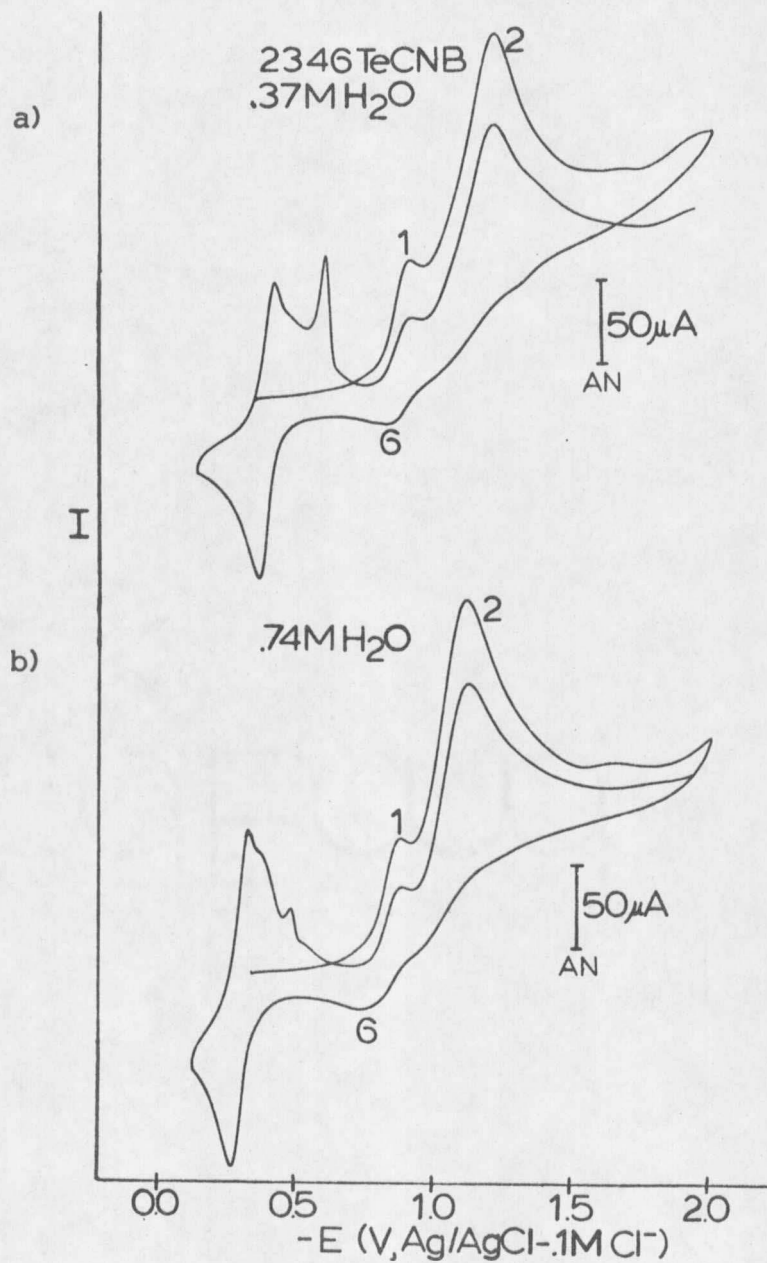


Figure 83. Cyclic voltammograms of 2,3,4,6-tetrachloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

the second sweep. There may be competition between formation of the 3,4-DCNB dianion and the 2,5 DCNB dianion. At .74 M, the irreversible wave shifts +97mV from the position of wave 3. It is difficult to determine if there is formation of a dichloro dianion. There does not appear to be nitroso formation.

2,3,5,6-Tetrachloronitrobenzene. The cyclic voltammograms of 2,3,5,6-tetrachloronitrobenzene in DMSO with ethanol are shown in Figure 84. Observing voltammograms at low ethanol concentrations, it is apparent that wave 6 disappears and wave 5 shifts into wave 4 causing an increase in peak height. Wave 4 shifts +185mV between no ethanol and .35 M ethanol. Wave 3 is steady but wave 2 shifts cathodically by -51mV. The wave (2) is broad without ethanol but is sharper with it. It is easy to assume that more than one process is occurring; but, another process would have to occur prior to the tetrachloro dianion formation. This is not likely to happen. It may be possible that chloride loss is occurring so rapidly that it causes the wave to be broad; but, with ethanol present, the rapid chloride loss slows down. Wave 3 also appears to have shifted cathodically by -30mV. This is due to competition between loss of a meta and an ortho chlorine. As the 2,3,5-TCNB dianion starts to form, a small amount loses the meta chloride. The potential of the shoulder is exactly between the potential of the 2,3,5-TCNB and the 2,5-DCNB

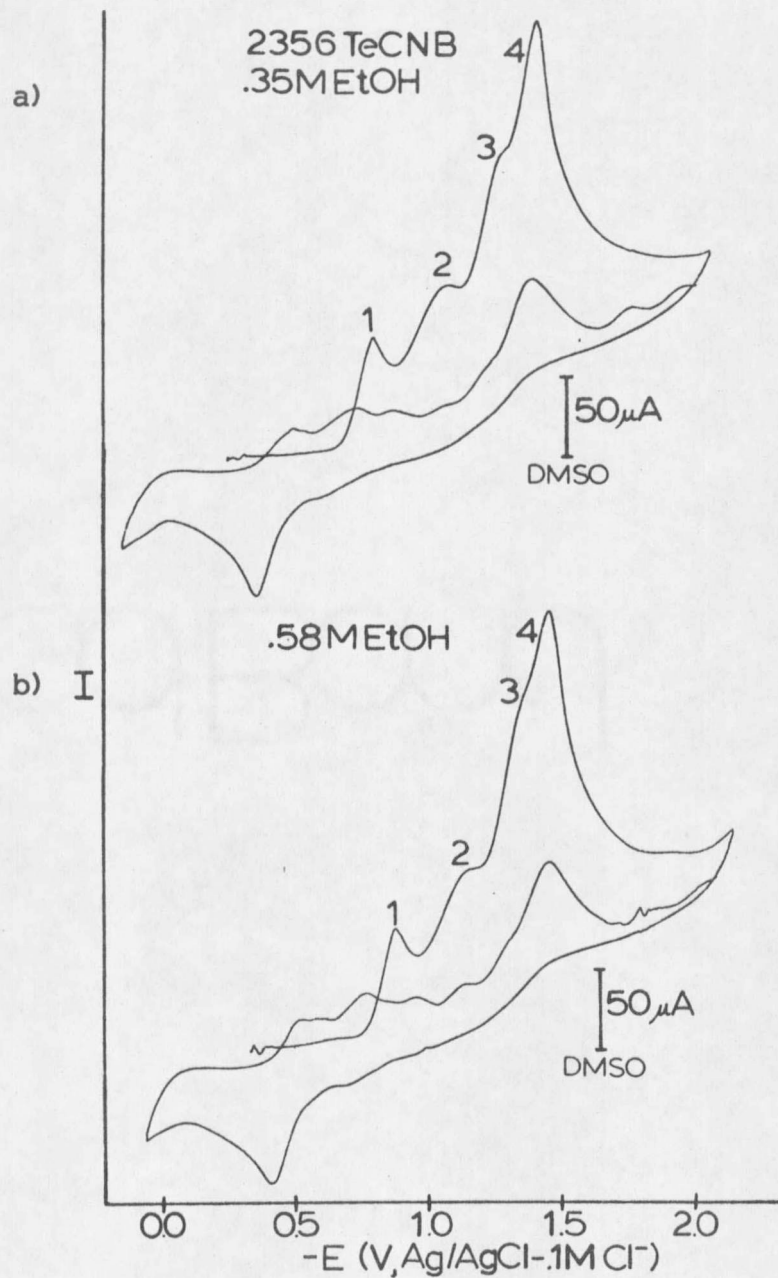


Figure 84. Cyclic voltammograms of 2,3,5,6-tetrachloronitrobenzene in DMSO with a) .35 M EtOH; b) .58 M EtOH.

dianions. The ortho chlorine is lost, for the most part, and forms the dianion for 3,5-DCNB at wave 4. With more ethanol (.58 M), the potential of wave 4 shifts slightly and the reductive waves of the mercury complex become more apparent.

Cyclic voltammograms of 2,3,5,6-TeCNB in DMF with water additions are shown in Figure 85. The wave 5 process decreases while wave 4 shifts +217mV. Wave 3 is stable and appears to be the 2,3,5-TCNB dianion. At .74 M, wave 2 shifts +30mV and still corresponds with the 2,3,5-TCNB dianion while wave 4 moves +91mV proving its the 3,5-DCNB dianion. The rate of chloride loss may decrease and nitroso formation increases along with the mercury complex wave. The second sweep shows some formation of the 3-CNB dianion.

In AN, Figure 86, 2,3,5,6-TeCNB with water addition yields a decrease in nitroso formation. Wave 3 shifts +222mV as it moves into wave 2. Wave 4 decreases but may also shift into wave 3, corresponding to the 2,3,5-TCNB dianion. There may be formation of either the 2,3- or 2,5-DCNB dianion. At .74 M, wave 3 shifts to the potential of wave 2. Wave 2 remains steady but wave 1 has shifted slowly with increasing water addition.

2,3,4,5,6-Pentachloronitrobenzene. The cyclic voltammograms of 2,3,4,5,6-pentachloronitrobenzene in DMSO with ethanol are shown in Figure 87. Waves 1 and 2 are very steady and wave 1 has a

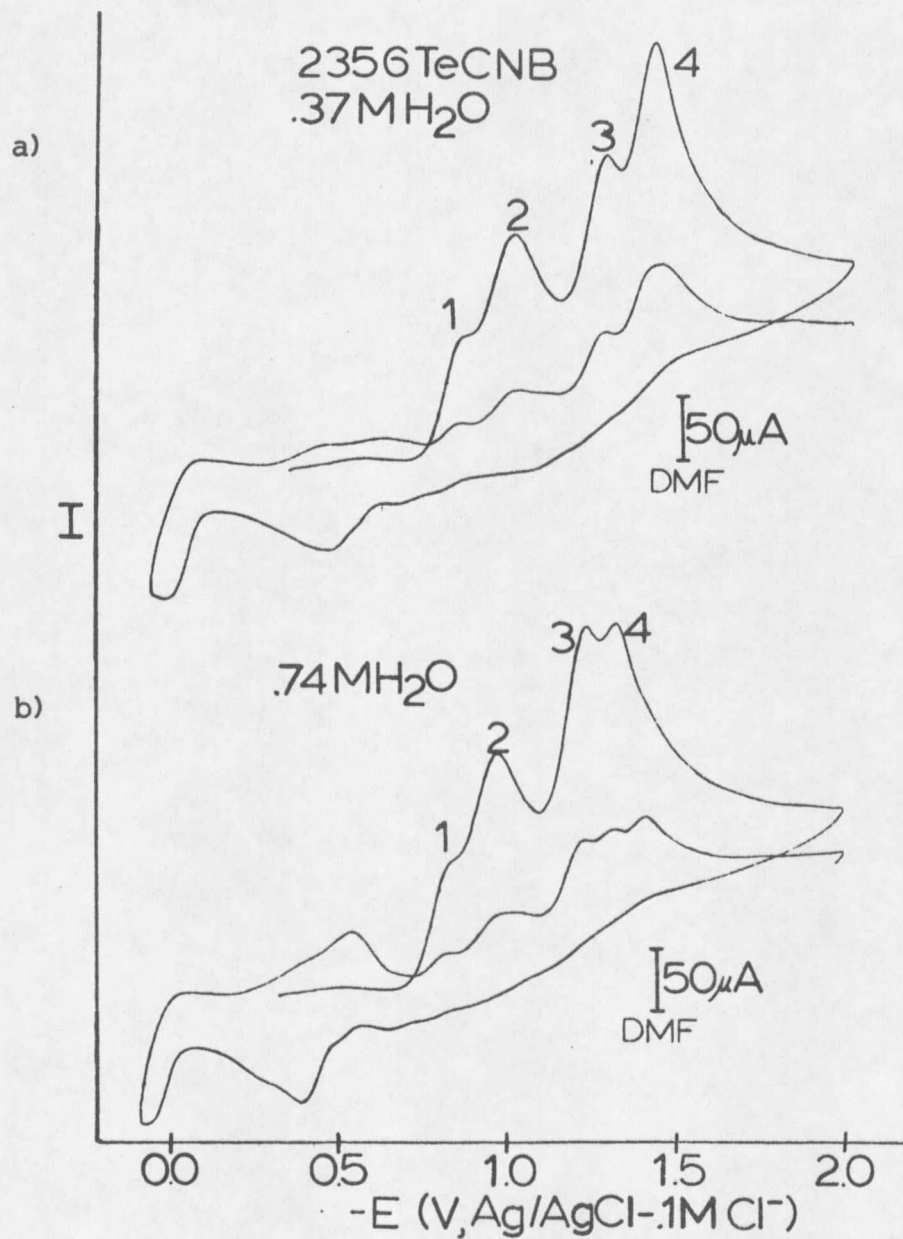


Figure 85. Cyclic voltammograms of 2,3,5,6-tetrachloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

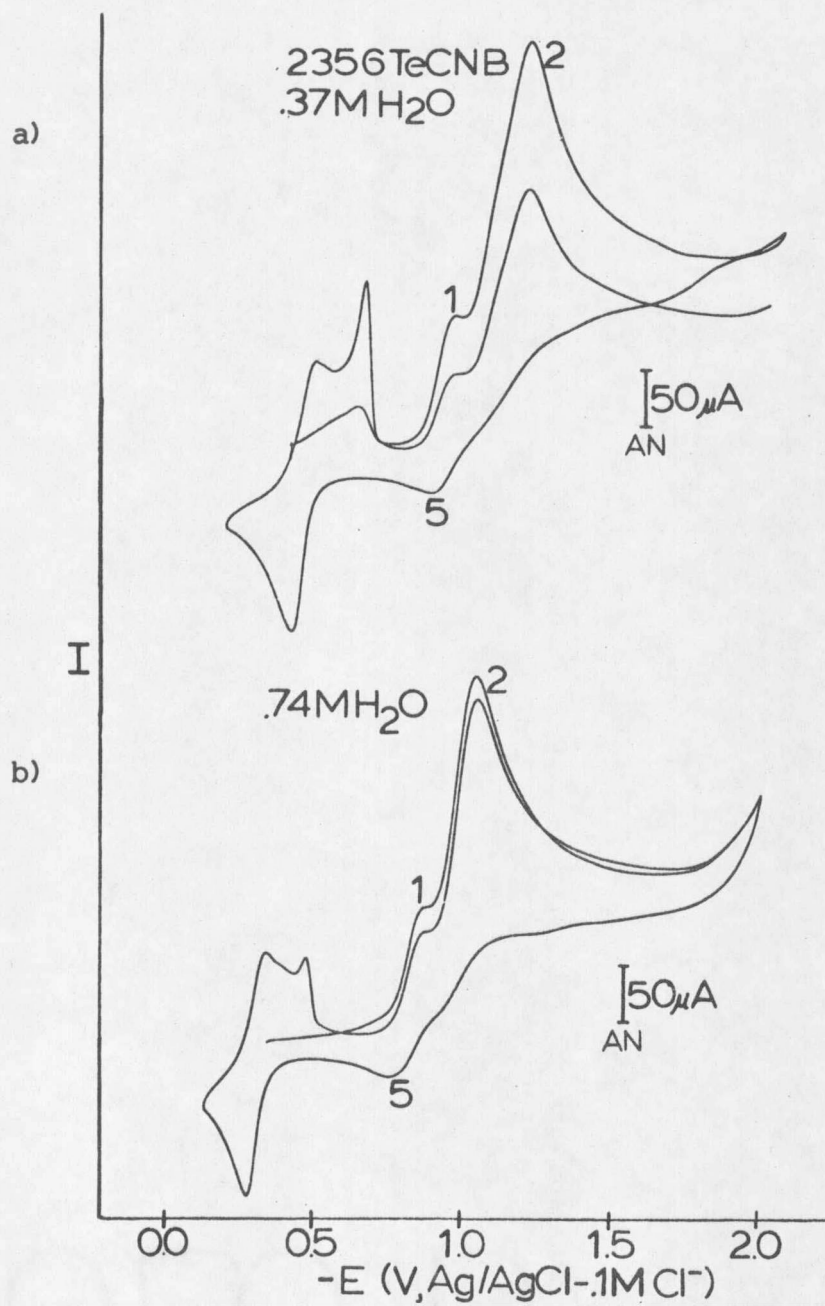


Figure 86. Cyclic voltammograms of 2,3,5,6-tetrachloronitrobenzene in AN with a) .37 M H₂O; b) .74 M H₂O.

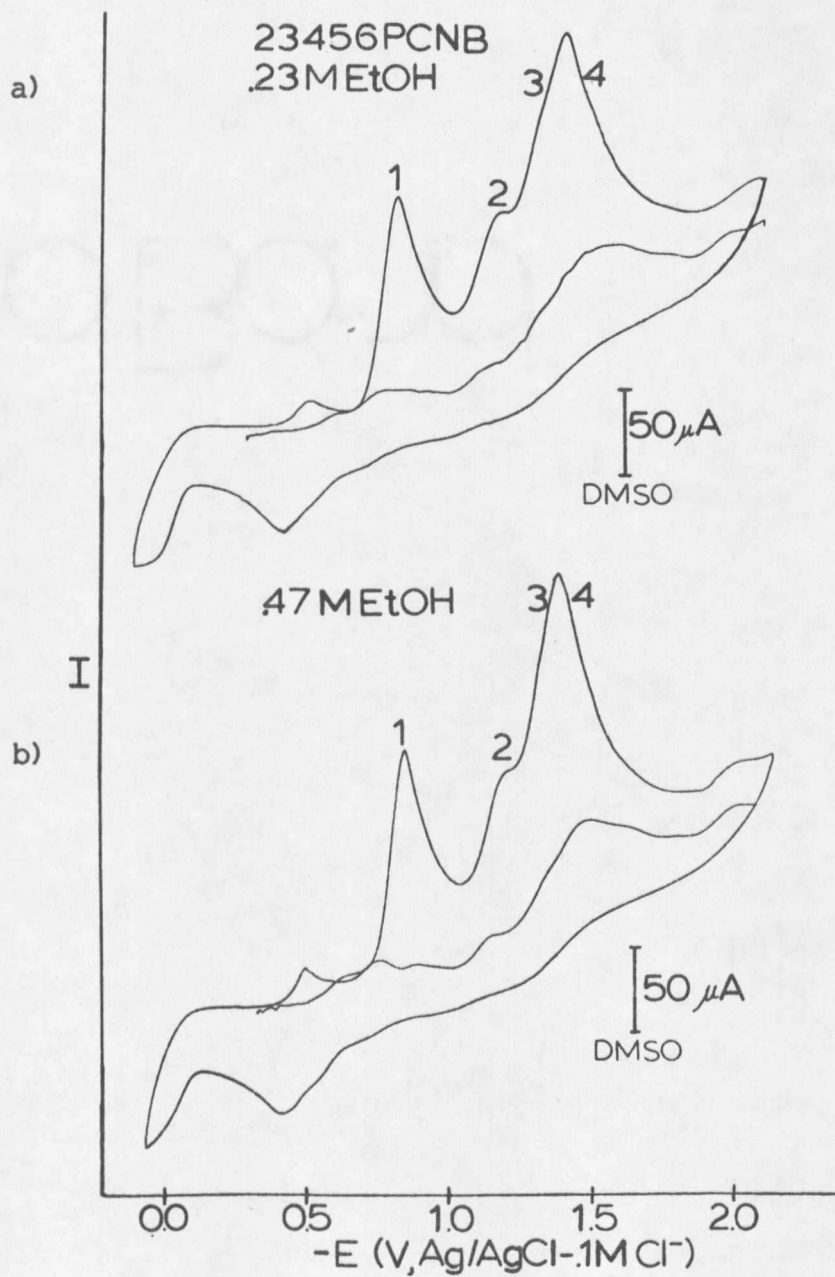


Figure 87. Cyclic voltammograms of 2,3,4,5,6-pentachloronitrobenzene in DMSO with a) .23 M EtOH; b) .47 M EtOH.

preprotonation wave but wave 5 merges into wave 4 while it shifts into wave 3. Wave 4 shifts +146mV while wave 3 is on the anodic tail of wave 4. Wave 2 is the dianion formation of 2,3,4,5-TeCNB at .23 M ethanol. At lower ethanol concentrations, wave 3 appeared to be due to the 2,3,5-TCNB dianion with competition between the 2,5-DCNB dianion and the 3,5-DCNB dianion, causing a shift in the potential of wave 3. Wave 3 is still occurring but it's under wave 4. Wave 4 is the 3,5-DCNB dianion. At higher concentrations, wave 4 merges with wave 3 and wave 3 does not move, so that the pathway is loss of the para chlorine to yield 2,3,5-DCNB. This, in turn, reduces and loses a meta chlorine to yield 2,5-DCNB, which is also reduced. It may lose a chlorine but the dianion does not form.

In DMF, Figure 88, 2,3,4,5,6-PCNB with water demonstrates shifts in potentials, but not as dramatic as might be expected. This is due to the continued rapid chlorine loss and little nitroso formation. Wave 4 shifts +116mV, merging into a stable wave 3. With more water, it shifts +39mV while wave 3 shifts about the same. This compound follows the 2,3,4,5-TeCNB reduction scheme. There is a large chloride wave, but no apparent mercury complex wave. Since there is probably no nitroso formation due to the rapid chlorine loss, there is no hydroxide loss.

In AN, the addition of water to 2,3,4,5,6-PCNB does not change

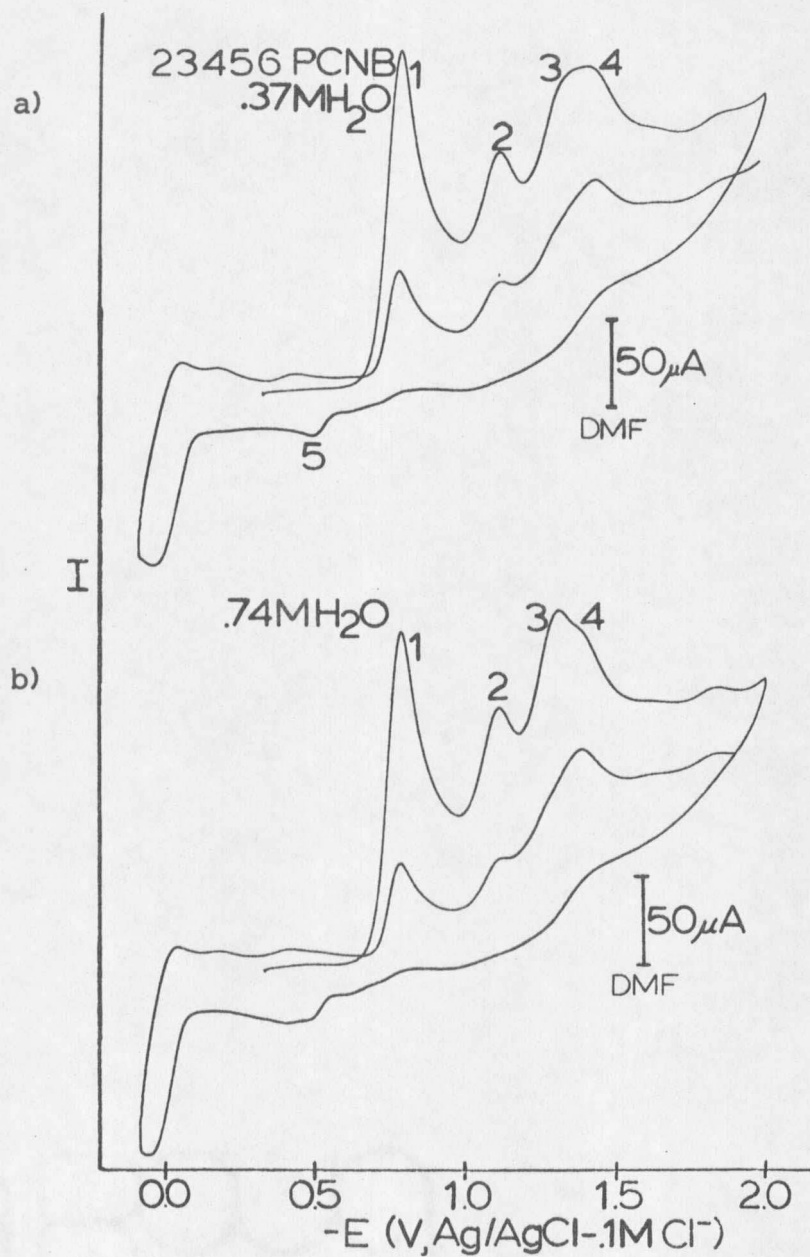


Figure 88. Cyclic voltammograms of 2,3,4,5,6-pentachloronitrobenzene in DMF with a) .37 M H₂O; b) .74 M H₂O.

the pathway (Figure 89). Waves 3 and 4 decrease and shift toward wave 2. The potentials of the shifted waves correspond to the mechanism found without added water. With the water concentration at .74 M, the waves past the 2,3,4,5-TeCNB dianion formation are not visible. However, since they decrease in size they could be occurring under the dominant wave 2. Their decrease shows chloride loss decreases and there is still no nitroso formation. Waves 5 and 6 correspond to the oxidation of the 2,3,5,6-TeCNB radical anion and the 2,3,5-TCNB or the 3,5-DCNB radical anion.

Sweep Rate Studies

Changes in sweep rate are very helpful in determining if a process is rate-limited. The work done in DMF and AN is observed at a variety of sweep rates as was some of the DMSO studies. Figure 90 shows the voltammograms of 2,5-dichloronitrobenzene in DMF at .37 M water. At a sweep rate of 503.7mV/sec (Figure 90a), there is one irreversible wave on both sweeps and a small oxidative "hump" for the protonated dianion (C3E2). At 64.2mV/sec, (Figure 90b), the irreversible wave shows a cathodic shoulder on the second sweep and the oxidative hump has grown considerably. Note that the slower sweep rate has allowed more material to diffuse to the surface so that the second sweep follows the first sweep more closely (this is shown more clearly in Figure 90a). The growth of the oxidative

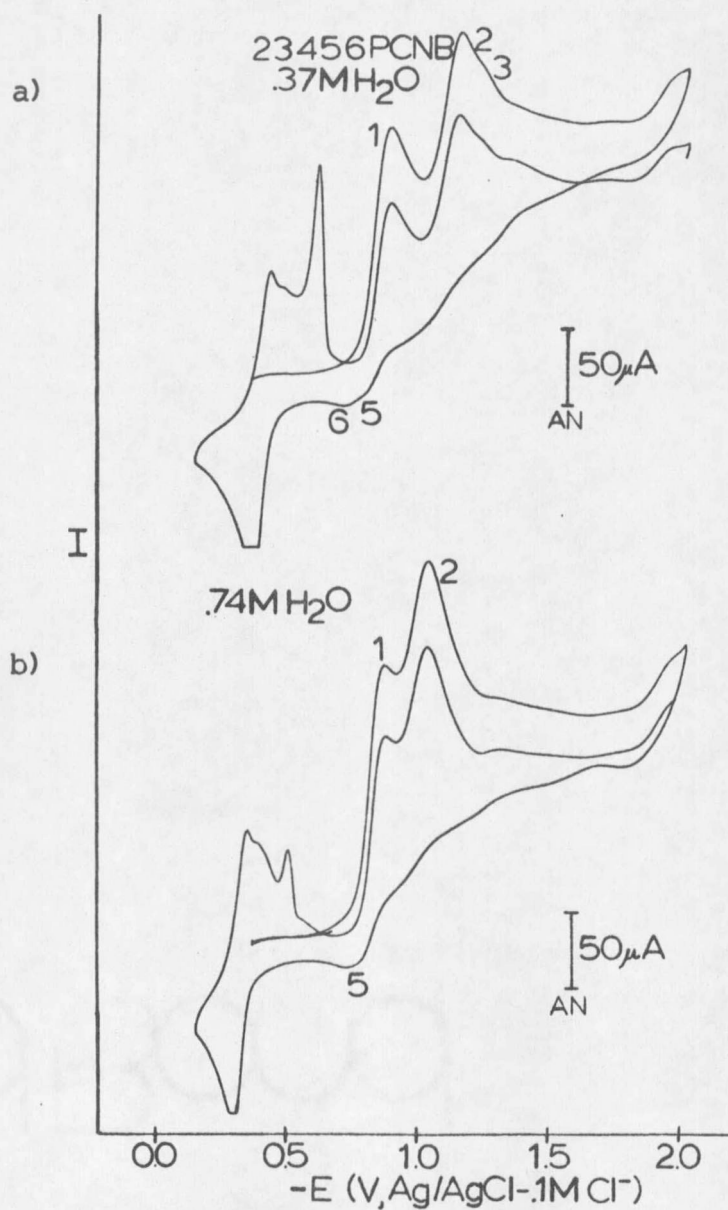


Figure 89. Cyclic voltammograms of 2,3,4,5,6-pentachloronitrobenzene in AN with a) $.37\text{M H}_2\text{O}$; b) $.74\text{M H}_2\text{O}$.

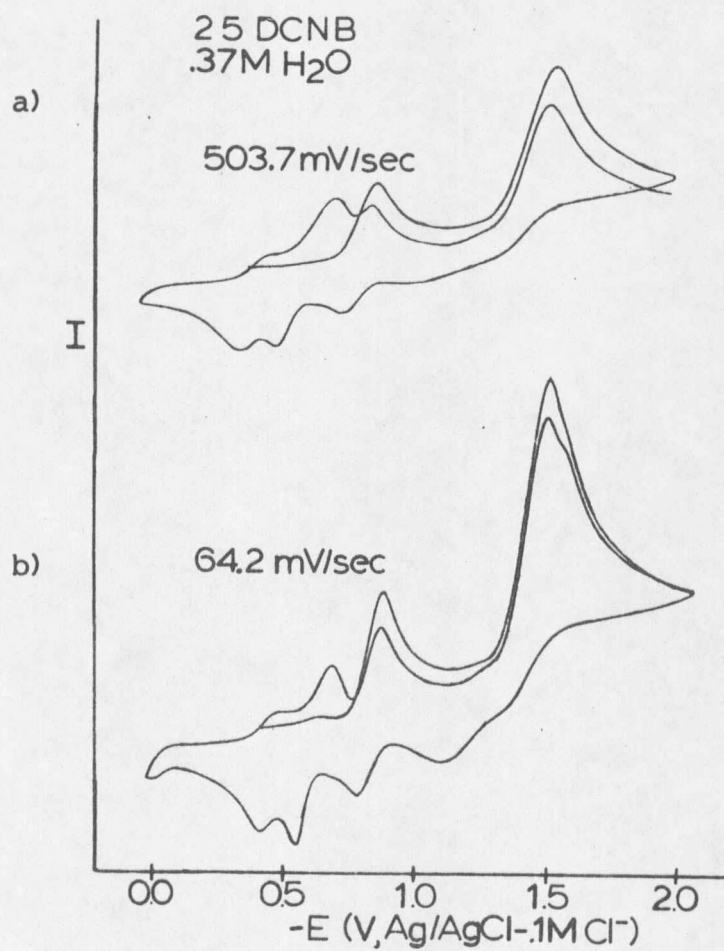


Figure 90. Sweep rate variations for 2,5-dichloronitrobenzene with .37 M H₂O in DMF.

"hump" is indicative of a slow protonation process. The slower sweep rate also allows processes that occur under a wave to be seen. For 3,5-dichloronitrobenzene in DMF, a sweep rate of 32.6mV/sec allows observation of three irreversible processes and a front shoulder (Figure 91a). There is some nitroso formation but actual peaks are not seen. At 252.6mV/sec the first irreversible process appears as a shoulder on the first sweep and as a peak on the second (Figure 91b). The nitroso waves have grown. At 1004mV/sec (Figure 91c), there is a front shoulder on the irreversible waves but the first irreversible wave is not present. The nitroso waves occur as one large wave. The nitroso process must occur fast enough that it dominates at rapid sweep rates while the slow rates allow for diffusion and for chemical reactions to occur. The lower sweep rates are most accurate as a plot of sweep rate vs potential of 2-CNB in DMF yields an exponential curve (Figure 92).

Sigma Rho Calculations

Sigma rho studies help to study the effect of adjacent chlorine on dianion formation and changes due to different solvents. Using the method of R. Geer and H. Byker,⁷⁰ calculations are performed using linear regression. Initial sigma constants used are $\sigma_{\text{para}} = .23$, $\sigma_{\text{ortho}} = .20$ and $\sigma_{\text{meta}} = .37$. The uncorrected calculated values for rho (ρ) and the correlation coefficients are in Table 8 for DMF

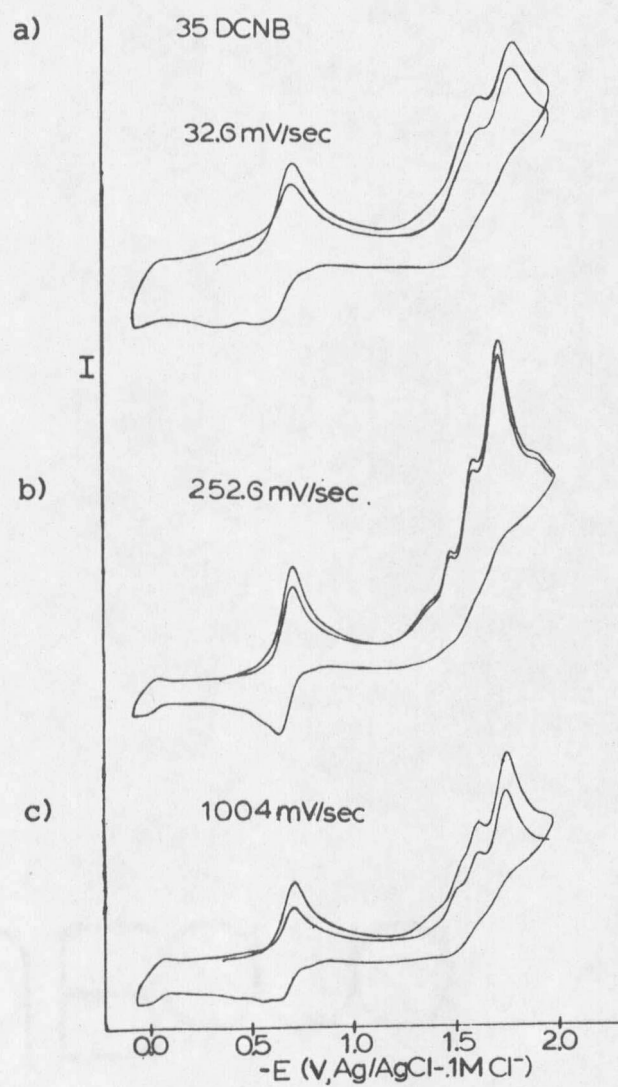


Figure 91. Sweep rate variations for 3,5-dichloronitrobenzene in DMF.

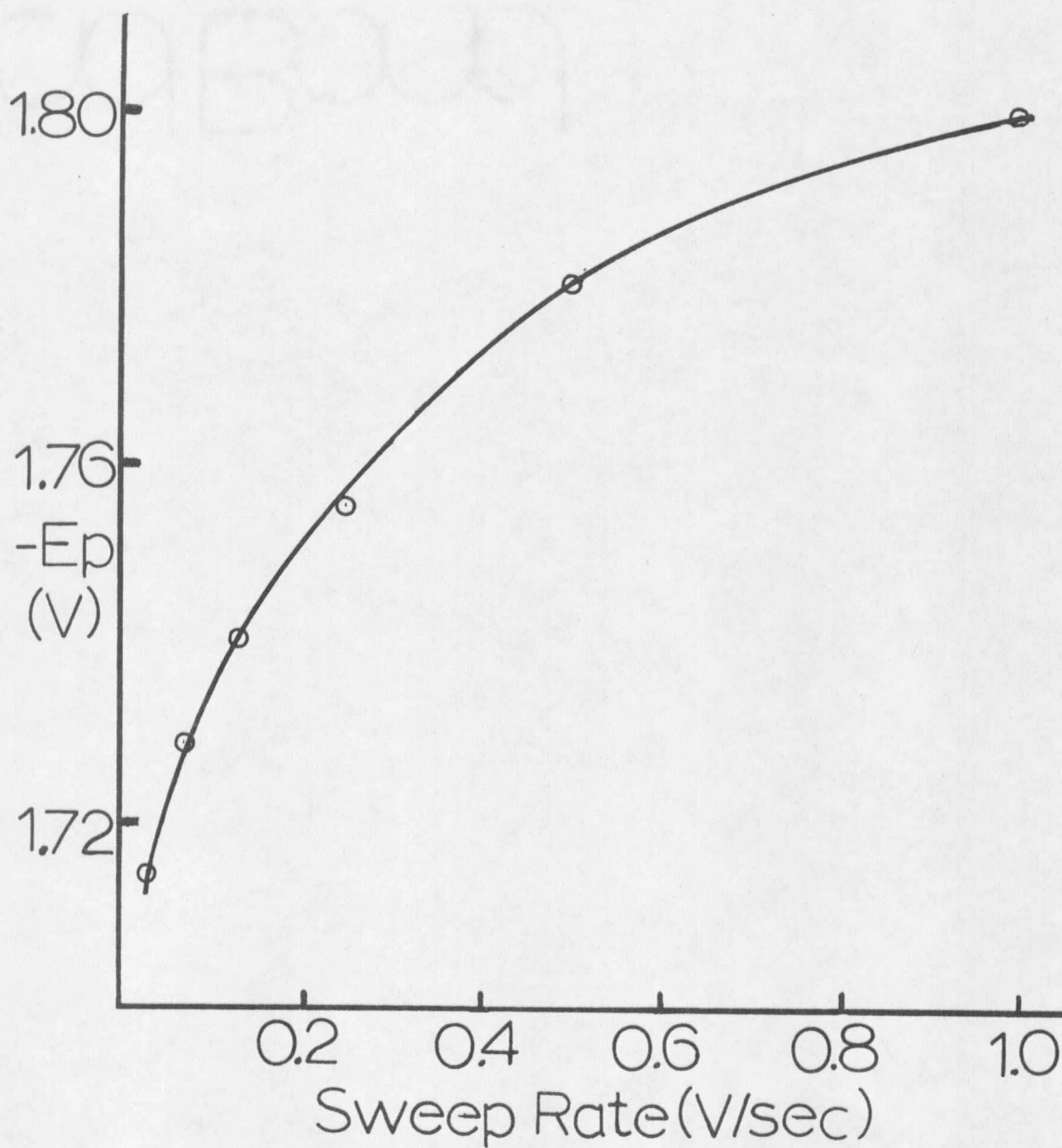


Figure 92. Plot of sweep rate (V/sec) vs peak potential (V) using 2-chloronitrobenzene data in DMF.

without water added. Each series of compounds are taken individually and a correction constant, σ_{α} , for compounds with adjacent chlorines is determined. This is found by determining the reaction constant (slope = ρ) for each series using only compounds without adjacent chlorines (Table 7), finding the total deviation from the line of compounds with adjacent chlorines and dividing by the number of adjacent chlorines to find the average deviation per adjacent chlorine. This is divided by the reaction constant (ρ) to yield σ_{α} for each series. These are averaged to yield one correction constant (Table 8). The correction factor is subtracted for each adjacent chlorine interaction from the $\Sigma\sigma$ value for each compound.

Using the new $\Sigma\sigma$ values, a new σ_{para} is determined since the σ_{para} value originally used is too small compared with σ_{meta} . Linear regression on all data in a series is done and the average deviation from the line for all compounds with a para chlorine is found and a new σ_{para} is calculated from $(2(\text{Avg. dev})/\rho) + \sigma_{\text{para}}^0$ where σ_{para}^0 is the original value (.23). Values found are in Table 9. Another σ_{α} is calculated using the new σ_p then both corrections, σ_{α} and σ_p , are applied and the linear regression reveals the final correlation coefficient, showing excellent agreement for the data (Table 9).

The same calculations are repeated for AN without water (Tables 10-12), for DMF and AN at low concentrations of water (Tables 13-15

Table 7. Hammett σ_p correlations using primary σ constants in DMF.

	<u>With all data</u>			<u>Data without adjacent chlorine</u>		
O-Cl's	0	1	2	0	1	2
# compounds	6	8	6	4	3	2
$\sigma = 0$, mV	-989	-1003	-1086	-995	-1022	-1174
ρ_e , mV	351	275	199	382	334	378
r	.995	.973	.978	.997	.990	1.000

(a) $\sigma_O = 0.20$, $\sigma_m = 0.37$, $\sigma_p = 0.23$

Table 8. Empirical determination of Adjacent Chlorine Correction Factor, σ_α^a in DMF.

O-Cl's	0	1	2
Set of Adj Cl's	3	8	2
Avg. Dev., mV	-17.0 $\pm$ 1.7	-23.6 $\pm$ 10.1	-45.7 $\pm$ 11.6
ρ_e , mV	382	334	378
σ_α^b	-.045 $\pm$.005	-.071 $\pm$.030	-.121 $\pm$.031

(a) $\sigma_O = .20$, $\sigma_m = .37$, $\sigma_p = .23$, $\sigma_\alpha = \text{avg dev}/\rho_e$

(b) $\sigma_\alpha (\text{avg}) = -.079\pm.039$

Table 9. Re-evaluation of Hammett Correlation Using the Empirical σ_{α} (avg) corrections^a in DMF.

	with $\sigma_p = .23$ and $\sigma_{\alpha} = .079$			with $\sigma_{pc}^{\circ} = .293$ and $\sigma_{\alpha}^{\circ} = .070$		
O-Cl's	0	1	2	0	1	2
$\sigma = O$, mV	-998	-1027	-1130	-1003	-1030	-1115
ρ_e , mV	403	356	289	384	332	267
r	.996	.964	.975	.998	.994	.976
σ_p^{ob}	.036	.082	.072			

(a) $\sigma_o = .2$, $\sigma_m = \sigma_m^{\circ} = .37$, $\sigma_p^{\circ} = \frac{2 \times \text{avg dev}}{\rho}$

(b) $\sigma_{p\text{avg}}^{\circ} = .063(\pm .024) + .23 = .293$

(c) σ_{α} (calculated using $\sigma_p = .293$) = $.070 \pm .009$

Table 10. Hammett σ_{ρ} Correlations Using Primary σ Constants,^a in AN.

	<u>With all data</u>			<u>Data without adjacent chlorine</u>		
O-Cl's	0	1	2	0	1	2
# compounds	6	8	6	4	3	2
$\sigma = O$, mV	-1043	-1043	-1103	-1046	-1077	-1169
ρ_e , mV	308	235	153	327	340	287
r	.997	.967	.981	.998	.999	1.000

(a) $\sigma_o = 0.20$, $\sigma_m = 0.37$, $\sigma_p = 0.23$

Table 11. Empirical Determination of Adjacent Chlorine Correction Factor, σ_{α}^a in DMF with .34 M water.

O-Cl's	0	1	2
Sets of Adj. Cl's	3	8	2
Avg. Dev., mV	-11.0 $\pm$ 0.0	-37.4 $\pm$ 11.4	-34.6 $\pm$ 7.1
ρ_e , mV	327	340	287
σ_{α}^b	-.034 $\pm$ 0.0	-.110 $\pm$.034	-.121 $\pm$.025

(a) $\sigma_o = .20$, $\sigma_m = .37$, $\sigma_p = .23$, $\sigma_{\alpha} = \text{avg.dev}/\rho_e$

(b) $\sigma_{\alpha}(\text{avg}) = -.088 \pm .047$

Table 12. Re-evaluation of Hammett Correlation Using the Empirical $\sigma_{\alpha}(\text{avg})$ correction^a in AN.

	with $\sigma_p = .23$ and $\sigma_{\alpha} = .088$			with $\sigma_p^{\circ} = .284$ and $\sigma_{\alpha}^{\circ} = .089$		
O-Cl's	0	1	2	0	1	2
$\sigma = 0$, mV	-1050	-1072	-1144	-1056	-1073	-1144
ρ_e , mV	356	319	235	349	307	228
r	.922	.986	.983	.996	.994	.996
$\sigma_{p\text{cor}}^{\text{ob}}$	.049	.044	.068			

(a) $\sigma_o = .2$, $\sigma_m = \sigma_m^{\circ} = .37$, $\sigma_p^{\circ} = \frac{2 \times \text{avg dev}}{\rho}$

(b) $\sigma_{p\text{avg}}^{\circ} = .054 (\pm .013) + .23 = .284$

(c) $\sigma_{\alpha}(\text{calculated using } \sigma_{p\text{avg}}^{\circ} = .284) = .089 \pm .023$

Table 13. Hammett σ_p Correlations Using Primary σ constants^a in DMF with .34 M water.

	<u>With all data</u>			<u>Data without adjacent chlorine</u>		
O-Cl's	0	1	2	0	1	2
# compounds	6	8	6	4	3	2
$\sigma = 0$, mV	-978	-995	-1071	-983	-1018	-1157
ρ_e , mV	348	272	187	375	342	357
r	.996	.975	.979	.998	.991	1.000

(a) $\sigma_o = 0.20$, $\sigma_m = .037$, $\sigma_p = 0.23$

Table 14. Empirical Determination of Adjacent Chlorine Correction Factor, σ_α^a in DMF with .34 M water.

O-Cl's	0	1	2
Sets of Adj. Cl's	3	8	2
Avg. Dev., mV	-15.3 $\pm$.3	-25.4 $\pm$ 12.9	-41.9 $\pm$ 10.1
ρ_e , mV	375	342	357
σ_α^b	-.041 $\pm$.001	-.074 $\pm$.038	-.117 $\pm$.028

(a) $\sigma_o = .20$, $\sigma_m = .37$, $\sigma_p = .23$, $\sigma_\alpha = \text{avg.dev}/\rho_e$

(b) $\sigma_\alpha(\text{avg}) = -.077\pm.038$

Table 15. Re-evaluation of Hammett Correlation Using the Empirical σ_{α} (avg) correction^a in DMF with .34 M water.

	with $\sigma_p = .23$ and $\sigma_{\alpha} = .078$			with $\sigma_p^{\circ} = .271$ and $\sigma_{\alpha}^{\circ} = .070$		
O-Cl's	0	1	2	0	1	2
$\sigma = 0$, mV	-987	-1023	-1113	-991	-1025	-1108
ρ_e , mV	399	353	272	392	345	257
r	.996	.986	.980	.999	.995	.980
σ_{pcor}^{ob}	.040	.061	.022			

(a) $\sigma_o = .2$, $\sigma_m = \sigma_m^{\circ} = .37$, $\sigma_{\alpha}^{\circ} = \frac{2x_{avg} \text{ dev}}{\rho}$

(b) $\sigma_p^{\circ} \text{ avg} = 0.41 (\pm .020) + .23 = .271$

(c) σ_{α} (calculated using $\sigma_p^{\circ} \text{ avg} = .271$) = $.080 \pm .015$

and Tables 16-18, respectively) and for DMF and AN at higher concentrations of water (Tables 19-21 and Tables 22-24, respectively). Note that sigma rho calculations are not done for DMSO. The DMSO data recorded by H. Byker⁸⁹ yielded better results because they were taken under drier solvent conditions and the sigma rho calculations reported by Geer and Byker⁷⁰ yield a much better fit.

Table 16. Hammett σ_p Correlations Using Primary σ constants^a in AN with .34 M water.

	<u>With all data</u>			<u>Data without adjacent chlorine</u>		
O-Cl's	0	1	2	0	1	2
# compounds	6	8	6	4	3	2
$\sigma = 0$, mV	-996	-1004	-1039	-1001	-1040	-1091
ρ_e , mV	282	217	120	311	324	222
r	.997	.964	.975	.999	.995	1.000

(a) $\sigma_o = 0.20$, $\sigma_m = .037$, $\sigma_p = 0.23$

Table 17. Empirical Determination of Adjacent Chlorine Correction Factor, σ_α^a in AN with .34 M water.

O-Cl's	0	1	2
Sets of Adj. Cl's	3	8	2
Avg. Dev., mV	-13.7 $\pm$ 1.2	-36.6 $\pm$ 11.5	-25.1 $\pm$ 3.1
ρ_e , mV	311	324	222
σ_α^b	-.044 $\pm$.004	-.112 $\pm$.036	-.113 $\pm$.014

(a) $\sigma_o = .20$, $\sigma_m = .37$, $\sigma_p = .23$, $\sigma_\alpha = \text{avg.dev}/\rho_e$

(b) $\sigma_\alpha(\text{avg}) = -.090 \pm .040$

Table 18. Re-evaluation of Hammett Correlation Using the Empirical σ_{α} (avg) correction^a in AN with .34 M water.

	with $\sigma_p = .23$ and $\sigma_{\alpha} = .079$			with $\sigma_p^{\circ} = .293$ and $\sigma_{\alpha}^{\circ} = .070$		
O-Cl's	0	1	2	0	1	2
$\sigma = 0$, mV	-994	-1027	-1075	-1010	-1037	-1075
ρ_e , mV	335	295	190	329	292	185
r	.994	.964	.993	.997	.992	.998
$\sigma_{p\text{cor}}^{\text{ob}}$	.042	.076	.042			

(a) $\sigma_o = .2$, $\sigma_m = \sigma_m^{\circ} = .37$, $\sigma_p^{\circ} = \frac{2 \times \text{avg dev}}{p}$

(b) $\sigma_{p\text{avg}}^{\circ} = 0.5341 (\pm .020) + .23 = .283$

(c) σ_{α} (calculated using $\sigma_{p\text{avg}}^{\circ} = .283$) = $.093 \pm .026$

Table 19. Hammett σ_p Correlations Using Primary σ constants^a in DMF with .74 M water.

	<u>With all data</u>			<u>Data without adjacent chlorine</u>		
O-Cl's	0	1	2	0	1	2
# compounds	6	8	6	4	3	2
$\sigma = 0$, mV	-963	-983	-1055	-967	-996	-1151
ρ_e , mV	338	264	178	359	310	370
r	.997	.972	.973	.998	.987	1.000

(a) $\sigma_o = 0.20$, $\sigma_m = .037$, $\sigma_p = 0.23$

Table 20. Empirical Determination of Adjacent Chlorine Correction Factor, σ_{α}^a in DMF with .74 M water.

O-Cl's	0	1	2
Sets of Adj. Cl's	3	8	2
Avg. Dev., mV	-13.0 $\pm$.9	-21.0 $\pm$ 8.3	-47.9 $\pm$ 10.8
ρ_e , mV	359	310	370
σ_{α}^b	-.036 $\pm$.002	-.068 $\pm$.027	-.130 $\pm$.029

(a) $\sigma_o = .20$, $\sigma_m = .37$, $\sigma_p = .23$, $\sigma_{\alpha} = \text{avg.dev}/\rho_e$ (b) $\sigma_a(\text{avg}) = -.078 \pm .048$ Table 21. Re-evaluation of Hammett Correlation Using the Empirical $\sigma_{\alpha}(\text{avg})$ correction^a in DMF with .74 M water.

	with $\sigma_p = .23$ and $\sigma_{\alpha} = .078$			with $\sigma_p^{\circ} = .278$ and $\sigma_{\alpha}^{\circ} = .078$		
O-Cl's	0	1	2	0	1	2
$\sigma = 0$, mV	-970	-1010	-1095	-977	-1012	-1096
ρ_e , mV	385	342	259	378	332	251
r	.995	.985	.977	.988	.994	.987
$\sigma_{p\text{cor}}^{\text{ob}}$	.043	.069	.0322			

(a) $\sigma_o = .2$, $\sigma_m = \sigma_m^{\circ} = .37$, $\sigma_p^{\circ} = \frac{2 \times \text{avg. dev}}{\rho}$ (b) $\sigma_{p\text{avg}}^{\circ} = .048 (\pm .019) + .23 = .278$ (c) $\sigma_{\alpha}(\text{calculated using } \sigma_{p\text{avg}}^{\circ} = .278) = .078 \pm .024$

Table 22. Hammett σ_p Correlations Using Primary σ constants^a in AN with .74 M water.

	<u>With all data</u>			<u>Data without adjacent chlorine</u>		
O-Cl's	0	1	2	0	1	2
# compounds	6	8	6	4	3	2
$\sigma = 0$, mV	-971	-990	-1004	-974	-1023	-1051
ρ_e , mV	278	221	110	294	321	200
r	.996	.964	.970	.996	.995	1.000

(a) $\sigma_o = 0.20$, $\sigma_m = .037$, $\sigma_p = 0.23$

Table 23. Empirical Determination of Adjacent Chlorine Correction Factor, σ_α^a in DMF with .74 M water.

O-Cl's	0	1	2
Sets of Adj. Cl's	3	8	2
Avg. Dev., mV	-9.3 $\pm$.6	-35.5 $\pm$ 13.9	-21.1 $\pm$ 3.18
ρ_e , mV	294	321	200
σ_α^b	-.032 $\pm$.002	-111 $\pm$.043	-.107 $\pm$.16

(a) $\sigma_o = .20$, $\sigma_m = .37$, $\sigma_p = .23$, $\sigma_\alpha = \text{avg.dev}/\rho_e$

(b) $\sigma_a(\text{avg}) = -.083\pm.046$

Table 24. Re-evaluation of Hammett Correlation Using the Empirical σ_{α} (avg) correction^a in AN with .74 M water.

	with $\sigma_p = .23$ and $\sigma_{\alpha} = .083$			with $\sigma_p^{\circ} = .275$ and $\sigma_{\alpha}^{\circ} = .085$		
O-Cl's	0	1	2	0	1	2
$\sigma = 0$, mV	-977	-1015	-1034	-982	-1017	-1033
ρ_e , mV	319	293	168	312	287	162
r	.992	.982	.992	.997	.993	.993
$\sigma_{p\text{cor}}^{\circ}$	.053	.065	.028			

(a) $\sigma_o = .2$, $\sigma_m = \sigma_m^{\circ} = .37$ $\sigma_p^{\circ} = \frac{2 \times \text{avg dev}}{\rho}$

(b) $\sigma_p^{\circ} \text{ avg} = .049 (\pm .019) + .23 = .279$

(c) σ_{α} (calculated using $\sigma_p^{\circ} \text{ avg} = .275$) = $.084 \pm .027$

CONCLUSIONS

Cyclic Voltammograms Without Proton Addition

The mechanistic pathways of reduction of the chlorinated nitrobenzenes appear to be characteristic of a particular solvent. Voltammograms run in DMSO and DMF often had similar mechanistic pathways though DMF had a series of prewaves attributable to strong product adsorption and/or protonation. Voltammograms run in AN showed fewer waves, showed less nitroso formation and the wave separation was not as great as in DMSO or DMF. AN does not hydrogen bond and the nitrile group is not very reactive towards water so that the dianion protonates rapidly and causes the waves to appear more positive and closer together. We noticed an increase in peak height in AN compared to DMF or DMSO when equal molar amounts of substrate are added to each. Runner et.al., found the ratios of wave heights in AN for the reduction of stilbene and other hydrocarbons in the presence of water were consistently greater than the same ratio in DMF.⁹⁸ They attributed this to the effect of the water on AN which would cause it to behave more acidically than DMF. We noted from the literature that AN has a lower viscosity than DMF or DMSO. Since viscosity is inversely related to the diffusion coefficient, the diffusion coefficient of AN should be greater than the values for DMF or DMSO.

This would allow material to move through AN to the surface of the electrode more rapidly than in DMSO or DMF and could account for the increased sensitivity in AN.

It has also been reported that the enthalpy of mixing of water and AN is endothermic so that breaking water-water hydrogen bonds occur and "free" water is present.⁸⁷ It was also noted that the enthalpy of mixing of DMF and DMSO with water is exothermic. The viscosity increases, the current decreases, which is what theory described since the diffusion coefficient is directly related to the diffusion current by the square root of the diffusion coefficient and the diffusion coefficient is inversely related to viscosity. The viscosity of DMSO was found to double and the viscosity of DMF was found to quadruple suggesting that the diffusion coefficient in DMF decreases with water addition.⁸⁷ This may account for the adsorption waves in DMF because a decrease in the diffusion coefficient would allow material to remain at the surface of the electrode longer. DMF may also solvate the anions less than AN or DMSO.

We have seen that the pathways for reduction of the chlorinated nitrobenzenes compete with each other. The competitive pathways are protonation vs chloride loss vs hydroxide loss as well as chlorine loss being competitive with loss of chloride from another position.

The protonation process (C3) competes with loss of chloride (C4) and the 4-chloronitrobenzene voltammogram in DMSO is a good example of this (Figure 10a). There is only one irreversible wave representing the 4-CNB dianion by the E2' wave and the oxidative "hump" are present. This means that the C3 predominates while for 3,5-dichloronitrobenzene in DMSO (Figure 13a), there is formation of the 3-CNB dianion but no further loss of chloride. However, the E2' wave is present, indicating that chloride loss competes with protonation. Loss of hydroxide competes with return of the protonated dianion by the E2' or C3E2 process. The hydroxide loss can be very slow and is dependent on the solvent. Our data show hydroxide loss is fastest in DMSO and slowest in AN. Loss of chlorine has been discussed above. The competition between the position of chloride loss has been seen in many cases. We have seen in some cases (Figure 18b, for example) that loss of the para and ortho chlorines are easier than loss of the meta chlorine. However, when meta chlorines are adjacent, there is appreciable loss of the meta chlorine which is not seen when it is isolated as in the 2,5-CNB case. Another example where adjacent chlorine interactions cause a change in the expected pathway is 2,3,5-DCNB in AN where the 3,5-DCNB dianion is formed compared to the 2,3-DCNB dianion in DMF and the 2,5- and 3,5-DCNB dianions in competition in DMSO. There are many other examples of adjacent chlorine inter-

actions which differ according to solvent (Table 25). DMSO studies yielded competitive processes in all but one compound while the other solvents usually had a definite process. DMSO may protonate more slowly thus allowing for competition between chlorines.

Sigma rho calculations were done to help determine the effects of adjacent chlorine interactions, the effect of changing solvents and to try to correlate the dianion behavior with the radical anion behavior. Sigmarho calculations use the radical anion data because the dianion peak potentials are modified due to more than one process occurring and no equilibrium is obtained. However, the sigma rho calculations from the radical anion can be compared with the behavior of the second wave. The corrected data for AN and DMF are plotted in Figures 93 and 94. All compounds now fit the line or are within one standard deviation of the line yielding excellent correlation. For these data, it is apparent that the slopes of the lines (ρ) for each series of compounds are different. The slope qualitatively measures the amount of charge on the nitro group (radical anion). It has been shown in another study that the reduction of nitrobenzene to its radical anion yields a different ρ in AN than in DMF.⁴⁷ This appears to be the case in our study where the slope for each set of data in each solvent is unique. In AN, the slope of the series 2 compounds is 1.18 times larger than the series 3 slope and 1.04 times longer than

Table 25. Effects of adjacent chlorines and solvent on position of chloride loss.

Compound with adjacent Cl's	# Adj. Cl's	Position # of Chloride loss*		
		DMSO	DMF	AN
23	1	<u>2</u> ;3	<u>2</u>	<u>2</u>
34	1	3; <u>4</u>	3; <u>4</u>	<u>4</u>
234	2	3; <u>4</u>	<u>4</u>	<u>2</u> ;3
235	1	<u>2</u> ;3	<u>2</u>	<u>2</u>
236	1	<u>2</u> ;6	<u>2</u> ;6	<u>6</u>
245	1	<u>4</u>	<u>2</u>	<u>4</u>
345	2	3; <u>4</u>	<u>4</u>	<u>4</u>
2345	3	<u>4</u>	<u>2</u>	<u>2</u>
2346	2	(<u>6</u> ;3), <u>4</u>	(<u>6</u>), <u>4</u>	(<u>6</u>), <u>2</u>
2356	2	5; <u>6</u>	<u>6</u>	<u>6</u>
23456	4	(<u>6</u>), <u>4</u>	(<u>6</u>), <u>2</u>	(<u>6</u>), <u>2</u>

* Position numbers underlined are position of major loss. Number in parenthesis indicate first chlorine loss when change in position of chlorine loss occurs after one or more chlorines is lost.

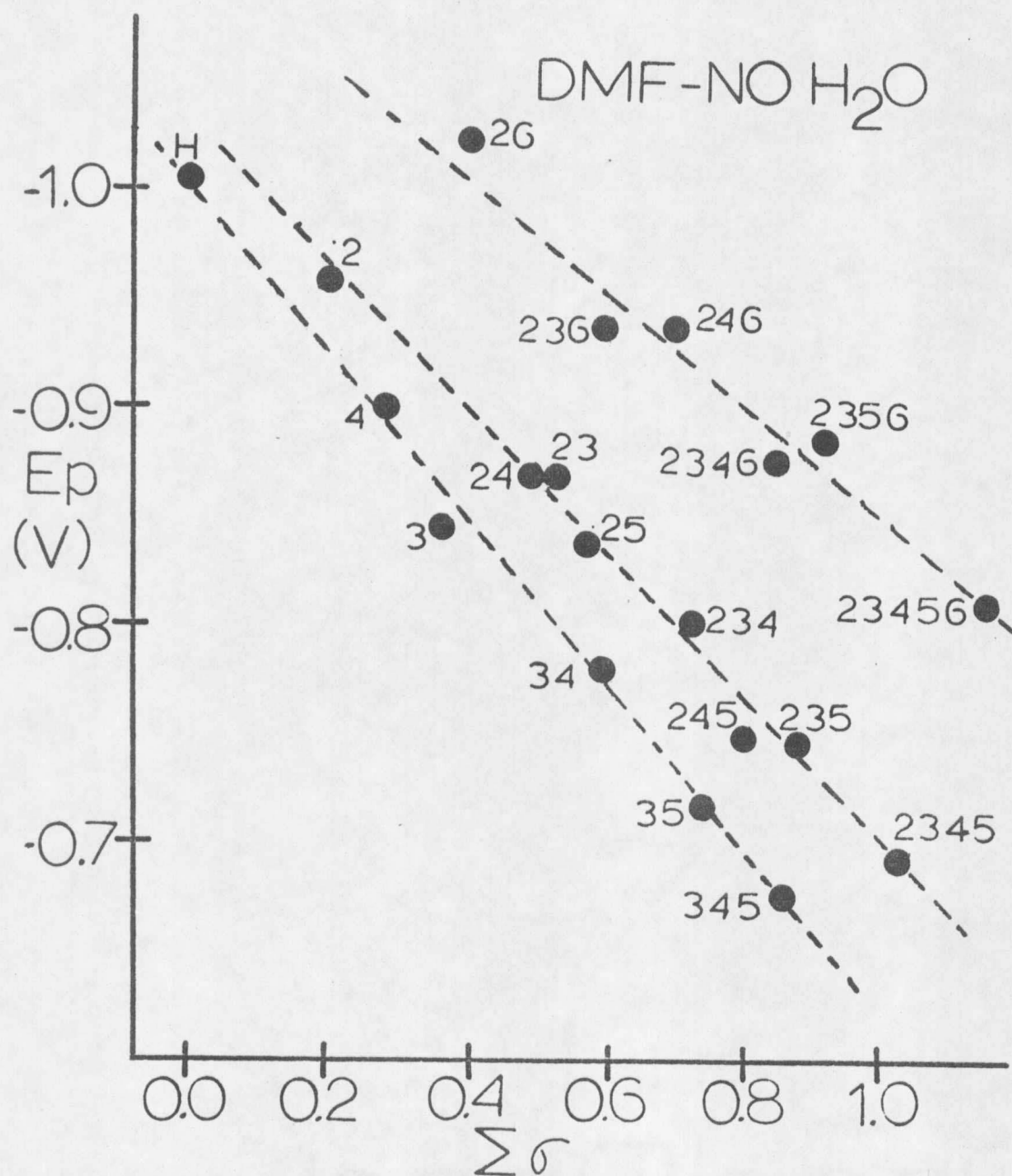


Figure 93. Plot of $\Sigma \sigma_{\text{corrected}}$ vs peak potential (V) for all compounds in DMF without water added.

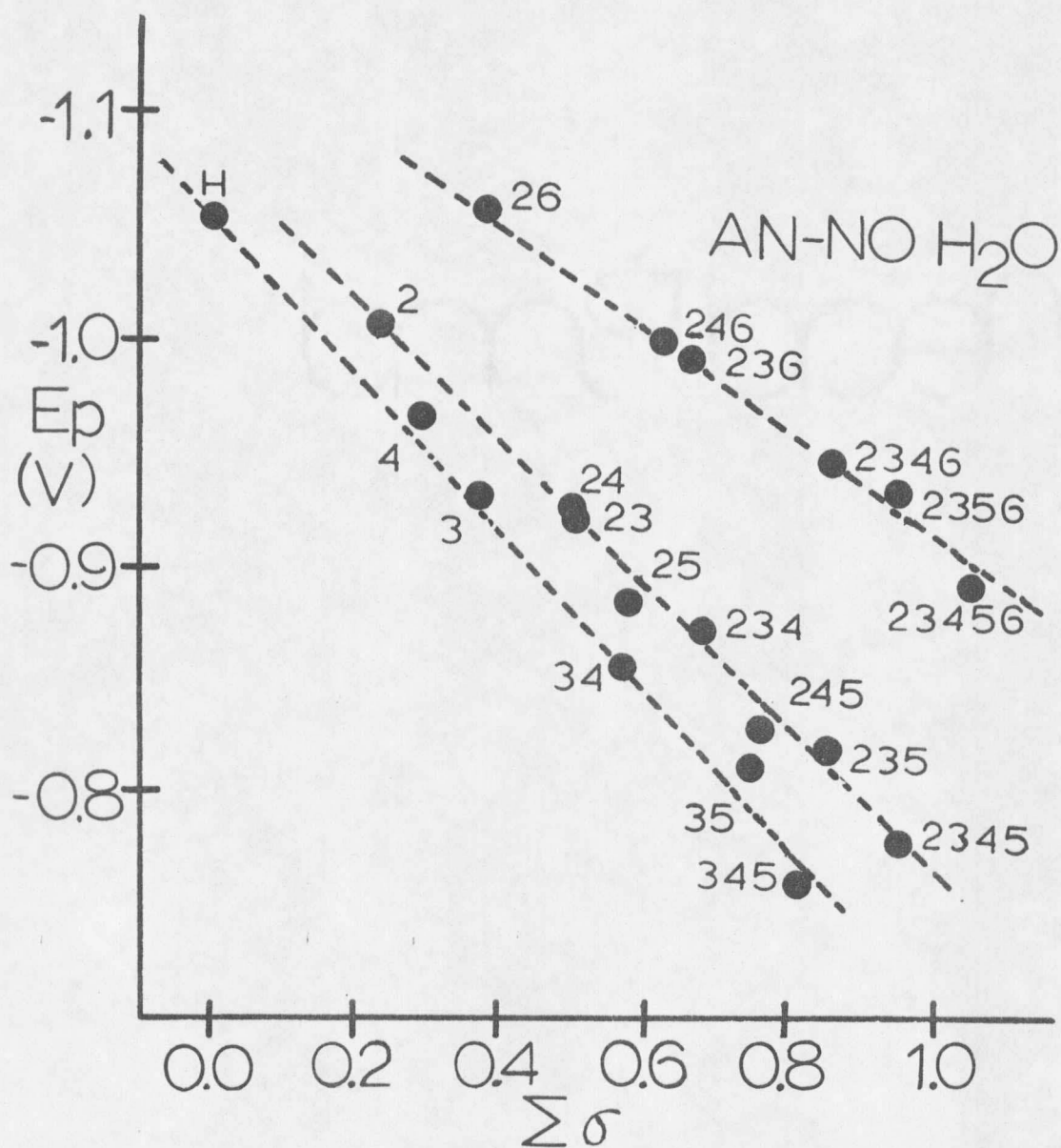


Figure 94. Plot of $\Sigma \sigma_{\text{corrected}}$ vs peak potential (V) for all compounds in AN without water added.

the series 1 slope. In DMF, the slope of the series 2 compounds is 1.24 times larger than the series 2 slope but .86 times smaller than the series 1 slope. Note that in AN, the potentials are all more negative than in DMF (Nitrobenzene reduces at -1.004V in DMF and -1.053V in AN), indicating that the compounds should be easier to reduce in DMF. The comparison of energy in terms of joules is $9.7 \times 10^4\text{J/mole}$ for the nitrobenzene radical anion in DMF compared to $1 \times 10^5\text{J/mole}$ in AN. The reduction of nitrobenzene is easier in DMF by 3000J/mole .

As stated above, the series 3 (two ortho chlorines) slope in DMF is much smaller than the other slopes. This is apparently due to the twisting of the nitro group from the plane of the aromatic ring because of the presence of two ortho chlorines. Series 2 (one ortho chlorine) has a shallower slope (more charge localized on the nitro group) than series 1 (no ortho chlorines). This is again probably due to the effect of the twisting of the nitro-group which allow less charge to be delocalized onto the ring. Chlorine usually develops strong dipoles with the carbon it's bonded to due to its large electronegativity.⁷⁰ Chlorines delocalize the electron density from a reaction center due to their inductive effect. When adjacent chlorines are present in a molecule, a strong electrostatic repulsion occurs due to the localized charge of adjacent dipoles. This can

cause bond bending, stretching and/or a decrease in the amount of charge the chlorine can carry so that the chlorine is not as effective with withdrawing electron density from the ring as shown by sigma rho data. This can also cause the chlorine bond to be weaker and more prone to bond breaking which can cause a change from the normally expected route of chlorine loss. DMSO studies reveal the same sort of phenomena but to a much lesser degree.⁷⁰

Cyclic Voltammograms with a Proton Source

The competitive processes have already been discussed and will play an important role when a proton source is added to the system. An increase in nitroso formation is noted upon addition of a proton source. Apparently, the rate of protonation of the dianion increases and in some cases, competes effectively with chloride loss reducing the amount of lower chlorinated species. We have observed the decrease of wave heights as this occurs. It also allows a greater opportunity for hydroxide loss from the dianion therefore increasing the size of the nitroso wave. However, on the electrochemical time scale, nitroso formation is still a slow process. The nitroso wave in DMSO is always larger, corresponding to the order of hydroxide loss from the dianion which decreases from DMSO to DMF to AN. The increase in the rate of protonation is not surprising but it does vary among solvents. AN protonates much more rapidly than DMF or DMSO⁹² though

other studies found the order of ease of hydrogen abstraction by the phenyl radical decreases in the order DMF>AN>DMSO.⁹⁹

Competition between position of chloride loss in compounds with adjacent chlorides is noted when a proton source is added (Table 26). Some positions of chloride loss for a particular compound and solvent have not changed with proton addition while others show a marked change.

In DMF, the Hammett plots (Figures 95 and 96) show a lowering of the energy required for reduction upon the addition of a proton source for the series 1 and 2 compounds. Though the actual potentials of the radical anions don't reflect this lowering, the dianions do. Series 1 and 2 compounds at .74 M show an energy change of 3.2×10^3 J/mole for series 1 and 9.6×10^3 J/mole for series 2. The irreversible waves shift positively while the reversible wave does not. This process is typical of protonation of the dianion but not the radical anion and it is apparently dependent on the proton concentration as was observed in a study of addition of phenol or benzoic acid to benzophenone in DMF.^{100,101} In our study, the slope (ρ) changes by only 1.5% between the no water and .74 M water plots for series 1 and 2 which indicates that the chlorines' inductive effect was not modified by the addition of water.

Series 3 compounds (two ortho chlorines) in DMF show a slight (6%)

Table 26. Effects of adjacent chlorines and solvent on position of chloride loss with a proton source added.

Compound with adjacent Cl's	# Adj. Cl's	Position # of Chloride loss*		
		DMSO	DMF	AN
23	1	2;3	-	-
34	1	4	4	4
234	2	2;3	2;3	2
235	1	2;3	2;5	3;5
236	1	2	2	3
245	1	4	2;4	4
345	2	4	4	4
2345	3	(2;3),4	(2),4	(2),4
2346	2	(2), (2),4	(2),2	2
2356	2	2;4	(6),2;5	(6)3;5
23456	4	(6), (4),2;3	(6),4	(6),4

* Number in parenthesis indicate previous chlorine(s) lost prior to competition.

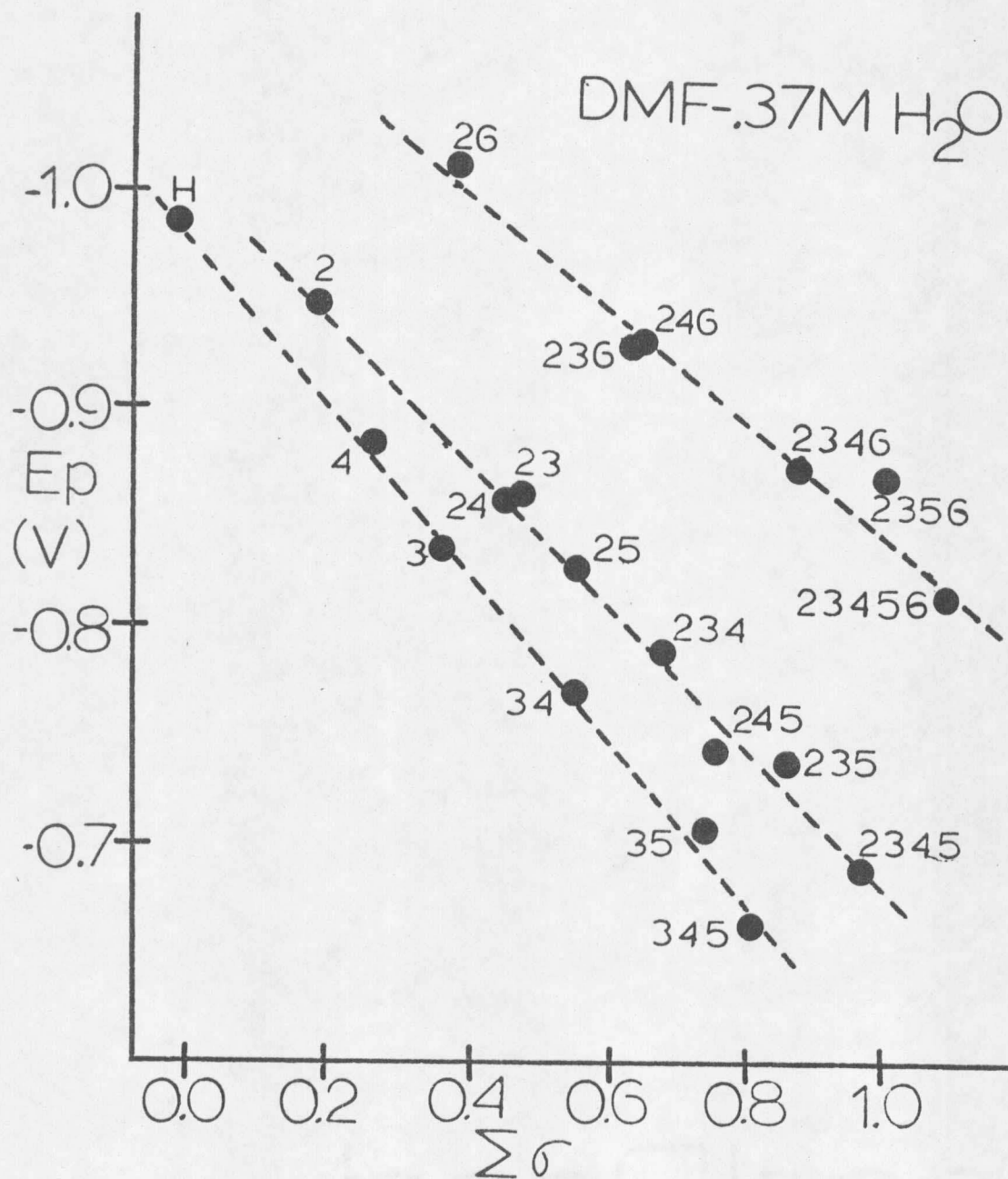


Figure 95. Plot of $\Sigma\sigma_{\text{corrected}}$ vs peak potential (V) for all compounds in DMF with .37 M H₂O.

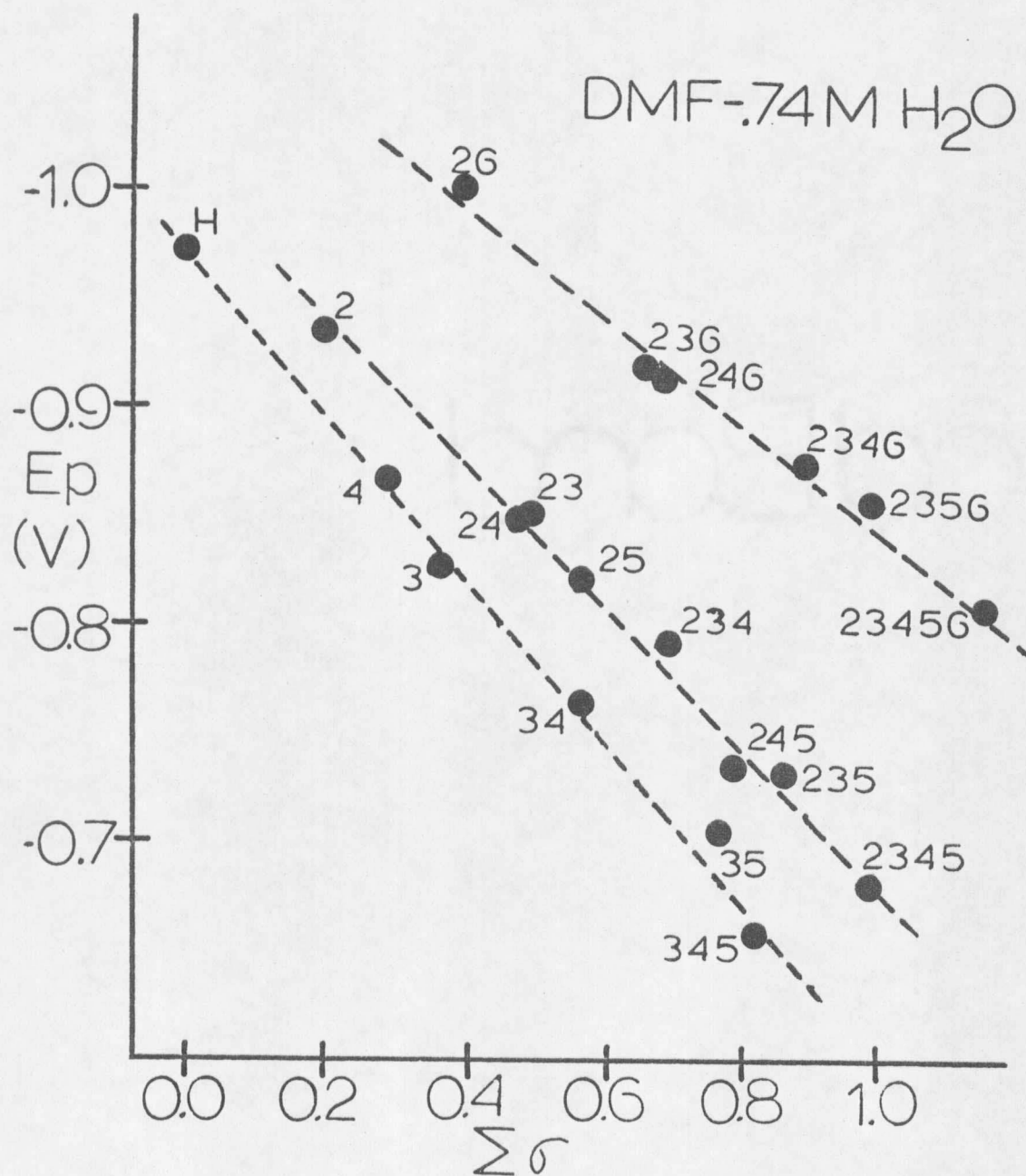


Figure 96. Plot of E_p vs peak potential (V) for all compounds in DMF with .74 M H₂O.

change in slope but no change in energy. The same process occurs in DMSO. Relating this slope change which indicates more charge on the nitro group to the dianion, we note that for this series the first irreversible wave remains steady. The two ortho chlorines cause the nitro group to twist 65° out of the plane of the ring which allows less delocalization of the charge.

In AN, the effect of an increase in proton availability differs from the effect in DMF (Figure 97 and 98). Compounds in Series 1 and 2 shift to a lower energy level as the same compounds did in DMF, but to a greater degree. Series 1 had an energy change of $4.6 \times 10^4 \text{ J/mole}$ for the dianion and series 2 changes $3.7 \times 10^4 \text{ J/mole}$. The voltammograms revealed shifts in both the reversible and irreversible waves upon water addition. The energy change of the radical anion is therefore 5790 J/mole for series 1 and 4150 J/mole for series 2. The slope of the Hammett plot has been modified by a decrease of 11% for series 1 and 16% for series 2. This may be representing rapid protonation of both waves which would result in a lower probability of chloride loss and more charge on the nitro group. Though the series 2 compounds do not normally cause twisting of the nitro group, the change in the slope may be a result of rapid protonation while the other effects which cause the slope to change may be secondary.

The series 3 compounds in AN show a 29% slope change in the

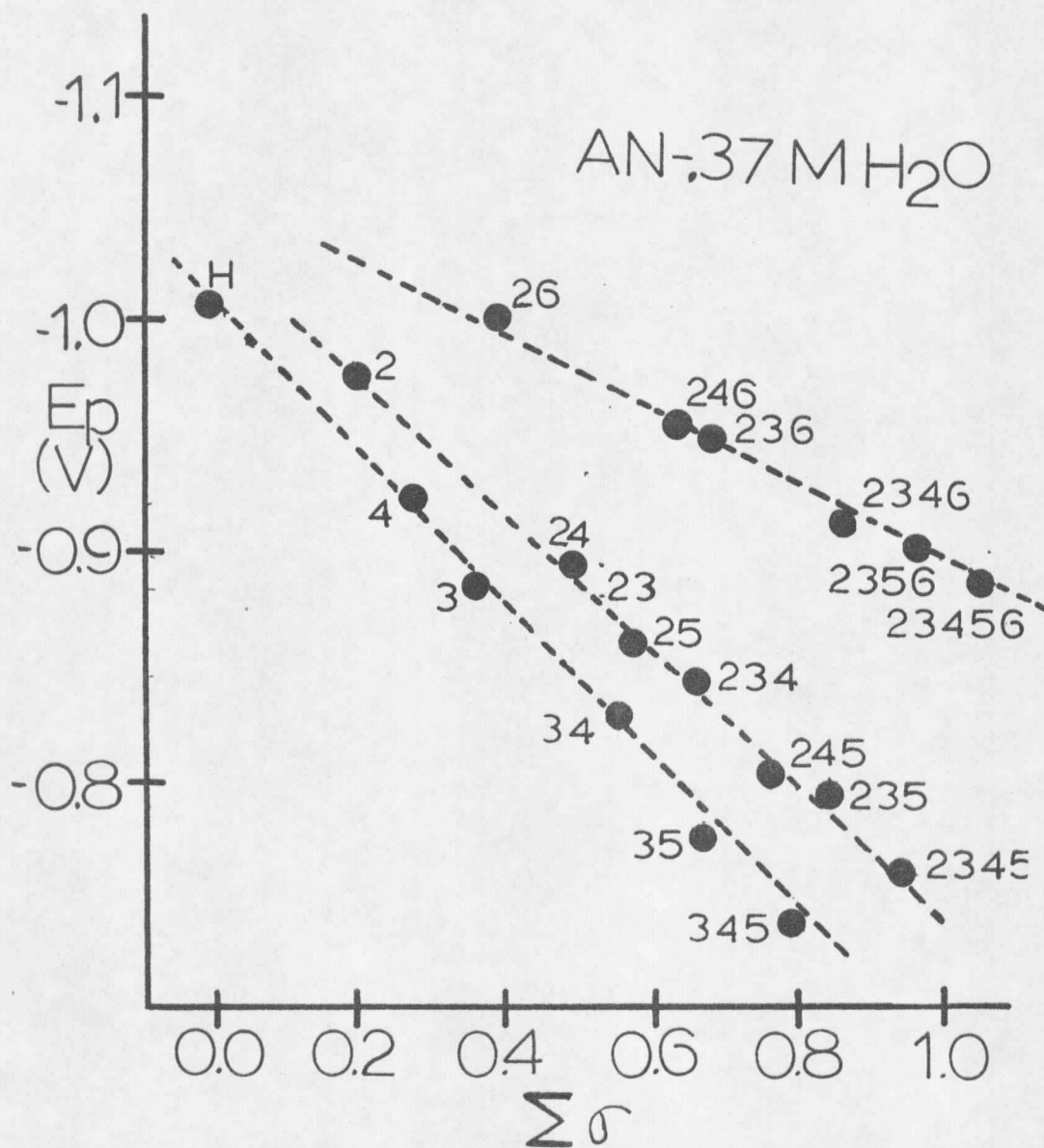


Figure 97. Plot of $\Sigma \sigma_{\text{corrected}}$ vs peak potential (V) for all compounds in AN with .37 M H₂O.

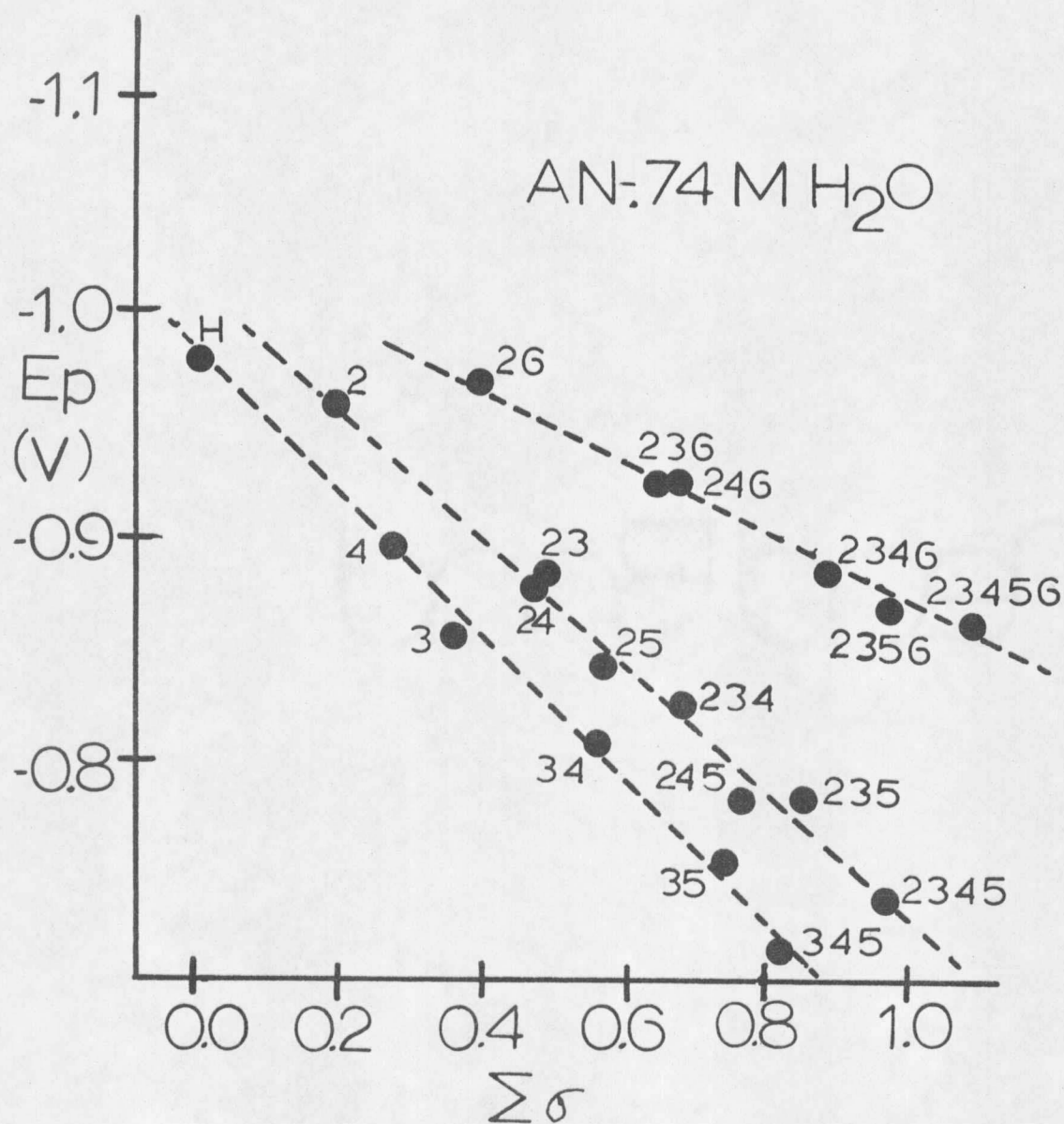


Figure 98. Plot of $\Sigma \sigma_{\text{corrected}}$ vs peak potential (V) for all compounds in AN with .74 M H₂O.

Hammett plots with water added and an energy change of $2.5 \times 10^4 \text{ J/mole}$ for the dianion and 8010 J/mole for the radical anion. At the same time, the voltammograms show a positive shift of all waves indicating that proton addition becomes competitive with chloride loss. The more chlorinated compounds do not show as great a shift of the dianion potentials, indicating chloride loss occurs more readily. However, another explanation of these shifts in AN which involve both the radical anion and dianion is a change in solvation with added proton source. Apparently, the "free" water molecules replace AN in the solvation sphere of the radical anion lowering its energy and cause it to reduce earlier. The dianion would also be easier to protonate since water molecules would already be associated with it.

Pathways of electrochemical reductions in DMSO with a proton source added do not appear to differ significantly from that described in DMF. However, there appears to be more competition between adjacent chlorine loss in DMSO which may be a reflection of the relatively less stable radical anion (than in AN or DMF) thus indicating adjacent chlorine interactions are increased in the dianion.

A final point of our study is to disagree with a previous study⁸⁷ which stated that solvents (DMSO, DMF, AN) do not have to be dried for polarographic studies since the radical anion is not affected until high concentrations of water (10-20 mole % (1.7-3.3M) in AN, 60-70%

mole % in DMF and DMSO). Jezorek and Mark failed to notice the effect water has on the irreversible waves. However, at very low concentrations of water (.05M), we observed a shift in the irreversible waves. This shift is due to a mechanism change relative to the rate of chloride loss, increased protonation, and competition between processes. They also noted that the addition of methanol did not yield the expected result. Since methanol has one proton capable of hydrogen bonding and does not form a rigid structure with the solvent, the mole % of methanol added would need to be greater to achieve the same effect. They found they needed to add 35 mole% to achieve the same results as the addition of 60-70 mole% water. We found that very low concentration of ethanol yielded minor shifts but a much greater amount was necessary to observe the dianion shifts equivalent to those observed with water addition.

If experimental difficulties and time had allowed for an extension of this study, it would have included the effect of proton addition to the chlorinated nitrosobenzenes. This would be helpful in determining where the nitroso compound lies and how it behaves. Chronocoulometry would be extremely useful since it records the electrochemical response by integrating the current and records it against time. It allows separation of current due to reactions of adsorbed species and current due to diffusing species reacting.

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