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Electrochemical Reduction of Nitrobenzene and Substituted Nitrobenzenes on Lead Electrode

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Electrochemical reduction of nitrobenzene and substituted nitrobenzenes on lead electrode was studied by galvanostatic measurements and cyclic voltammetry in basic ethanol-water solvents. Nitroso compounds or hydroxylamines were detected as the main reduction product depending on the potential. Mechanisms of production and further reduction of substituted and unsubstituted nitrosobenzenes are deduced from Tafel slope, pH dependence and reaction order. The reduction of most of the substituted nitrobenzenes to corresponding nitrosobenzene derivatives seemed to follow the reaction mechanism of nitrobenzene reduction with a few exceptions. A Hammett type relationship between the magnitude of the reduction current and the kinds of substituents was found with the ρ value of 0.54.

Introduction

Since Haber^{1,2} studied in 1898 the electrochemical reduction of nitrobenzene with platinized platinum electrode, a number of investigators³⁻¹⁹ have used polarographic and other methods to study the reaction paths for the electrochemical reduction of nitrobenzene to phenylhydroxylamine, aniline and coupled products such as azoxy-, azo- and hydrazobenzene. The course of reactions were varied depending on the choice of electrode material, electrode potential and electrolyte solutions. There have been reports²⁰⁻²³ on studies of reduction of some substituted nitrobenzenes by ESR and polarographic experiments.

In a previous paper²⁴ we reported a study on the reduction of nitrobenzene ($C_6H_5NO_2$) at lead electrode in ethanol-water solvents. In basic solutions ($pH > 8.5$) the first reduction product was nitrosobenzene (C_6H_5NO) contrary to the previous reports^{4-6,11-13} that C_6H_5NO can not be obtained since its reduction is faster than its formation at the reduction potential of $C_6H_5NO_2$.

Based on kinetic evidences we proposed in the previous paper²⁴ a reaction mechanism in which the rate determining step at lower polarization is a chemical dehydration of an adsorbed intermediate $C_6H_5N(OH)_{2ads}$ which is in potential-dependent equilibrium with $C_6H_5NO_2$.

At more negative potentials C_6H_5NO was further reduced supposedly through an adsorbed radical intermediate ($C_6H_5\dot{N}OH$)_{ads} which is hydrolyzed in a rate determining step to a cation radical $C_6H_5\dot{N}HOH^+_{ads}$ which subsequently accepts an electron to become C_6H_5NHOH . However, at extremely negative potentials coupled products such as

O
|
 $C_6H_5\dot{N}=NC_6H_5$

were produced through condensation because of higher coverage of electrode by ($C_6H_5\dot{N}OH$)_{ads}.

To supplement the previous study we expanded the scope of the investigation to include cyclic voltammetry of $C_6H_5NO_2$ and C_6H_5NO , and also the kinetic measurements of cathodic reduction of 10 substituted nitrobenzenes in basic ethanol-water solutions in order to study the effect of the substituents. The evidences from these experiments are discussed in this paper with regards to the previously proposed reaction mechanisms of nitrobenzene.

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Experimental

Chemicals and Materials. Reagent grade nitrobenzene (Eastman Kodak) was purified by vacuum distillation²⁵. Nitrosobenzene which was chemically synthesized²⁶ was purified by recrystallization from ethanol. The substituted nitrobenzenes were of the highest purity available from Eastman Kodak. They were checked for purity by measurement of the melting point and recrystallized from ethanol before use, if necessary. All electrolytic solutions were prepared from reagent grade absolute ethanol (Malinkrodt) and doubly distilled water (80 percent alcohol by volume) with lithium chloride (Baker analyzed) and sodium hydroxide (Baker analyzed) as the electrolyte without further purification. The total concentration of the electrolytes used were 0.1 M. The solutions were deaerated with stream of nitrogen purified by passing through a tube of hot copper shred.

Smooth electroplated lead wire or mesh was used as the working electrode. Lead was electroplated in a fluoborate bath²⁷ on platinum wire or platinum mesh on which copper was first electroplated. These electrodes were chemically polished in a solution of 80% glacial acetic acid and 20% hydrogen peroxide for a few seconds²⁸. After the electrodes were withdrawn from the bath, they were immediately degreased by washing with isopropyl alcohol followed by washing with stream of doubly distilled water.

Apparatus and Measurements. The electrochemical cell used for all measurements was a three compartment pyrex glass cell. The main compartment which contained the working electrode had a capacity of about 15 ml and the counter electrode compartment about 10 ml. The working electrode compartment was separated by a fritted glass disc from the counter electrode and connected to the reference electrode compartment by a Luggin capillary. The general construction of the cell was similar to the one described elsewhere.²⁹

The reference electrode was a saturated calomel electrode and all the potential data given here are referred to this electrode. Measurements of pH of the electrolytes used in these experiments were made before and after electrolysis.

After desired period of electrolysis, the products were identified by TLC technique and UV spectroscopy from an aliquot portion of sample removed from the solution being electrolyzed. Kieselgel GF₂₅₄ (Merck) and chloroform were used for the fixed phase and eluent, respectively, in the TLC. Identification by TLC was made by matching positions of the spots against those of known reference compounds.

The UV spectrophotometric confirmation was made by comparing spectra obtained with a Beckman DK-2A spectrophotometer with the standard spectral data in the literature³⁰.

Steady state current-potential curves (Tefel plots) were obtained by applying constant currents from the galvanostatically operating electrochemical control unit and reading the potential after the latter reached a steady value while the solution was continuously stirred by the stream of

bubbling nitrogen. The steady value of the potential did not change appreciably with the rate of stirring

Results

Cyclic Voltammetry. The cyclic voltammograms that are shown in Figure 1 (for nitrobenzene) and Figure 2 (for nitrosobenzene) were obtained with scan rate of 20 mV/sec in the buffered solution of pH=10.60 within the range of -0.5 to -0.9 volt. In the cyclic voltammograms obtained by potential-sweeping in the unstirred solutions (dashed lines), there were both the reduction and oxidation waves. However, oxidation waves disappeared in the stirred solutions (solid lines). The cyclic voltammograms of C₆H₅NO₂ and C₆H₅NO with various scan rates are shown in Figures 3 and 4, respectively. For C₆H₅NO₂ (Figure 3) the height of reduction wave was unchanged with scan rate while the oxidation wave increased with increasing scan rate. However, in Figure 4 both the reduction and oxidation waves for C₆H₅NO increased with scan rate. Furthermore, single oxidation wave (b) of Figure 4 splitted into two waves (c) as the potential sweeping rate was increased.

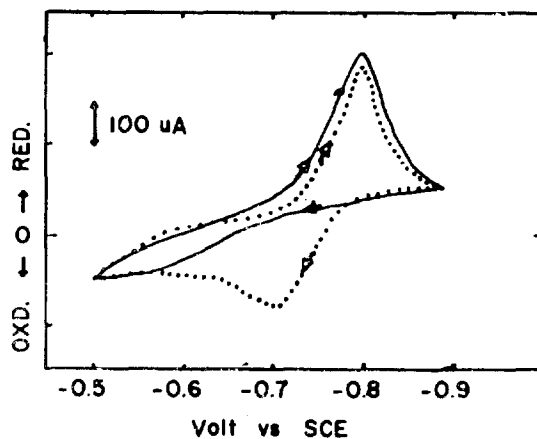


Figure 1. Cyclic voltammogram of $10^{-3} M$ C₆H₅NO₂ in unstirred (dashed line) and stirred (solid line) solutions at pH=10.60. Scan rate was 20 mV/sec. Potential against saturated calomel electrode.

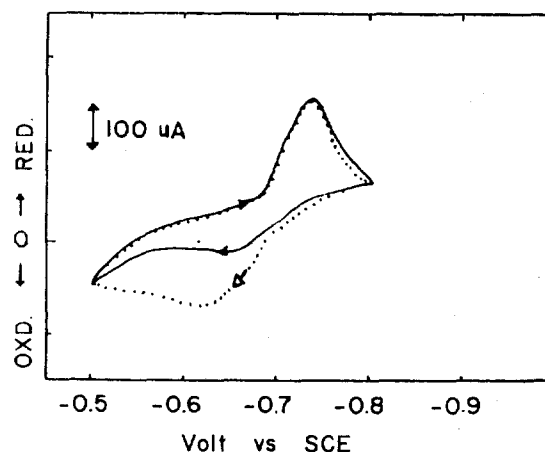


Figure 2. Cyclic voltammogram of $10^{-3} M$ C₆H₅NO in unstirred (dashed line) and stirred (solid line) solutions at pH10.60. Scan rate was 20 mV/sec.

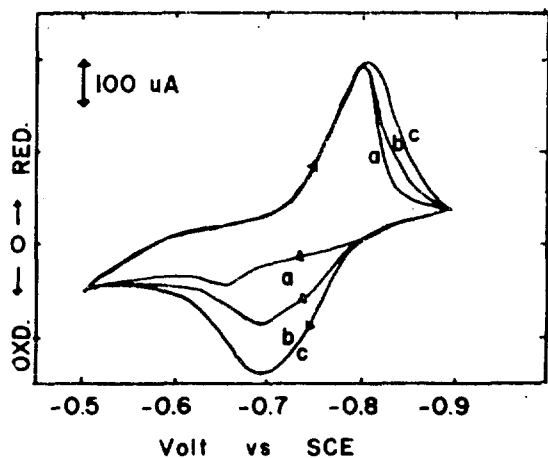


Figure 3. Cyclic voltammogram of $10^{-3} M$ $C_6H_5NO_2$ in the unstirred solution at $pH=10.60$. Scan rates were 2 mV/sec (a), 20 mV/sec (b), and 200 mV/sec (c).

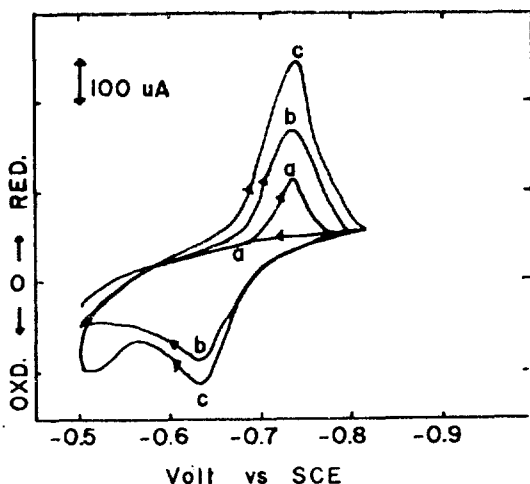


Figure 4. Cyclic voltammogram of $10^{-3} M$ C_6H_5NO in unstirred solution at $pH=10.60$. Scan rates were 2 mV/sec (a), 20 mV/sec (b), and 200 mV/sec (c).

Polarization Curves. The steady state current-potential relationships for the reduction of nitrobenzene and nitrosobenzene are shown in Figure 5. The Tafel line of C_6H_5NO coincides with that of $C_6H_5NO_2$ in the solution of same pH at higher polarization. In Figure 6, it is shown that the reduction rate of $C_6H_5NO_2$ was independent of its concentration but dependent on pH. The steady state current-potential curves of substituted nitrobenzenes are compared with that of nitrobenzene in Figures 7 and 8. At lower polarization, Tafel slopes for the substituted nitrobenzenes used in this work were about 30 mV, close to the value for the unsubstituted. Also the concentrations of the substituted nitrobenzenes had no effect on the current at a fixed potential. It can therefore be assumed that nitro groups in the substituted nitrobenzenes are reduced in the first Tafel region to nitroso groups via processes similar to that of nitrobenzene.²⁴ At higher polarization, Tafel slopes for *p*- CH_3 , *m*- CH_3 , *p*- $COOH$ and *p*- Cl nitrobenzenes shown in Figure 7 (group I compounds) were about 60 mV as in the case of nitrobenzene while with other compounds

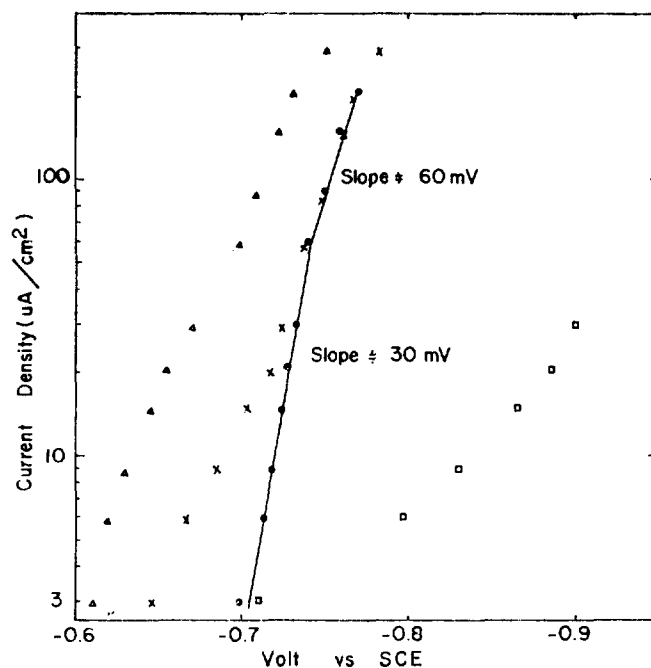


Figure 5. Steady state polarization curves, for nitrobenzene and nitrosobenzene. \square : Electrolyte only; \bullet : $10^{-4} M$ $C_6H_5NO_2$ at $pH=10.60$; \times : $10^{-4} M$ C_6H_5NO at $pH=10.60$; \triangle : $10^{-4} M$ C_6H_5NO at $pH=9.90$.

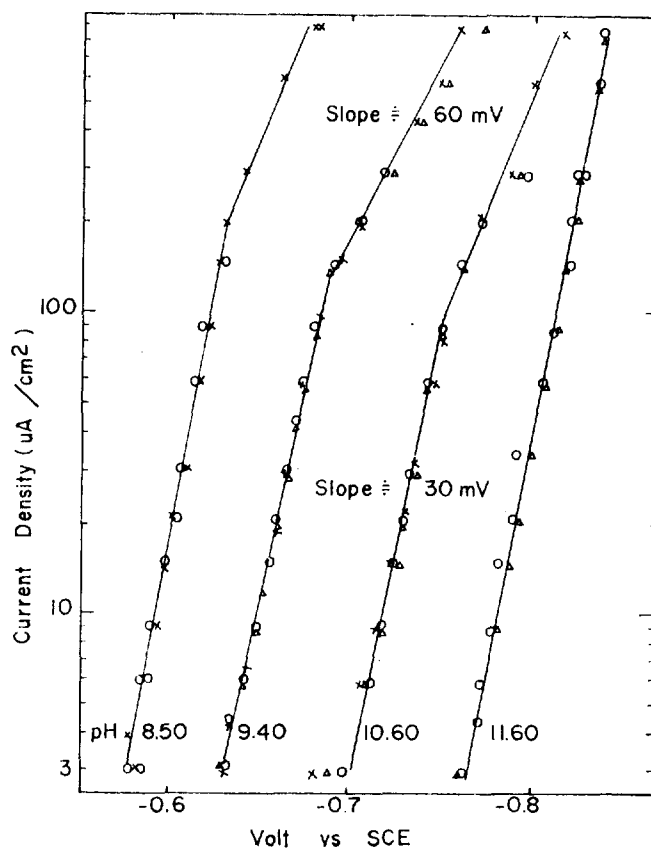


Figure 6. Steady state polarization curves for nitrobenzene at various pH's. \circ : $10^{-4} M$ $C_6H_5NO_2$; \triangle : $10^{-3} M$ $C_6H_5NO_2$; \times : $10^{-2} M$ $C_6H_5NO_2$.

(group II compounds) in Figure 8 there were sharp rises in potential when the current reached beyond certain limits.

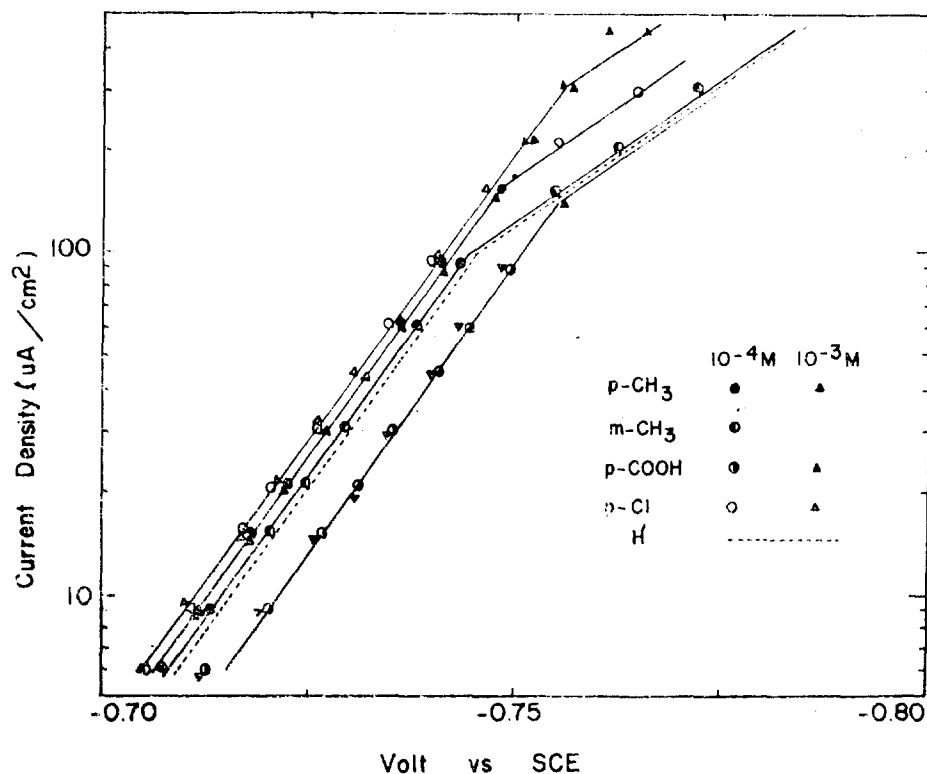


Figure 7. Steady state polarization curves of substituted nitrobenzenes (group I) at pH=10.60.

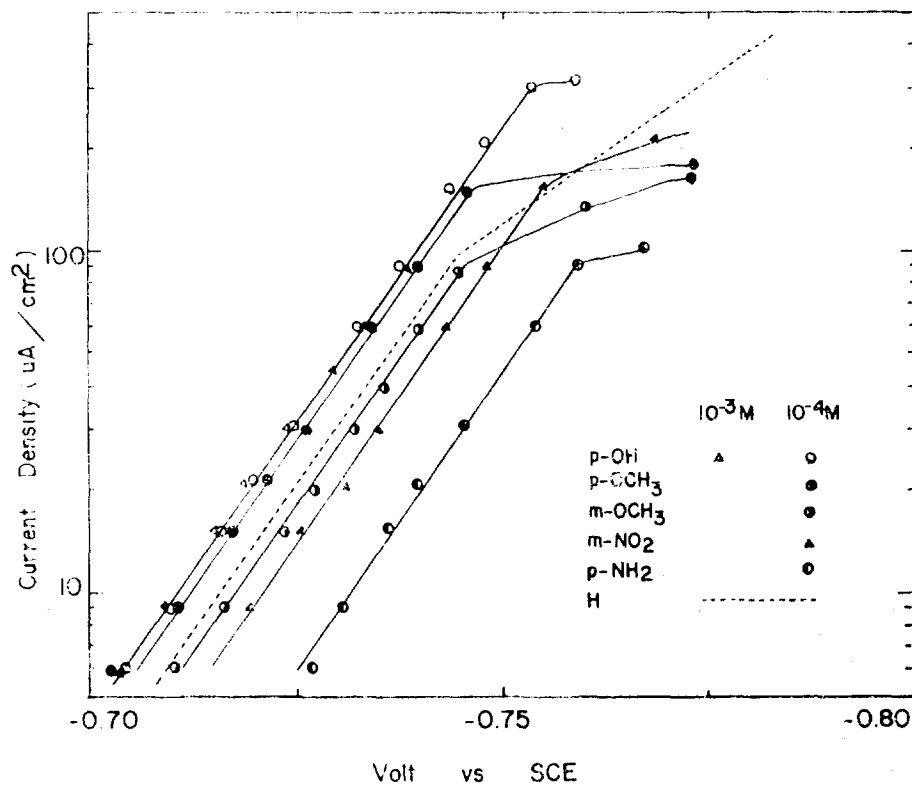


Figure 8. Steady state polarization curves of substituted nitrobenzenes (group II) at pH=10.60.

The logarithm of the ratio i_x/i_H at -725 mV and pH=10.60, where i_x and i_H stand for the reduction currents of a substituted and the unsubstituted nitrobenzenes, respectively, was calculated for each substituent as shown in Table I and was used in drawing the Hammett plots of Figure

9. The Hammett substituent constants (σ) are taken from Jaffé³¹. The Hammett linear free energy relationship is followed by most of the substituted nitrobenzenes with $\rho = -0.54$ except for $p\text{-NH}_2$ and $p\text{-Cl}$. Points for $p\text{-NH}_2$ and $p\text{-Cl}$ nitrobenzenes lie on another straight line with a positive

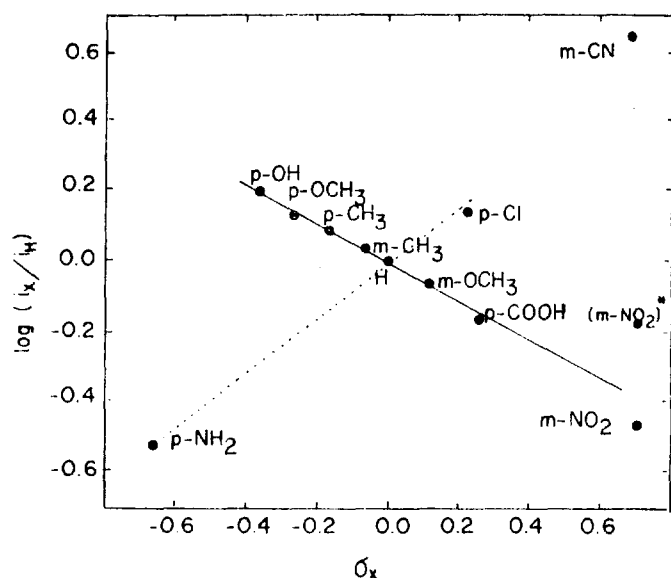


Figure 9. Hammett plot for the electro-reduction of substituted nitrobenzenes.

TABLE 1: Hammett Table for the Electro-Reduction of Substituted Nitrobenzenes, at pH=10.60, -725 mV

Substituted	σ_x	i_x	$\log(i_x/i_H)$
<i>p</i> -OCH ₃	-0.268	25.7	+0.132
<i>p</i> -OH [†]	-0.357	30.3	+0.203
<i>p</i> -CH ₃	-0.170	23.0	+0.083
<i>m</i> -CH ₃	-0.069	20.3	+0.031
H	0.000	19.0	0.000
<i>m</i> -OCH ₃	+0.115	16.5	-0.600
<i>p</i> -COOOH [†]	+0.265	12.8	-0.170
<i>m</i> -NO ₂	+0.710	12.7	-0.175
		$\frac{1}{2}i_x = 6.35^*$	-0.476
<i>p</i> -NH ₂ [†]	-0.660	5.60	-0.529
<i>p</i> -Cl	+0.226	26.0	+0.139
<i>m</i> -CN ^{**}	+0.678	88.0	+0.665

[†]These substituents were confirmed not to be in ionic forms in the solutions used. ^{*} i_x is divided by 2 to account for the fact that there are 2 NO₂ groups in a molecule. ^{**}Tafel slope of *m*-CNC₆H₄NO₂ was 90 mV.

slope in the Hammett plot.

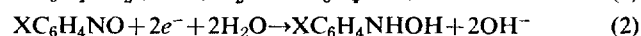
Analyses of Products. Reduction Products were identified by comparing the absorption spectra with the standard spectral data in the literature^{30*} and were confirmed by the TLC experiments.

*The nitroso compounds produced from the corresponding nitrocompounds were identified by the absorption maxima at their characteristic wavelengths; *p*-CH₃(C₆H₄)NO: 288 and 315 nm, *p*-OH(C₆H₄)NO: 280 and 305 nm, *p*-Cl(C₆H₄)NO: 226, 288 and 313 nm, *p*-CH₃O(C₆H₄)NO: 345 nm, *m*-NO₂(C₆H₄)NO 265 and 320 (S) nm, *p*-NH₂(C₆H₄)NO: 240 and 355 nm. The hydroxylamines were identified by their respective absorption peaks; *p*-CH₃(C₆H₄)NHOH: 285 to 288 nm; and 315 nm, *p*-Cl(C₆H₄)NHOH: 231 and 255 nm to 288, and 313 nm, which gradually shifted to those of nitroso compounds due to oxidation.

At potentials more negative than -750 mV, the main reduction products of the group I compounds (polarization presented in Figure 7) were corresponding nitroso compounds (XC₆H₄NO) along with small amounts of hydroxylamino compounds (XC₆H₄NHOH). But, at less negative potential than -750 mV corresponding hydroxylamines were the major products, which changed gradually to XC₆H₄NO by air oxidation.

However, during the reduction of the group II compounds (presented in Figure 8) hydroxylamines were not detected at any potential. Coupled compounds of the type XC₆H₄N(O)NC₆H₄X or XC₆H₄NNC₆H₄X resulted when *p*-CH₃O, *p*-OH, *p*-NH₂ or *m*-NO₂ substituted nitrobenzenes were used.

The main reactions can therefore be summarized as follows:



in the cases of group I compounds where X is H, *p*-CH₃, *m*-CH₃, *p*-COOH or *p*-Cl, and



or



in the cases of group II compounds where X is *p*-OCH₃, *m*-OCH₃, *p*-NH₂, *p*-OH or *m*-NO₂.

The group I compounds (X=H, *p*-CH₃, *p*-COOH, *p*-Cl) seem to be reduced through reactions (1) and (2). Reaction (1) is slower at lower polarization but more potential dependent than (2), and becomes eventually faster at higher polarization. Therefore, one can expect that at lower polarization XC₆H₄NHOH are obtained as the main product and at higher polarization XC₆H₄NO are accumulated before they are further reduced.

However, the group II compounds (X=*p*-OCH₃, *m*-OCH₃, *p*-NH₂, *p*-OH, *m*-NO₂) seem to be further reduced through reaction (3a) or (3b) after reduction (1) because of higher coverage of the electrode by XC₆H₄NO. Thus, at lower polarization XC₆H₄NO is obtained without XC₆H₄NHOH, but at higher polarization along with the coupled compounds. (Refer to the Mechanism section)

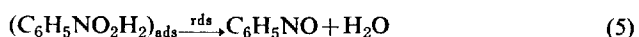
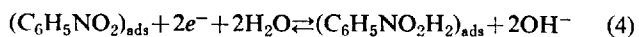
Discussion

Electroactive Forms and Intermediates. Several adsorbed intermediate species such as (C₆H₅NO₂)_{ads},⁷ (C₆H₅NO₂H⁺)_{ads},³² and (C₆H₅NO₂H₂²⁺)_{ads},⁶ have been proposed in the literature. Preprotonated species C₆H₅NO₂H₂⁺ and C₆H₅NO₂H₂²⁺ were reported to be reduced at less negative potential than C₆H₅NO₂. *pK_a* of C₆H₅NO₂H₂²⁺ was found to be 5.6 by polarographic experiments¹⁹. Therefore, in a basic solution unprotonated species C₆H₅NO₂ is probably dominant over the protonated species. The substituted nitrobenzenes can be supposed to behave in a similar way.

The electrode reactions can be reasonably assumed to take place through a strongly adsorbed species, (C₆H₅NO₂)_{ads} or (XC₆H₄NO₂)_{ads} since the rate obtained in Figures 6 and 8 are independent of C₆H₅NO₂ or XC₆H₄NO₂ concentration down to the lowest concentration used. These

assumption agrees with results of adsorption studies³³⁻³⁵ on various metal electrodes indicating that the adsorption of similar organic molecules is more favorable than that of water near the potential of zero charge, which is reported to be -0.7 volts for lead³³.

According to the ESR studies,^{17,18} the reduced radical anions such as $C_6H_5\dot{N}O_2^-$ and $XC_6H_4\dot{N}O_2^-$ can be immediately protonated by water molecule to become neutral radicals such as $C_6H_5\dot{N}O_2H$ and $XC_6H_4\dot{N}O_2H$. The electron transfer to these neutral radicals is expected to be rapid at the potential at which the radical anions are formed³⁶. As the second electron transfer occurs, protonation is also expected to be rapid. Therefore, the reaction scheme is given by the following equations:



Although the polarographic reduction potentials of $(C_6H_5NO_2)$ and $(C_6H_5\dot{N}O_2^-)$ in an aprotic solvent are widely separated¹¹, in the protic solvent of the present case reduction seems to take place by a two-electron transfer step.

The intermediate $C_6H_5N_2OH_2$ assumed in this work was also proposed by workers who used electrochemical³⁷ and pulse radiolysis^{38,39} techniques to study similar systems. $C_6H_5NO_2H_2$ is produced by the reversible reaction (4) during the cathodic sweep represented in Figure 3. Since the surface coverage by $C_6H_5NO_2H_2$ at the end of the cathodic sweep should be larger when the sweep rate is slower (longer reduction time), the fact that the oxidation wave observed on reversing the sweep decrease with slower sweep rate can be explained only by the removal of $C_6H_5NO_2H_2$ through the chemical reaction (5).

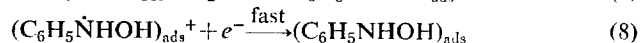
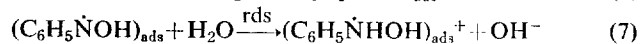
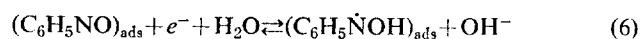
Further evidence supporting the assumption of $C_6H_5N(OH)_2$ as the intermediate comes from a separate finding in our laboratory. When the reduction was carried out in dry CH_3CN with excess $NaClO_4$ (or $KClO_4$) as electrolyte, a reddish brown solid was produced as the reduction product whose formula was found to be $C_6H_5NO_2Na_2$ (or $C_6H_5NO_2K_2$) by elementary analysis. It seems to be ionic salt of $C_6H_5NO_2^{2-}$ anion since on dissolving this compound in DMSO the conductivity of DMSO increased greatly. Furthermore, this solid readily changed to C_6H_5NO and C_6H_5O

$N=NC_6H_5$ in deaerated water. $p-CH_3C_6H_4NO_2$ also resulted in a sodium salt by reduction in the aprotic solvent. In an aqueous solution, $XC_6H_4N(OH)_2$ will obviously result from the electron transfer step instead of $XC_6H_4NO_2^{2-}$.

The adsorbed C_6H_5NO is generally supposed to be more basic than the adsorbed $C_6H_5NO_2$ ^{7,11}. However, it was found that the pK_a of $C_6H_5NOH^+$ is 3.3 by polarographic technique⁷. Therefore, in a basic solution the unprotonated species C_6H_5NO should be dominant as the electroactive form. During the reduction of nitrobenzene in a solvent containing water, an ESR study¹⁸ showed that the radicals are both $C_6H_5\dot{N}OH$ and $C_6H_5\dot{N}HOH^+$. The formation of $C_6H_5\dot{N}OH$ is expected to be rapid when the potential is favorable while its protonation is slow since C_6H_5NOH

should be less basic than $C_6H_5\dot{N}O^-$. $C_6H_5\dot{N}HOH^+$ should be an electroactive species and its reduction will be fast. Thus, $C_6H_5\dot{N}OH$ is believed to be an intermediate in the reduction process of C_6H_5NO .

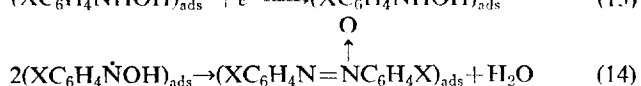
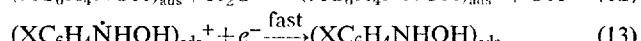
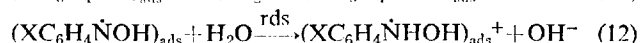
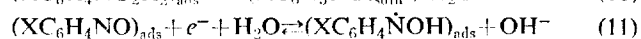
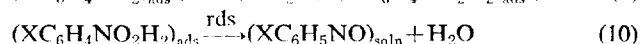
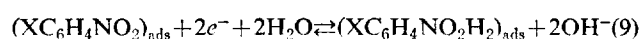
The cyclic voltammograms of Figure 4 can be interpreted by the reaction scheme of equations (6) to (8). We propose the reaction scheme as follows.



The reduction wave increases with increasing scan rate presumably because the adsorption of C_6H_5NO is fast enough. The first oxidation wave is due to the oxidation of $(C_6H_5\dot{N}OH)_{ads}$ and the second oxidation wave is due to oxidation of $(C_6H_5NHOH)_{ads}$. With a slow scan rate the second oxidation wave decreases or disappears since $(C_6H_5NHOH)_{ads}$ desorbs.

According to reported polarographic experiments⁴⁰, $C_6H_5NO_2$ is irreversibly reduced to C_6H_5NHOH at more negative potential than C_6H_5NO is reversibly reduced. Thus, although C_6H_5NO was proposed to be an intermediate, C_6H_5NO has not been identified. In the present investigation, the reduction potential of $C_6H_5NO_2$ was also more negative than that of C_6H_5NO (See the cyclic voltammograms of Figures 1 and 2.). However, in the higher current regions of Figures 5 and 6, C_6H_5NO was obtained as the main product²⁴ since its formation rate is greatly enhanced with higher polarization. The substituted nitrobenzenes also resulted in nitroso compounds on reduction in the higher polarization region of Figure 7.

Mechanism. Based on the above facts, it is seen that aromatic nitro compounds are reduced to nitroso compounds by a strongly potential-dependent charge transfer step and subsequently to hydroxylamino compounds by a less potential-dependent charge transfer reaction. The substituted nitrobenzenes are generally found to be reduced through the same process as nitrobenzene, but at different rates (See Figures 7 and 8). Thus, the mechanism can be written in a generalized form for the substituted nitrobenzenes with exceptions of a few substituents.



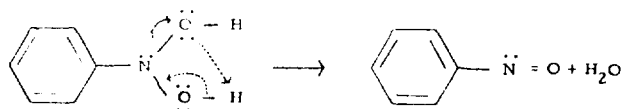
The reactions of equations (9) to (14) correspond to those of nitrobenzene studied in the previous work²⁴. From reactions (9) and (10), the current i_x for the production of substituted nitrosobenzenes can be written in the following way:

$$\log i_x = \log K_x k_x + \text{const.} - 2\text{pH} - \frac{2}{0.0592} E \quad (15)$$

where x stands for a substituent, and K_x and k_x are the equilibrium constant of reaction (9) and the rate constant of reaction (10), respectively. Under a fixed potential and pH, the ratio of the reduction current of a substituted nitrobenzene given by equation (15) to that of the unsubstituted nitrobenzene should be related to the nature of the substituents by a Hammett type equation:

$$\log \left(\frac{i_x}{i_H} \right)_{\text{pH}, E} = \log \left(\frac{K_x k_x}{K_H k_H} \right)_{\text{pH}, E} = \rho \sigma \quad (16)$$

The negative ρ value from Figure 9 may be taken as a supporting evidence for reaction (10) and not reaction (9) as the rate determining step. The dehydration may take place through a concerted electron shift involving 6 electrons in which the breaking of N-O bond is the most difficult part:



The reaction constant ρ for the electrochemical formation of radical anions in CH_3CN solvent was found to be a positive value by some investigators^{22, 36, 41}. However, the chemical dehydration steps (such as formation of semicarbazones) have been reported to hold negative ρ values⁴².

Reduction of $p\text{-NH}_2$, $p\text{-Cl}$ and $m\text{-CN}$ nitrobenzenes seems to be carried out through a path different from the proposed reactions (9) to (14), since the substituent-current relations for these compounds do not follow the same Hammett type relationship with a negative ρ as the other compounds.

According to a study on the conformation of aromatic nitro groups⁴³, the nitro groups tend to lie in or near the plane of aromatic ring except those in $p\text{-OH}$, $p\text{-NH}_2$, or $p\text{-NO}_2$ substituted nitrobenzenes, in which case the nitro groups are twisted away from the aromatic plane. The non-planar substituted nitrobenzenes can therefore be assumed to be less adsorbable than the planar ones which can attach themselves flat to the electrode surface.

If the substituted nitrobenzenes such as $p\text{-OCH}_3$, $m\text{-OCH}_3$, $p\text{-OH}$, $m\text{-NO}_2$ and $p\text{-NH}_2$ nitrobenzenes are less adsorbable species than the other nitrobenzenes the corresponding nitroso compounds will be accumulated on the electrode surface. Therefore, coupling reaction (14) will be more favorable than reaction (12). In fact, small amounts of coupled compounds such as p , p -dimethoxy azoxybenzene, p , p -dihydroxy, m , m -dinitro and p , p -diamino azobenzenes were detected along with the nitroso compounds during the reduction of $p\text{-OCH}_3$, $p\text{-OH}$, $m\text{-NO}_2$ and $p\text{-NH}_2$ nitrobenzenes.

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References

- (1) F. Harber, *Z. Electrochem.*, **22**, (1898).
- (2) F. Harber and O. Schmidt, *Z. Phys. Chem.*, **32**, 193 (1900).
- (3) P. Zuman and C. L. Perrin, "Organic Polarography", Interscience, Interscience, New York, 1969.
- (4) A. J. Fry, "Synthetic Organic Electrochemistry", pp 224-236, pp 224-236, Harper and Row, New York, 1972.
- (5) F. D. Popp and H. P. Schultz, *Chem., Rev.*, **62**, 119 (1962).
- (6) S. K. Vijayalkshamma and R. S. Subrahmanya, *J. Electroanal. Chem.*, **23**, 99 (1969).
- (7) H. Sadek and B. A. Abd-El-Naby, *Electrochim. Acta*, **17**, 2065 (1972).
- (8) B. Kastening, *Electrochim. Acta*, **9**, 24 (1964).
- (9) L. Chuang, I. Fried and P. J. Elving, *Anal. Chem.*, **36**, 2426 (1964).
- (10) S. K. Vijayalkshamma and R. S. Subrahmanya, *Electrochim. Acta*, **47**, 471 (1972).
- (11) W. H. Smith and A. J. Bard, *J. Amer. Chem. Soc.*, **97**, 5203 (1975).
- (12) G. M. Fleishman, I. N. Petrov and W. F. K. Wynne-Jones, "Proc. 1st Australian Conference on Electrochemistry", p. 500, Pergamon, London, 1964.
- (13) M. Suzuki, *J. Electrochem. Soc. Japan*, **22**, 112 (1954).
- (14) L. H. Piette, P. Ludwig and R. N. Adams, *Anal. Chem.*, **34**, 916 (1962).
- (15) L. H. Piette, P. Ludwig and R. N. Adams, *J. Amer. Chem. Soc.*, **84**, 4212 (1962).
- (16) D. H. Geske and A. M. Maki, *J. Amer. Chem. Soc.*, **82**, 2671 (1960).
- (17) P. Ludwig, T. Layloff and R. N. Adams, *J. Amer. Chem. Soc.*, **86**, 4568 (1964).
- (18) P. B. Ayscough, F. P. Sargent and R. Wilson, *J. Chem. Soc., (B)*, 903 (1966).
- (19) H. Sadek and B. A. Abd-El-Naby, *Electrochim. Acta*, **17**, 511 (1972).
- (20) T. Kitagawa, T. P. Layloff and R. N. Adams, *Anal. Chem.*, **35**, 1086 (1963).
- (21) J. G. Lawless, D. E. Bartak and M. D. Hawley, *J. Amer. Chem. Soc.*, **91**, 7121 (1969).
- (22) D. E. Bartak, W. C. Danen, M. F. Marcus and M. D. Hawley, *J. Org. Chem.*, **35**, 1206 (1970).
- (23) P. Neta and D. Meisel, *J. Phys. Chem.*, **80**, 519 (1976).
- (24) J. Chon and W. Paik, *J. Korean Chem. Soc.*, **21**, 404 (1977).
- (25) A. I. Vogel, "Textbook of Practical Organic Chemistry", 3rd. Ed., Longmans, London, 1961.
- (26) E. C. Hornig, "Organic Synthesis", Coll. Vol. III, p. 668, Wiley, New York, 1958.
- (27) H. J. Wisner, "Modern Electroplating", Chap. II, F. A. Lowenheim, Ed., John-Wiley, New York, 1974.
- (28) T. N. Anderson, B. A. Miner, E. Dibble and H. Eyring, "Proc. of the International Conference on Tropical Oceanography", p. 229, Univ. of Miami, Inst. of Marine

Science, 1967.

- (29) J. Chon and W. Paik, *J. Korean Chem. Soc.*, **18**, 391 (1974).
- (30) H. E. Ungnade, "Organic Electronic Spectral Data", Vol. I-VI, Interscience, New York, 1946-1962.
- (31) K. B. Wiberg, "Physical Organic Chemistry", p. 401, John-Wiley, New York, 1964.
- (32) S. H. Cadle, P. R. Tice and J. Q. Chambers, *J. Phys. Chem.* **71**, 3517 (1967).
- (33) J. O' M. Bockris, and D. A. J. Swinkels, *J. Electrochem. Soc.*, **111**, 736 (1964).
- (34) J. O'M Bockris, M. Green and D. A. J. Swinkels, *J. Electrochem. Soc.*, **111**, 743 (1964).
- (35) E. Bromgren, J. O' M Bockris and C. Jesch, *J. Phys. Chem.*, **65**, 2000 (1961).
- (36) R. D. Allendoerfer and P. H. Rieger *J. Amer. Chem. Soc.*, **88**, 3711 (1966).
- (37) M. Heyrovsky and S. Vavricka, *J. Electroanal. Chem.* **28**, 409 (1970).
- (38) K. D. Asmus, A. Wigger and A. Henglein, *Ber. Bunsenges. Physik. Chem.*, **70**, 127 (1966).
- (39) E. J. Hart and M. Anbar, "The Hydrated Electron", p. 121, Wiley-Interscience, New York, 1970.
- (40) L. Meites and P. Zuman, "Electrochemical Data", Part I, Vol. A. p. 184-193, Wiley-Interscience, New York, 1974.
- (41) W. C. Danen, T. T. Kensler, J. G. Lawless, M. F. Marcus and M. D. Hawley, *J. Phys. Chem.*, **73**, 4389 (1969).
- (42) A. Liberles, "Introduction to Theoretical Organic Chemistry", p. 97-101, McGraw-Hill, New York, 1968.
- (43) J. R. Holden and C. Dickinson, *J. Phys. Chem.*, **81**, 1505 (1977).

A New Empirical Potential Function and Its Application to Hydrogen Bonding

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A new potential function based on spectroscopic results for diatomic molecules is presented and applied to the hydrogen bonding systems. The potential energy of interaction is supposed to have electrostatic, polarization, dispersion, repulsion and effective charge-transfer contributions. Estimates of the effective charge-transfer quantity have been made based on the average charge of the proton donor and the acceptor atoms. For dimers such as water, methanol, acetic acid and formic acid, the vibrational stretching frequencies and dimerization energies are calculated and discussed in connection with Badger-Bauer rule.

Introduction

There is a great deal of works about the hydrogen bonding because of its significant role in determining the structure and properties of molecular systems of importance to chemistry and biology. The phenomenon of the hydrogen bonding has been investigated extensively by a variety of spectroscopic and other physical methods and by theoretical considerations¹⁻⁸.

In early theoretical works, it had been suggested by Coulson *et al.*^{9,10} and independently by Tsubomura¹¹ that the significant nature of the hydrogen bonding is brought about by a complicated superposition of the following four contributions which are of similar magnitude; (a) electrostatic energy, (b) exchange repulsion, (c) polarization energy, (d) dispersion energy and (e) charge transfer energy or covalent contribution.

They thought that the success of the electrostatic models in the calculation of the hydrogen bonding energies in certain systems is possibly due to the fact that the other contributions are not significant, which met exactly other

calculations.^{12,13}

On the basis of these interpretations, first we will propose a new empirical potential function for diatomic molecules, and next calculate the vibrational frequencies and the interaction energies for several dimers by using this function.

Potential Energy Function

In earlier papers¹⁴⁻¹⁸, a number of authors have examined various potential functions for diatomic molecules with the spectroscopic measurements, but there are few simple forms to satisfy fairly well those results.

In the present work, we suggest a new function;

$$U(r) = D_e \left\{ 1 - \left(\frac{r}{r_e} \right)^n e^{-a(r-r_e)} \right\}^2 \quad (1)$$

where r is the internuclear distance, r_e is the equilibrium internuclear distance and D_e is the dissociation energy. Here two constants n and a are obtained from the following relationship;

$$ar_e = n + \Delta^{1/2} \quad (2)$$