ione, $E_7{}^1 = -0.20$ V[11]) may be a more favorable sensitizer.[31] The apparent limit of sensitization at the oxygen redox potential may lie in the capability of the cell to dispose of O_2^- radicals by the superoxide dismutase enzyme and consequently of other radicals which transfer electron to oxygen.

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Electrochemical Reactions of Organic Compounds in Liquid Ammonia. II. Nitrobenzene and Nitrosobenzene

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Abstract: The electrochemical behavior of nitrobenzene and nitrosobenzene in anhydrous liquid ammonia was investigated by cyclic voltammetry and controlled potential coulometry. In the absence of added protonating agents, nitrosobenzene and nitrobenzene are both reversibly reduced in two one-electron transfer steps to yield the stable radical anion and stable dianion species. In the presence of the weak acid isopropyl alcohol, the dianion of nitrosobenzene adds a single proton to form the anionic species, which can be reversibly oxidized back to parent compound. The dianion of nitrobenzene also adds a single proton and then rapidly decomposes with the loss of hydroxyl ion to neutral nitrosobenzene, which undergoes further reduction and protonation. The overall reduction process consists of the addition of a single electron to yield a stable radical anion followed by addition of three electrons and two protons to yield the protonated dianion of nitrosobenzene. In the presence of strong acid (ammonium ion), nitrosobenzene is reduced in a single two-electron reduction process to yield phenylhydroxylamine. Nitrobenzene is reduced in two steps, involving the addition of one and three electrons, to yield the same final product, phenylhydroxylamine. Estimates of the equilibrium or rate constants for several of these reactions associated with the electrode reactions are given.

The mechanism of the electrochemical reduction of nitrobenzene to phenylhydroxylamine and aniline has received considerable attention over the past 25 years.[1-14] Most of this work involved the use of aqueous solutions containing alcohol or an ether to aid in the dissolution of the relatively insoluble organic compound. Attempts at elucidating the reduction mechanism were made by correlating changes in electrochemical behavior of the system with changes in pH, which was adjusted through the use of various buffer systems. Some studies have also been undertaken in nonaqueous solvent systems with addition of proton sources of varying proton-donating strength. In aqueous solution, nitrobenzene is reduced to phenylhydroxylamine in a single four-electron reduction step at all pH values. At pH values less than 4.7, nitrobenzene is assumed to be pre-protonated giving the species $C_6H_5NO_2H_2{}^{2+}$, while analysis of the polarographic wave shows that the rate-determining step involves the addition of two electrons and a single proton.[8,9] The mechanism of reduction is given as:

$$C_6H_5NO_2H_2{}^{2+} + 2e^- + H^+ \longrightarrow C_6H_5NOH^+ + H_2O \quad \text{(slow)}$$
$$C_6H_5NOH^+ + 2e^- + 2H^+ \longrightarrow C_6H_5NH_2OH^+ \quad \text{(fast)}$$

The reduction product of the rate-determining step ($C_6H_5NOH^+$) is reducible at a less negative potential than the starting compound ($C_6H_5NO_2H_2{}^{2+}$), which explains why this intermediate has never been detected during the course of an experiment. A second wave at a more negative potential occurs in acid solution corresponding to reduction of the protonated phenylhydroxylamine species $C_6H_5NH_2OH^+$, to yield aniline in a single two-electron transfer step:

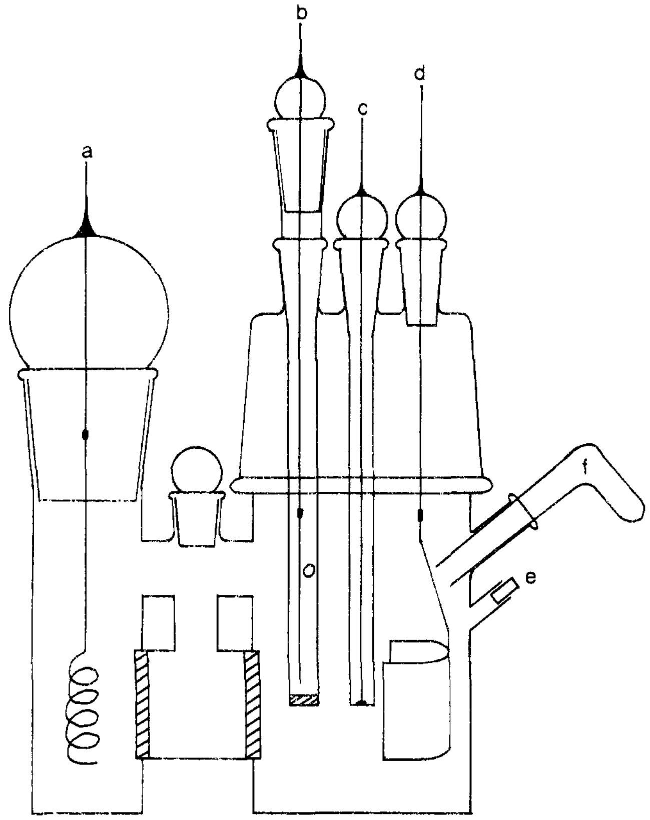


Figure 1. Electrochemical cell for voltammetric and coulometric studies: (a) Pt wire auxiliary electrode; (b) Ag wire reference electrode in separate compartment; (c) Au voltammetric working microelectrode; (d) Pt foil coulometric working electrode; (e) silicon gum rubber septum for sample injection; (f) rotatable side arm for solid sample addition. Arm and joint for attachment of cell to the vacuum line are not shown.

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

In neutral and alkaline solution, there is no evidence for pre-protonation of the parent molecule, and polarographic analysis again shows a rate-determining step consisting of the addition of two electrons and a single proton. The mechanism is given as:

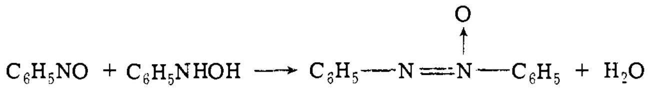
$$C_6H_5NO_2 + 2e^- + H_2O \longrightarrow C_6H_5NO_2H^- + OH^- \quad \text{(slow)}$$
$$C_6H_5NO_2H^- + 2e^- + 2H_2O \longrightarrow C_6H_5NHOH + 3OH^- \quad \text{(fast)}$$

At values of pH greater than 4.7, there is no wave observed corresponding to the reduction of phenylhydroxylamine. In aqueous alkaline solutions (pH greater than 10), electron spin resonance (ESR) studies showed the presence of a short-lived intermediate corresponding to the nitrobenzene radical anion.[5]

In the nonaqueous solvents dimethylformamide[11] and acetonitrile,[6] the nitrobenzene radical anion is very stable, and the reduction to phenylhydroxylamine occurs in two steps: a single electron addition to form the radical anion followed by a three-electron addition and protonation to form phenylhydroxylamine. Incremental addition of a proton donor, such as benzoic acid, causes an increase in the first reduction wave at the expense of the second wave until, at a ratio of acid to nitrobenzene of 4 to 1, a single four-electron reduction wave is observed equivalent to that obtained in aqueous solutions.[11]

Parallel to studies of the reduction mechanism of nitrobenzene, studies of the proposed intermediate nitrosobenzene have also been undertaken.[13-18] In aqueous alkaline solution, nitrosobenzene undergoes a base-catalyzed self-condensation reaction to form azoxybenzene so that the polarogram is found to change with time.[18] In neutral and acidic aqueous solutions, the compound is reduced to phenylhydroxylamine in a single two-electron transfer step. Bulk electrolysis gives an overall electron addition of somewhere between one and two with the formation of azoxybenzene which was attributed to the reaction of the reduction product phenylhydroxylamine with parent compound:

$$C_6H_5NO + 2e^- + 2H^+ \longrightarrow C_6H_5NHOH$$



$$C_6H_5NO + C_6H_5NHOH \longrightarrow C_6H_5{-}\overset{\overset{\displaystyle O}{\uparrow}}{N}{=}N{-}C_6H_5 + H_2O$$

In anhydrous dimethylformamide, nitrosobenzene is reduced in a single one-electron transfer step to yield an unstable radical anion.[16] A second reduction wave corresponding to the reduction of azoxybenzene appears at a more negative potential. In all of the solvent systems studied, nitrosobenzene is reduced at a less negative potential than nitrobenzene and, as a result, it has never been detected as an intermediate in the reduction of nitrobenzene to phenylhydroxylamine. The dianions of nitrosobenzene and nitrobenzene have also apparently never been prepared.

Previous studies in our laboratories[19] have demonstrated the unique properties of liquid ammonia as a solvent for electrochemical investigations of organic compounds and allowed the observation of the dianion of benzophenone. This allowed the determination of reaction mechanism by the purposeful addition of protonating agents and the elucidation of individual electron transfer and protonation steps. We report here an investigation of the electroreduction of nitrosobenzene and nitrobenzene in anhydrous liquid ammonia in the absence of protonating agents and in the presence of the weak acid, isopropyl alcohol, and in the presence of ammonium ion.

Experimental Section

Chemicals. Nitrobenzene, reaction grade quality (Matheson Coleman and Bell), was stored over molecular sieves to remove traces of moisture. Nitrosobenzene (Aldrich Chemical Co.) was considerably less pure than advertised (97%) and contained a large percentage of azoxybenzene and smaller amounts of nitrobenzene and azobenzene. A portion of this mixture was dissolved in benzene and purified by chromatography on an alumina column employing elution with benzene. The separation was facilitated by the fact that nitrosobenzene is blue in color, while the three other major components are yellow. The solvent was removed from the nitrosobenzene fraction with a rotary evaporator and was replaced with benzene that had been distilled from sodium metal to ensure dryness. The sample was placed in a flask sealed with a serum cap and stored frozen until use, when the sample was allowed to thaw to room temperature, and aliquots were removed with a 100-μl syringe without exposing it to the air. Incremental addition of ammonium ion to the solution was made by adding glacial acetic acid, which reacted with liquid ammonia to form the soluble salt, ammonium acetate. Reagent grade isopropyl alcohol (MCB) was used as received.

Potassium iodide which was used as supporting electrolyte in this study was obtained in reagent grade quality from Baker and Adamson. The large crystals were ground into a fine powder, dried at 110° for 48 hr, and stored in a desiccator over phosphorus pentoxide. The handling and purification of liquid ammonia has been described previously.[19]

Apparatus and Techniques. The type of electrochemical cell used for all measurements in the study is shown in Figure 1. The main compartment which contains the working electrodes had a total volume of 50 ml, the middle compartment contained approximately 15 ml, and the auxiliary compartment approximately 25 ml. The compartments were separated by medium porosity sintered-glass disks which allowed passage of currents up to 250 mA during bulk

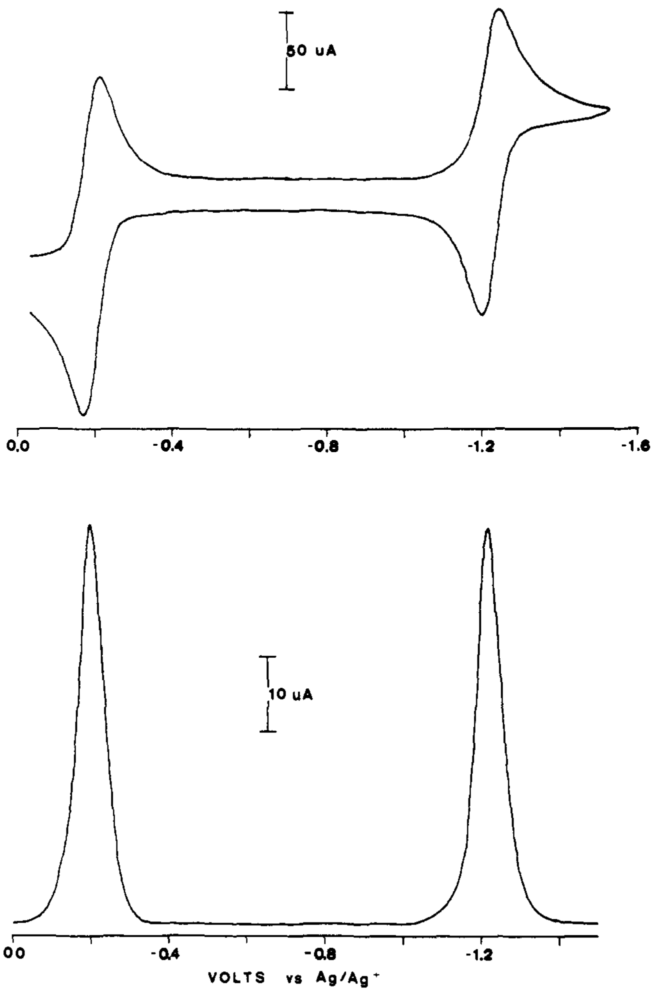


Figure 2. Cyclic and alternating current voltammetry of 4.3 mM nitrosobenzene in anhydrous liquid ammonia—0.1 M KI at −40°. Scan rate was 200 mV/sec. For ac voltammetry, ac frequency was 38.5 Hz with 5 mV amplitude (PP).

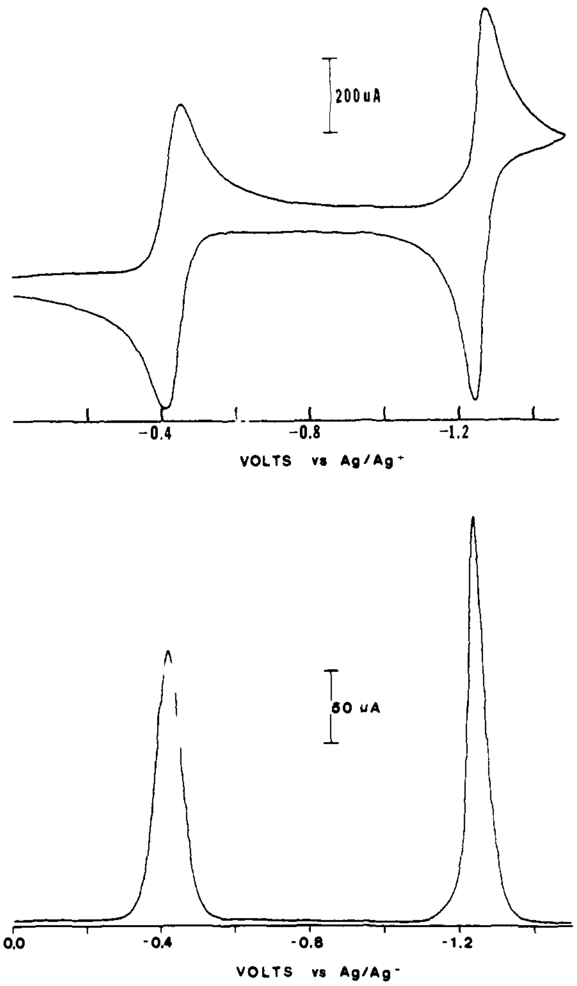


Figure 3. Cyclic and alternating current voltammetry of 9.5 mM nitrobenzene in anhydrous liquid ammonia—0.1 M KI at −40°. Conditions same as Figure 2.

electrolysis before excessive heating and solution boiling occurred, yet, which were sufficiently nonporous to hinder diffusion of components from one compartment to another. For example, coulometric generation of a stable radical anion with subsequent regeneration of starting material in ammonia occurred with a typical reoxidation efficiency of 97%. The working electrode for cyclic voltammetry and alternating current voltammetry was a 2.6-mm gold disk sealed in soft glass. Electrode pretreatment consisted of polishing the gold with an alumina slurry (0.3 μm particle size) on a felt cloth, then rinsing with deionized water, and wiping with an absorbent tissue. For coulometry, a 5.7 × 2.7 mm platinum foil was used as the working electrode; it was allowed to stand in dilute sulfuric acid when not in use. Just before the cell was assembled, the electrode was rinsed in deionized water and wiped dry with an absorbent tissue. Both electrodes exhibited very reproducible behavior. The reference electrode system consisted of a silver wire in a narrow glass tube with approximately 1-ml volume and sealed at the end with a fine porosity glass frit. The tube had a small hole above the solution level of the cell so that ammonia could condense and fill the electrode. Initially, silver nitrate was added to the electrode to establish the Ag|Ag^+ redox couple; however, it was found that substituting supporting electrolyte for the silver salt gave the same potential readings which did not vary by more than ±15 mV for successive experiments. A platinum wire wound into a helix served as the auxiliary electrode. Above the solution levels of the main compartment were two glass joints; one held a silicon gum rubber septum for injection of liquid samples with a syringe, the other an L-shaped glass tube that was used to introduce solid samples without opening the cell to the atmosphere. For solid samples which sublime under vacuum, an alternate sample introductory system was used which consisted of an L-shaped tube that was fitted with a Teflon plug. The top of the plug was threaded so that it could be lowered to seal off the sample holder from the rest of the cell during evacuation and, at the appropriate time, the plug could be raised and the tube rotated, thus allowing the sample to fall into the cell.

All electrochemical experiments were performed with a Princeton Applied Research Corp. Model 170 electrochemistry system using positive feedback to compensate for the ohmic drop between the working and reference electrode. Current-time curves were obtained on a Mosely-Autograf Model 1700 B variable speed strip-chart recorder. Current-potential curves for cyclic voltammetry at scan rates greater than 500 mV/sec were obtained with a Tektronix Type 564 storage oscilloscope.

Results and Discussion

Electrochemical Behavior in the Absence of Proton Donors. In liquid ammonia, both nitrosobenzene and nitrobenzene are reduced in two successive reversible one-electron transfer steps as shown by cyclic voltammetry and alternating current voltammetry (Figures 2 and 3). Values for the diagnostic parameters describing the nature of the electron transfer processes for the two compounds are listed in Table I. Nitrosobenzene is reduced during controlled potential coulometry in two steps, yielding solutions of the reddish-brown radical anion and deep red dianion, with each step giving an n_{app} value of 1.0. The dianion can be reoxidized back to parent compound, again in two successive steps, with an overall n_{app} value of 1.92. Nitrobenzene also shows a controlled potential coulometric reduction of two steps with the first step giving an n_{app} value of 1.0, resulting in a bright orange solution of the radical anion. The second elec-

Table I. Summary of Voltammetric Parameters for Reduction of Nitrobenzene and Nitrosobenzene in Anyhdrous Liquid Ammonia[a]

Diagnostic parameter	Nitrobenzene First wave	Nitrobenzene Second wave	Nitrosobenzene First wave	Nitrosobenzene Second wave	Theoretical values for Nernstian behavior
		Cyclic Voltammetry			
E_{p_c}, V vs. Ag|Ag$^+$	−0.44	−1.26	−0.22	−1.24	
$E_{p_c} - E_{p/2}$, mV	46 ± 5	30 ± 5	52 ± 5	46 ± 5	44.2
$E_{p_a} - E_{p_c}$, mV	50 ± 5	35 ± 5	50 ± 5	47 ± 5	45.4
i_{p_a}/i_{p_c}	1.0	1.15 ± 0.05	1.0	1.0	1.0
$i_p/v^{1/2}C$, (A sec$^{1/2}$ cm^3)/(V mol)	111		106		
Diffusion coefficient, cm^2/sec	2.8×10^{-5}		2.6×10^{-5}		
		Ac Voltammetry			
E_p, V vs. Ag|Ag$^+$	−0.42	−1.24	−0.20	−1.22	
$E/\log \left\{\left(\frac{i_p}{i}\right)^{1/2} \pm \left(\frac{i_p - i}{i}\right)^{1/2}\right\}$, mV	99	50; 100[b]	105	98	92.4

[a] 0.1 *M* KI; gold working electrode. [b] First value represents slope of current function for front side of curve; second value represents slope of back side of curve.

tron-transfer step takes place with unusual current–time, and therefore *Q* vs. time, behavior. The initial current for the second reduction step is approximately the same as that for the first reduction step, but the current decay much more rapidly during the second step in a nonexponential manner. At a value of n_{app} of 2.0, a deep blood red suspension is observed, and there is a low steady state current still flowing in the reaction cell. Stepping the potential back to the region of formation of the radical anion causes a large current spike followed by rapid decay to a relatively high steady state current, which eventually decays to zero. Another oxidation step, showing normal *i–t* behavior, yields a colorless solution of the parent compound. Typically, the n_{app} value for each oxidation step is 0.90. A cyclic voltammogram of the solution after coulometric reduction and reoxidation is essentially identical with that of the original solution with an approximate 10% decrease in the peak currents. Coulometric generation of the radical anion of nitrobenzene followed by reoxidation to the parent species proceeds with n_{app} values of 1.0 and 0.97, respectively.

The experimental values for the diagnostic parameters listed in Table I indicate that both reduction waves of nitrosobenzene and the first reduction wave of nitrobenzene are characterized by reversible (Nernstian) electron transfers. For the second electron-transfer step of nitrobenzene, the large value for i_{p_a}/i_{p_c} suggests an adsorption or precipitation process since, for a diffusion-controlled reversible electron transfer, this parameter has a maximum value of 1.0. The formation of the blood red suspension on coulometric generation of the dianion demonstrates that the potassium dianion salt is indeed insoluble. Precipitation of the species from solution is equivalent to removal of reduction product due to a following chemical reaction which in cyclic voltammetry causes a sharpening of the reduction wave as measured by a decrease in the value of the parameter ($E_p - E_{p/2}$). Since the precipitate does not diffuse away from the electrode surface, the dianion concentration builds up so that, on scan reversal, a sharp reoxidation wave is observed, giving an i_{p_a}/i_{p_c} value of greater than unity. The unusual coulometric behavior observed for this electron-transfer step can also be explained by this precipitation. Normal *i–t* behavior is observed until the electrode becomes coated with the insoluble dianion salt; the current then drops sharply because no further reduction can occur until agitation in the cell causes removal of some of the precipitate from the electrode surface. The high current spike at the beginning of the reoxidation step is caused by oxidation of the dianion salt adhering to the electrode surface, and the steady-state current that follows is a function of the rate of dissolution of the precipitate in solution. The low n_{app} value of 0.9 for this reoxidation process is caused by loss of some of the dianion salt precipitate which adheres to the wall of the cell above the solution line and cannot be redissolved and because of a very slow chemical reaction of dianion with solvent, which is suggested by the existence of a low steady state current beyond n_{app} values of 2.0. The dianion of nitrosobenzene is apparently more stable than that of nitrobenzene as evidenced by a current decay to zero at an n_{app} value of 2.0.

It is interesting to compare the stabilities of electrogenerated species in liquid ammonia with their stabilities in other solvent systems. To our knowledge, in no other solvent investigated so far by electrochemical techniques, including aprotic solvents, have dianions of nitrobenzene and nitrosobenzene been observed which are stable on the cyclic voltammetric time scale. In liquid ammonia on the other hand, both of these compounds not only form stable dianions on the cyclic voltammetric time scale but, since the dianion species react only slowly with the solvent, they can almost be considered stable even on the much longer coulometric time scale. This high stability allows straightforward calculation of rate constants or equilibrium constants for following chemical reactions of radical anion or dianion upon addition of reactants based on shifts in peak potentials of the reduction waves.

Electrochemical Behavior in the Presence of Isopropyl Alcohol. The first reduction wave of nitrosobenzene is unaffected by the addition of isopropyl alcohol. The second reduction wave decreases with increasing alcohol concentration and is replaced by a new reversible wave approximately 120 mV positive of the original wave. This new wave grows in height with increasing alcohol concentration and approaches a maximum corresponding to the height of a single electron transfer at a mole ratio of alcohol to nitrosobenzene of 1 to 1 (Figure 4). Further addition of alcohol causes the wave to shift in a positive direction but with no significant increase in the peak current. In the presence of alcohol, nitrosobenzene is reduced coulometrically in two successive one-electron transfer steps and is reoxidized in a similar manner. The only difference in the voltammograms of the solution before and after electrolysis is the presence of a small wave at −0.79 in the electrolyzed solution, which occurs at the same potential as that for azoxybenzene.

The first reduction wave of nitrobenzene is also unaffected by the presence of isopropyl alcohol. The second wave exhibits a shoulder on its positive side at low alcohol con-

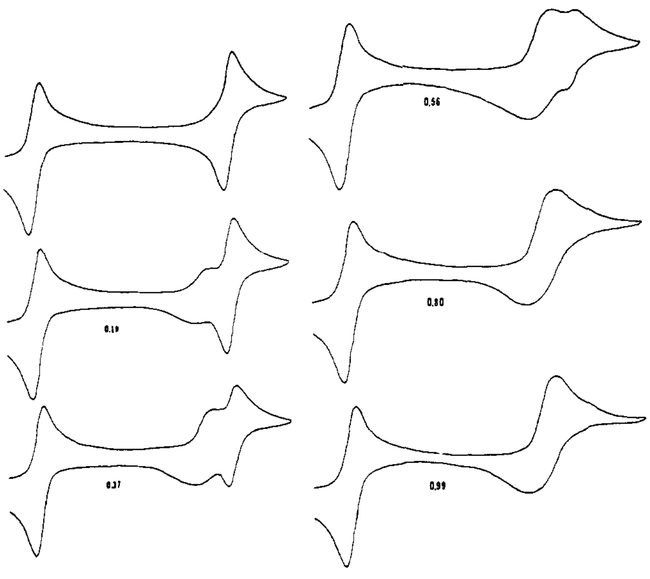


Figure 4. Cyclic voltammetry of nitrosobenzene in the presence of isopropyl alcohol. Solution contained 5.0 m*M* C_6H_5NO, 0.1 *M* KI, and the indicated mole ratio of *i*-PrOH/C_6H_5NO. Scan rate = 200 mV/sec.

centrations, and the height of the two combined waves increases with increasing amounts of the proton donor (Figure 5). At a high ratio of alcohol to substrate, the two waves coalesce, and the peak current becomes a function of scan rate and no longer increases with further addition of the alcohol (Figure 6). A cyclic voltammogram of nitrobenzene in the presence of an excess of alcohol gives no anodic wave on reverse scan corresponding to the oxidation of the dianion. However, two new oxidation waves appear whose peak potentials are the same as those obtained on the reverse scan of a solution of nitrosobenzene in the presence of alcohol. A new reduction wave positive of the first reduction wave of nitrobenzene is observed on the second scan on repetitive cycling. Controlled potential coulometry of nitrobenzene at the first reduction wave gives an n_{app} value of 1.0 at all alcohol concentrations. Reduction at the second wave yields an n_{app} value of 3.0 for all solutions containing alcohol in a mole ratio of 2/1 or greater and smaller n_{app} values for lower alcohol mole ratios.

The failure of the addition of alcohol to influence the electrochemical behavior of the first reduction wave of nitrosobenzene indicates that the radical anion species is a very weak base so that the position of equilibrium for the reaction in (1) lies far to the left. The peak potential of the

$$C_6H_5NO^-\cdot + ROH \rightleftarrows C_6H_5NOH\cdot + RO^- \qquad (1)$$

new reduction wave is independent of scan rate which indicates that the rate of protonation of the dianion is very fast.[18] For this case the difference in peak potential between the new wave and the original wave (ΔE_p) is a measure of the equilibrium constant for the protonation reaction. The relationship between these two quantities is given by:

$$\Delta E_p = (RT/nF) \ln K \qquad (2)$$

$$K = [C_6H_5NOH^-][RO^-]/[C_6H_5NO^{2-}][ROH] \qquad (3)$$

At −70° the equilibrium constant has a value of approximately 700. The presence of anodic current for the new reduction wave on scan reversal indicates that the chemical reaction is limited to the addition of a single proton since addition of a second proton would yield phenylhydroxylamine which oxidizes at a much more positive potential. Protonation of the dianion does not facilitate further addition of electrons since the height of the new reduction wave approaches a maximum peak current corresponding to the transfer of a single electron, and since the coulometric n_{app} value is 1.0 for the second reduction step. The reduction consists of the stepwise transfer of two electrons followed by a rapid protonation of the dianion, an EEC type mechanism; the new reduction wave reaction can be represented by:

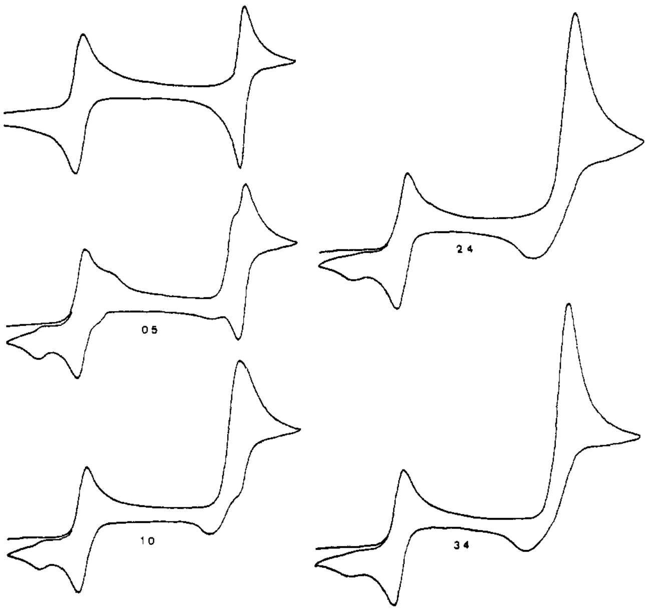


Figure 5. Cyclic voltammetry of nitrobenzene in the presence of isopropyl alcohol. Solution contained 5.0 m*M* $C_6H_5NO_2$, 0.1 *M* KI, and the indicated mole ratios of *i*-PrOH/$C_6H_5NO_2$ on curves.

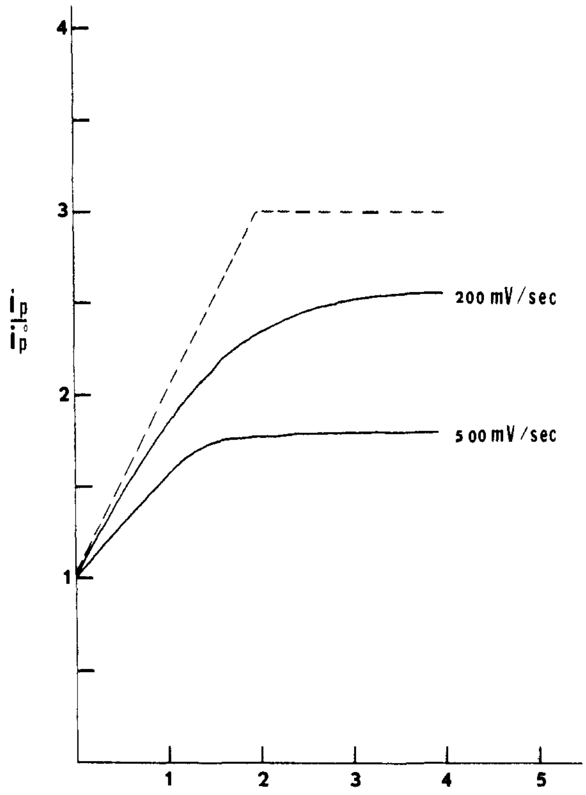


Figure 6. Peak current of second reduction wave of nitrobenzene as function of isopropyl alcohol concentration. The solution contained 5.0 m*M* $C_6H_5NO_2$, 0.1 *M* KI, and the indicated mole ratio of alcohol/$C_6H_5NO_2$. The dashed line represents theoretical behavior at slow scan rates.

$$C_6H_5NO^{-}\cdot + ROH + e^- \rightleftharpoons C_6H_5NOH^- + RO^- \quad (4)$$

The fact that the anodic portion of the first wave does not decrease with the addition of alcohol (Figure 4) suggests that the generation of the species $C_6H_5NOH\cdot$ under these conditions is followed by rapid loss of a proton to yield the radical anion as shown in (1). Furthermore, previous studies in acidic aqueous alcohol solutions show that the species, $C_6H_5NOH^+$ (which would result from oxidation of $C_6H_5NOH\cdot$), is reduced at a potential approximately 200 mV positive of the unprotonated parent compound. Moreover, if the $C_6H_5NOH\cdot$ were stable to deprotonation by the alkoxide anion, then coulometric generation of this species by oxidation of the protonated dianion would give a nearly quantitative yield of azoxybenzene, which is formed by a rapid dimerization of $C_6H_5NOH\cdot$. Only a trace of azoxybenzene is detected in the cyclic voltammogram of the solution after coulometric reduction at the second wave and reoxidation, indicating that deprotonation must be much more rapid than dimerization.

Since the first reduction wave of nitrobenzene is similarly unaffected by the addition of isopropyl alcohol, its radical anion is also stable with respect to protonation by the alcohol, and the position of equilibrium of reaction 5 lies far to

$$C_6H_5NO_2^{-}\cdot + ROH \rightleftharpoons C_6H_5NO_2H\cdot + RO^- \quad (5)$$

the left. The presence of a shoulder on the positive side of the second reduction wave of nitrobenzene is indicative of the following chemical reaction, the protonation of the dianion by the alcohol:

$$C_6H_5NO_2^{2-} + ROH \rightleftharpoons C_6H_5NO_2H^- + RO^- \quad (6)$$

The peak potential of the shoulder does not change with scan rate, indicating that the rate of protonation is high. The equilibrium constant for the reaction was difficult to estimate, because the peak potential of the second reduction wave is already shifted in the positive direction somewhat by precipitation of the dianion salt. K_{eq} for reaction 6 probably lies in the range of 20–60 which is considerably less than that calculated for nitrosobenzene, indicating that the dianion of nitrosobenzene is a stronger base than the dianion of nitrobenzene.

The significant increase in peak current for the second reduction wave upon addition of alcohol (Figure 5) indicates that more than a single electron is being transferred in the reduction process. However, it is unlikely that simple protonation of the dianion alone could facilitate the transfer of additional electrons. The nitrogen and oxygen atoms in the nitro group are all singly bonded and contain a full octet of electrons in their valence shells so that there is no vacancy for futher electron addition, and protonation does nothing to alleviate this saturated condition. Moreover, reduction of the aromatic ring at this potential is unlikely. The most likely mechanism calls for protonation of the dianion followed by rapid loss of hydroxide ion to yield a neutral molecule of nitrosobenzene. Since the dianion of nitrosobenzene is formed at the same potential as the dianion of nitrobenzene, an immediate transfer of two additional electrons would occur for a total of three electrons passed in the second reduction step. The coulometric data indeed indicate that $n_{app} = 3$ for the second reduction step, but only when 2 or more equiv of alcohol are present instead of just 1 equiv. This can be explained by the fact that the dianion of nitrosobenzene also protonates so that a competition for the available proton is established between the two dianion species with nitrosobenzene taking preference since it is the stronger base. At 2 equiv of added alcohol, there is a sufficient quantity of protons present for protonation of both dianion species allowing the reaction to go to completion. Furthermore, the appearance of the two oxidation waves in the cyclic voltammogram of nitrobenzene in the presence of alcohol that correspond to those obtained with nitrosobenzene in the presence of alcohol indicates that both reactions give the same final product, $C_6H_5NOH^-$, the protonated dianion of nitrosobenzene. The reduction follows an EEC-CEEC mechanism which can be written as shown in (7).

$$C_6H_5NO_2 \overset{e^-}{\rightleftharpoons} C_6H_5NO_2^- \overset{e^-}{\rightleftharpoons} C_6H_5NO_2^{2-} + ROH \longrightarrow$$
$$RO^- + C_6H_5NO_2H^- \longrightarrow OH^- + C_6H_5NO \overset{e^-}{\rightleftharpoons} C_6H_5NO^- \overset{e^-}{\rightleftharpoons}$$
$$C_6H_5NO^{2-} + ROH \longrightarrow C_6H_5NOH^- + RO^- \quad (7)$$

The transformation of nitrobenzene dianion to neutral nitrosobenzene occurs in two consecutive chemical steps: a second-order protonation reaction followed by a first-order decomposition reaction. The effect of increasing the alcohol concentration is to cause an increase in the rate of the second-order reaction but not that of the first-order one; thus at sufficiently high concentrations of alcohol, the first-order decomposition becomes the rate-determining step in the overall reduction process. This effect is clearly demonstrated in a plot of the ratio of peak current of the second reduction wave in the presence of alcohol to the peak current of pure nitrobenzene at the same concentration against mole ratio of alcohol to nitrobenzene (Figure 6). For a given scan rate, the peak current increases with increasing alcohol concentration to a maximum value. Further addition of alcohol produces no additional increase in peak current, showing that the rate of reaction is now controlled by another process not involving a molecule of proton donor. Moreover, at a given excess of alcohol, the peak current ratio is higher at a slower scan rate, because the longer time interval of the experiment allows the first-order reaction to proceed more nearly to completion. At a scan rate of 500 mV/sec, the conversion of nitrobenzene dianion to nitrosobenzene is only 40% complete during the scan as indicated by a maximum value of 1.8 for the peak current ratio, while a peak current ratio of 2.54 at a scan rate of 200 mV/sec indicates a 77% conversion. For still smaller experimental times, such as those used in dc polarography, complete conversion of the dianion can be expected, and the height of the second reduction wave should be exactly three times the height of the first wave; this is the reported behavior of this system in other nonaqueous solvents.[10,11] The mechanism involves the addition of two electrons and a single proton which is the postulated rate-determining step obtained by an analysis of the polarographic wave for this system in aqueous alcohol solution.[8,9] Calculations using the theory developed for an ECE-type mechanism[20,21] and experimental values for peak current as a function of scan rate yield a value of $k_f = 10\ \text{sec}^{-1}$ for the first-order decomposition.

Electrochemical Behavior in the Presence of Strong Acid. Two effects are noted in the electrochemical behavior of nitrosobenzene in the presence of the strong acid, ammonium ion. First a shoulder develops on the positive side of the first reduction wave and, second, a new reversible redox process is observed at −0.79 V, the reduction potential of azoxybenzene (Figure 7). The azoxybenzene wave grows in height with increasing addition of ammonium ion and reaches a maximum at a mole ratio of proton donor to substrate of 1 to 1. At this concentration, the peak current for the azoxybenzene wave is approximately one-half the height of the original nitrosobenzene wave. Further addition of ammonium ion results in a decrease in the height of the wave until, at a mole ratio of approximately 2 to 1, the wave has essentially disappeared. The first reduction wave of nitrosobenzene grows with addition of ammonium ion and reaches a maximum height equivalent to the transfer of two elec-

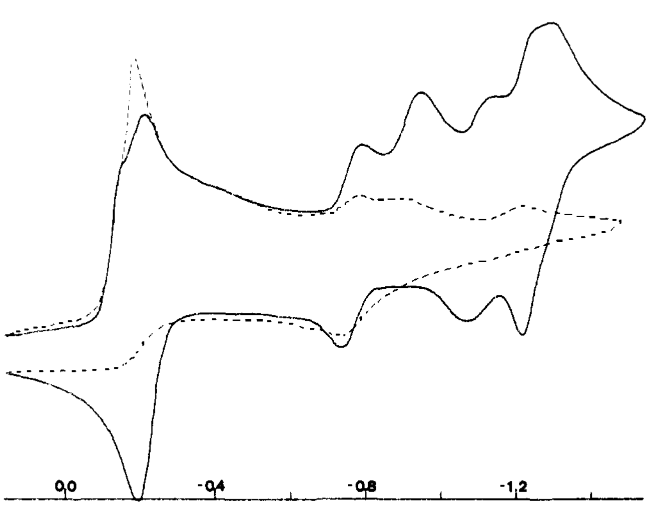


Figure 7. Cyclic voltammetry of nitrosobenzene in presence of strong acid. Solution contained 2.7 m*M* C_6H_5NO, 0.1 *M* KI, and (—) 1.2 m*M* or (– – –) 6.1 m*M* acetic acid at −40°. Scan rate = 200 mV/sec.

trons at mole ratios of ammonium ion to nitrosobenzene in excess of 2 to 1. At these concentrations, no anodic current corresponding to the reoxidation of radical anion is observed, but a new oxidation wave appears very close to the anodic potential limit of the solvent. Controlled potential coulometric reduction at the first wave with ammonium ion in excess of a 2 to 1 mole ratio gives an n_{app} value of slightly greater than 1 with formation of considerable amounts of azoxybenzene.

A cyclic voltammogram of nitrobenzene in the presence of ammonium ion shows that the first reduction wave is unaffected by the addition of a strong acid. A new wave develops at approximately −0.90 V which grows with increasing ammonium ion concentration and reaches a maximum height equivalent to the transfer of three electrons when the ratio of ammonium ion to nitrobenzene is 4 to 1 (Figure 8). A detailed study of this system was hampered by severe distortion of the reduction waves caused by adsorption processes so that a relationship between rate of growth of the new wave with rate of addition of ammonium ion could not be established accurately. Controlled potential coulometric analysis at the potential of the first reduction wave proceeded with the rapid transfer of a single electron followed by a very slow process involving the transfer of three additional electrons over a period of several hours. On the other hand, coulometric reduction at the potential of the new wave (−0.90 V) proceeded rapidly with the addition of four electrons in approximately 30 min. A cyclic voltammogram taken of the solution after reduction in both cases showed the presence of a single irreversible oxidation wave close to the anodic limits of the solvent (Figure 9).

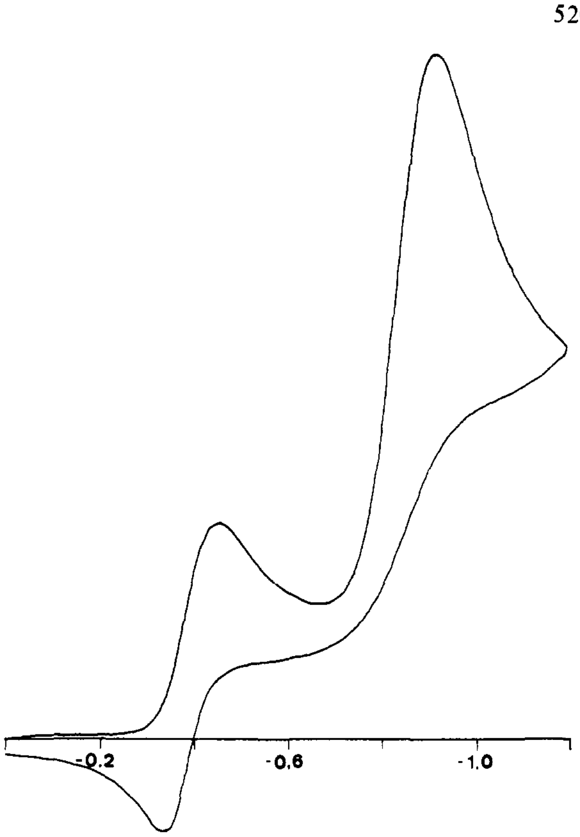


Figure 8. Cyclic voltammetry of nitrobenzene in presence of strong acid. Solution contained 5.0 m*M* $C_6H_5NO_2$, 0.1 *M* KI, and 41 m*M* acetic acid at −40°. Scan rate = 200 mV/sec.

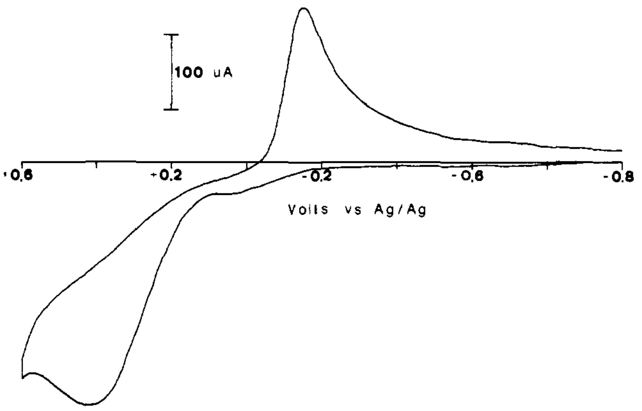
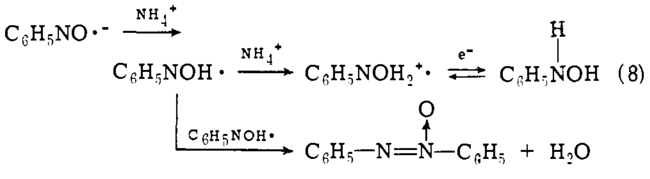


Figure 9. Cyclic voltammetry of phenylhydroxylamine in solution produced by coulometric reduction of a 0.8 m*M* $C_6H_5NO_2$ in the presence of excess acetic acid. Scan rate = 200 mV/sec.

The appearance of a shoulder on the anodic side of the first reduction wave of nitrosobenzene suggests that protonation of the radical anion to form the free radical species $C_6H_5NOH\cdot$ occurs. As was observed in the study of the electrochemical behavior of this compound in the presence of alcohol, the reduction potential for this free radical species is only slightly less than that for the radical anion. Thus addition of a single proton does not facilitate further reduction at the potential of the first wave, and the species must undergo another chemical step before further reduction can occur. There are two possibilities for further chemical reaction—addition of a second proton to form the species $C_6H_5NHOH\cdot^+$, which is reducible at the potential imposed, or dimerization of the free radical species with subsequent loss of a molecule of water to form azoxybenzene (eq 8). If the species $C_6H_5NO\cdot^-$ is more basic than $C_6H_5NOH\cdot$ then, for mole ratios of ammonium ion to nitrosobenzene of less than 1, the radical anion is necessarily limited to the addition of a single proton, allowing the fast dimerization reaction to occur. At mole ratios greater than 1, addition of a second proton can occur, decreasing reaction by the dimerization route and allowing addition of another electron to form phenylhydroxylamine. This mechanism is reflected in the results, showing that the azoxyben-



$$\begin{aligned} & C_6H_5NO\cdot^- \xrightarrow{NH_4^+} \\ & \quad C_6H_5NOH\cdot \xrightarrow{NH_4^+} C_6H_5NOH_2^{+}\cdot \overset{e^-}{\rightleftharpoons} C_6H_5\overset{H}{\overset{|}{N}}OH \qquad (8) \\ & \quad \xrightarrow{C_6H_5NOH\cdot} C_6H_5{-}N{=}\overset{O}{\overset{\uparrow}{N}}{-}C_6H_5 + H_2O \end{aligned}$$

zene reduction wave increases with increasing ammonium ion concentration until a 1 to 1 mole ratio of ammonium ion to nitrosobenzene is reached and then decreases with further addition of acid. The maximum peak current for azoxybenzene is one-half the peak current of the initial reduction wave of nitrosobenzene because two molecules of starting material react to form one molecule of the dimer. The coulometric behavior of this system is similar to that obtained in aqueous alcohol solutions at high pH; n_{app} values considerably less than 2 are found with formation of large quantities of azoxybenzene.[9] In this case, the mechanism of formation of azoxybenzene involves reaction of nitrosobenzene with phenylhydroxylamine.[22] Apparently, phenylhydroxylamine produced at the electrode surface diffuses into the bulk solution where it reacts with unreduced nitrosobenzene to form the dimeric species.

The radical anion of nitrobenzene is not readily protonated by ammonium ion on the cyclic voltammetric time scale since there is no change in the first reduction wave on addition of strong acid. This demonstrates that the radical anion of nitrosobenzene (which readily protonates under these conditions) is a stronger base than that of nitrobenzene, thus keeping with an earlier observation on the relative basicity of the dianion species. Since ammonium ion is a stronger acid than isopropyl alcohol, the peak shift caused by the protonation reaction with the dianion is much larger (approximately 300 mV with ammonium ion, while the shift caused by the alcohol was insufficient to cause separation of the two waves). The equilibrium constant for protonation of the dianion of nitrobenzene with ammonium ion calculated from this shift in peak potential is 3×10^6, five orders of magnitude greater than the equilibrium constant obtained for the same reaction using isopropyl alcohol as the proton source. The reduction mechanism is essentially the same as that given in (7), with NH_4^+ replacing ROH and the OH^- produced by decomposition of the protonated nitrobenzene dianion reacting with NH_4^+ to produce ammonia. Protonation of the $C_6H_5NOH^-$ species also probably occurs.

Coulometric reduction takes place with an overall n_{app} value of 4.0 giving a single reduction product, phenylhydroxylamine. The absence of azoxybenzene in the reduction mixture can probably be attributed to two factors. There is probably very little unreduced nitrosobenzene in the bulk solution for the phenylhydroxylamine to react with since the decomposition reaction to form nitrosobenzene near the electrode surface is rapid and further reduction occurs before the species is swept into the bulk solution. Furthermore, at the imposed potential, there is probably a two-electron addition to neutral nitrosobenzene followed by rapid addition of two protons so that the free radical species $C_6H_5NOH\cdot$ is not formed. On the coulometric time scale, the radical anion is capable of reacting with ammonium ion since an n_{app} value of 4.0 is also reached upon reduction at the potential of the first wave. The long time interval of the reduction process suggests that this reaction is of only minor importance in the overall reduction process, and it was not studied further. The reduction product, phenylhydroxylamine, oxidizes at approximately +0.4 V, very close to the anodic limit of the solvent, making wave analysis very difficult (Figure 9). An associated reduction wave appears at −0.2 V, which is the reduction potential of nitrosobenzene, and both oxidation and reduction waves shift with scan rate. It was impossible to determine if the wave shifts were caused by a quasi-reversible electron transfer or by the involvement of a following chemical reaction. One possibility for such a reaction would be a two-electron oxidation of phenylhydroxylamine followed by loss of two protons to form a neutral molecule of nitrosobenzene. Nitrosobenzene can then be reduced in a two-electron two-proton reaction, as was observed earlier, to yield phenylhydroxylamine, giving a chemically and electrochemically reversible system.

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