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.

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

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in

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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 Amphiprotic 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]

$$PhNO_2 + 4e^- + 4H^+ \longrightarrow PhNHOH + H_2O \qquad (1)$$

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

$$PhNO_2 + 4e^- + 4H^+ \longrightarrow PhNHOH + H_2O \qquad (2)$$

$$PhNHOH + 2e^- + 2H^+ \longrightarrow PhNH_2 + H_2O \qquad (3)$$

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 $PhNO_2H_2^{2+}$ ion that is reduced according to the following mechanism:[9]

$$PhNO_2H_2^{+2} + 2e^- + H^+ \xrightarrow{slow} PhNOH^+ + H_2O \tag{4}$$

$$PhNOH^+ + 2e^- + 2H^+ \xrightarrow{fast} PhNH_2OH^+ \tag{5}$$

$$PhNHOH^+ + 2e^- + 3H^+ \longrightarrow PhNH_3^+ + H_2O \tag{6}$$

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-Nabey[10] 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:

$$\phi\text{-}NO_2 + 2H^+ \xrightarrow{slow} \phi NO_2H_2^{2+} \tag{7}$$

$$\phi\text{-}NO_2H_2^{2+} + 4e^- + 2H^+ \xrightarrow{fast} \phi NHOH + H_2O \tag{8}$$

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.

$$\mathrm{PhNO_2} + e^- \longrightarrow \mathrm{PhNO_2^{\dot{-}}} \tag{9}$$

$$\mathrm{PhNO_2^{\dot{-}}} + e^- \xrightarrow{\text{slow}} \mathrm{PhNO_2^{2-}} \tag{10}$$

$$\mathrm{PhNO_2^{2-}} + 3\mathrm{H_2O} + 2e^- \xrightarrow{\text{fast}} \mathrm{PhNHOH} + 4\mathrm{OH^-} \tag{11}$$

In solutions of low proton donor concentration[11] and in alcohol-water solutions (concentration alcohol > 10 wt%)[9] there are two consecutive single electron transfer processes (Equations 12-13)

$$\mathrm{PhNO_2} + e^- \rightleftharpoons \mathrm{PhNO_2^{-}} \tag{12}$$

$$\mathrm{PhNO_2^-} + e^- \xrightarrow{\text{slow}} \mathrm{PhNO_2^{=}} \tag{13}$$

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 phenyhydroxylamine.[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]

$$PhNO + e^- \rightleftharpoons PhNO^{\dot{-}} \qquad (14)$$

$$PhNO^{\dot{-}} + H^+ \longrightarrow PhNHO^{\cdot} \qquad (15)$$

$$PhNHO^{\cdot} + H^+ + e^- \longrightarrow PhNHOH \qquad (16)$$

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 phenlyhydroxylamine.

$$\mathrm{PhNO_2} + e^- \longrightarrow \mathrm{PhNO}^{\dot{-}} \tag{17}$$

$$\mathrm{PhNO}^{\dot{-}} + 3e^- + 2\mathrm{H}^+ \longrightarrow \mathrm{PhNHOH} \tag{18}$$

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 Balog[18] 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.

$$\mathrm{PhNO_2} + \mathrm{H}^+ \xrightarrow{e^-} \mathrm{PhNO_2H}\cdot \tag{19}$$

$$\mathrm{PhNO_2H}\cdot + \mathrm{H}^+ \xrightarrow{e^-} \mathrm{PhNO} + \mathrm{H_2O} \tag{20}$$

$$\mathrm{PhNO} + \mathrm{H}^+ \xrightarrow{e^-} \mathrm{PhNOH}\cdot \tag{21}$$

$$\mathrm{PhNOH}\cdot + \mathrm{H}^+ \xrightarrow{e^-} \mathrm{PhNHOH} \tag{22}$$

$$\mathrm{PhNHOH} + 2\mathrm{H}^+ \xrightarrow{e^-} \mathrm{PhNH}_2^{+\cdot} + \mathrm{H}_2\mathrm{O} \qquad (23)$$

$$\mathrm{PhNH}_2^{+\cdot} \xrightarrow{e^-} \mathrm{PhNH}_2 \qquad (24)$$

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:

$$\mathrm{PhNO_2CF_3} + e^- \rightleftharpoons \mathrm{PhNO_2CF_3}^- \qquad (25)$$

$$\mathrm{PhNO_2CF_3}^- + e^- \rightleftharpoons \mathrm{PhNO_2CF_3}^= \qquad (26)$$

$$\mathrm{PhNO_2CF_3}^= + 2\mathrm{HS} \longrightarrow \mathrm{PhNOCF_3} + \mathrm{H_2O} + 2\mathrm{S}^- \qquad (27)$$

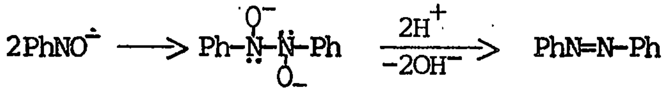
$$\mathrm{PhNOCF_3} + e^- \rightleftharpoons \mathrm{PhNOCF_3}^- \qquad (28)$$

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]

$$\mathrm{PhNO} \underset{}{\overset{e^-}{\rightleftharpoons}} \mathrm{PhNO}^{\dot{-}} \tag{29}$$



$$2\mathrm{PhNO}^{\dot{-}} \longrightarrow \mathrm{Ph{-}\underset{\cdot\cdot}{\overset{O^-}{N}}{-}\underset{O^-}{\dot{N}}{-}Ph} \xrightarrow[-2OH^-]{2H^+} \mathrm{PhN{=}N{-}Ph} \tag{30}$$

$$e^- + \mathrm{Ph{-}N{=}N{-}Ph} \rightleftharpoons (\mathrm{Ph{-}N{=}N{-}Ph})^- \tag{31}$$

$$\mathrm{PhNO}^{\dot{-}} \xrightarrow{e^-} \mathrm{PhNO}^{=} \tag{32}$$

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]

$$\mathrm{PhNO_2} + 2e^- + 2H^+ \xrightarrow{\text{slow}} \mathrm{PhNO} + H_2O \tag{33}$$

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.

$$PhNO_2 + e^- \xrightarrow{k_1} PhNO_2^{\dot{-}} \tag{34}$$

$$PhNO_2^{\dot{-}} + e^- \xrightarrow{k_2} PhNO_2^{=} \tag{35}$$

$$PhNO_2^{=} + 2H^+ \longrightarrow PhNO_2H_2 \tag{36}$$

$$PhNO_2H_2 \longrightarrow H_2O + PhNO \tag{37}$$

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:

$$PhNO_2^{2-} + ROH \longrightarrow PhNO_2H^- + RO^- \qquad (38)$$

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:

$$PhNO_2 \overset{e^-}{\rightleftharpoons} PhNO_2^{\dot{-}} \overset{e^-}{\rightleftharpoons} PhNO_2^{=} + ROH \qquad (39)$$

$$RO^- + PhNO_2H^- \rightleftharpoons OH^- + PhNO \overset{e^-}{\rightleftharpoons} PhNO^- \overset{e^-}{\rightleftharpoons} \qquad (40)$$

$$PhNO^{=} + ROH \rightleftharpoons PhNOH^- + RO^- \qquad (41)$$

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 pKa 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 nitrobenzene[11] 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 Belin[26] 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).

$$PhNO_2 + 4H^+ + 4e^- \longrightarrow PhNHOH + H_2O \qquad (42)$$

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:

$$PhNO^- + ROH + e^- \rightleftharpoons PhNOH^- + RO^- \qquad (43)$$

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:

$$\mathrm{ArX} + e^- \rightleftharpoons \mathrm{ArX}^{\dot{-}} \qquad (44)$$

$$\mathrm{ArX}^{\dot{-}} \xrightarrow{k_1} \mathrm{Ar}\cdot + \mathrm{X}^- \qquad (45)$$

$$\mathrm{Ar}\cdot + \mathrm{SH} \xrightarrow{k_2} \mathrm{ArH} + \mathrm{S}\cdot \qquad (46)$$

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 $\mathrm{PhH/Ph}^-$ 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]

$$S\cdot + e^- \longrightarrow S^- \tag{47}$$

$$S^- + Ar\cdot \longrightarrow ArS^- \tag{48}$$

$$ArS^{\dot{-}} + e^- \longrightarrow ArS \tag{49}$$

$$ArS^{\dot{-}} + ArX \longrightarrow ArS + ArX^{\dot{-}} \tag{50}$$

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-bromoquanoxaline and 6-iodoquinoxaline.

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

$$ArX + e^- \longrightarrow ArX^{\dot{-}} \tag{51}$$

$$ArX^{\dot{-}} \xrightarrow{k_1} Ar\cdot + X^- \tag{52}$$

$$Ar\cdot + e^- \longrightarrow Ar^- \tag{53}$$

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

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]

Wave 1 $PhNO_2I + 2e^- + H^+ \longrightarrow PhNO_2 + I^-$ (54)

Wave 2 $PhNO_2 + e^- \longrightarrow PhNO_2^{\dot{-}}$ (55)

Wave 3 $PhNO_2^{\dot{-}} + e^- \longrightarrow PhNO_2^{=}$ (56)

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:

$$\text{o-PhNO}_2\text{Cl} \xrightarrow{e^-} \text{o-Ph-}\dot{\text{N}}\text{O}_2\text{Cl} \xrightarrow{2e^- + H^+} \text{o-PhNO}_2^{\dot{-}} + \text{Cl}^- \qquad (57)$$

$$\text{p-PhNO}_2\text{Br} \xrightarrow{e^-} \text{p-Ph-}\dot{\text{N}}\text{O}_2\text{Br} \xrightarrow{2e^- + H^+} \text{-PhNO}_2^{\dot{-}} + \text{Br}^- \qquad (58)$$

$$\text{H}^+ + \text{PhNO}_2\text{I} \xrightarrow{2e^-} \text{PhNO}_2 + \text{I}^- \xrightarrow{e^-} \text{PhNO}_2^{\dot{-}} \qquad (59)$$

Lawless and Hawley interpreted the iodo reduction mechanism more precisely.[37]

$$PhNO_2I + e^- \rightleftharpoons PhNO_2I^{\dot{-}} \qquad (60)$$

$$PhNO_2I^{\dot{-}} \rightleftharpoons PhNO_2^{\bullet} + I^- \qquad (61)$$

$$PhNO_2^{\bullet} \xrightarrow[slow]{SH} PhNO_2 + S^{\bullet} \qquad (62)$$

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 $k_F<k_{Cl}<k_{Br}<k_I$.[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: km<kp<ko. 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-dichloronitrobenzene[38] 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.

$$PhNO_2X^{\dot{-}} + e^- \longrightarrow PhNO_2X^= \qquad (63)$$

$$PhNO_2X^= \xrightarrow{k_1} PhNO_2^- + X^- \qquad (64)$$

$$PhNO_2X^= + H^+ \xrightarrow{k_2} Products \qquad (65)$$

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.

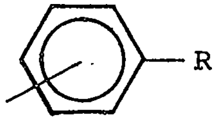
It has been observed that more resonance energy is lost between the nitro group and the ring due to the nitro group being decoupled as it twists out of the plane of the ring.[28]

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 $a^{N}_{NO_2}$, 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^{H}_{meta}, is not affected the same as the ortho and para constants which decrease when $a^{N}_{NO_2}$ 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^{H}_{ortho} and a^{H}_{para} than a^{H}_{meta}. In DMF, the para splitting constant, a^{H}_{para}, 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 $a^{N}_{NO_2}$ and a^{H}_{para} 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

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

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:

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

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 $D_{ox} \simeq D_{red}$,

$$E_{\frac{1}{2}} = E^\circ \qquad (68)$$

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

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

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

where K is the equilibrium constant of an oxidation reduction reaction and $\Delta\log K = \log K_X - \log K_o$ where K_o 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

$$\Delta E_{\frac{1}{2}} = \sigma\rho \qquad (71)$$

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 as[47]

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

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

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

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

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

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, $\sigma°$, 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.