니트로벤젠의 전해환원 반응 조건과 메카니즘

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Reaction Conditions and Mechanism of Electrolytic Reduction of Nitrobenzene

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요 약. 예한올-물을 혼합용매에서 납전극을 사용하여 니트로벤젠(©NO2)과 그 유도체의 전해환원반응을 조사하였다. 산성용액에서는 피텐셜에 따라 ©NH2H 및 ©NH2 가 생성되었으며 니트로벤젠(©NO)은 중간 채가 아닌것으로 보였다. 염기성 용액에서는 ©NO가 생성되며 더 낮은 피텐셜에서 환원시키면 ©N=©N 2 동락이 가능한 화합물이 생성됨을 확인하였다. 사용한 전해질 용액에서 ©NO와 ©NH2H 사이에 화학적 반응(coupling reaction)은 일어나지 않았다.

각각의 반응에 대의 전류-전압관계와 pH 의존도 및 반응물질에대한 반응 차수로부터 반응 메카니즘을 도출하였다. ©NO 가 생성되는 반응은 치환기가 있을 때도 같은 메카니즘을 따르는 것으로 보인다.

ABSTRACT. Electrochemical reduction of nitrobenzene (©NO2) and its derivatives on Pb electrode was studied by means of galvanostatic measurements and coulometric electrolysis in ethanol-water solvent. In acidic solutions phenylhydroxyl amine and aniline were produced while nitrosobenzene and coupled products such as azo- and hydrazobenzene were produced in basic solutions. Nitrosobenzene (©NO) was not found to be an intermediate in the reduction reactions of ©NO2 in acidic solutions. No direct coupling between ©NO and ©NH2H was observed to occur in the electrolyte solutions used.

Mechanisms of the production of phenylhydroxylamine and nitrosobenzene are deduced from Tafel slope, pH dependence and reaction order with respect to nitrobenzene. Mechanism for the reduction of substituted nitrobenzenes seems to be identical to that of nitrobenzene.

INTRODUCTION

Despite the growing interest in electrochemical organic reactions due to its potential as synthetic and analytical tool[1-4], one of the simplest reactions among the electroreduction of organic compounds does not seem to have received a full treatment of elucidating the reaction mechanisms.
and influence of experimental conditions such as electrode material and pH on the reaction course. It is the electroreduction reactions of nitrobenzene (\(\phi\text{NO}_2\)) and related compounds.

In 1898 Harber\(^{7,18}\) found that various reduction products of nitrobenzene could be obtained on platinized platinum electrode and proposed a reaction scheme which seems to be generally accepted at the present time. But it should be noted that Harber's reduction scheme refers to the reaction on platinized platinum and applies to the particular potentials at which the reduction was carried out.

Since these early studies by Harber, a number of investigators\(^{9-18}\) have proposed reduction mechanism of nitrobenzene based on their polarographic experiments and other methods. Polarographic reduction of nitrobenzene to phenylhydroxylamine in aqueous solutions\(^{11-15}\) occurred with a 4-electron wave at all pH's, and below pH 4.7 there appeared a second 2-electron wave corresponding to reduction of the phenylhydroxylamine to aniline at more negative potentials.

However, in aqueous basic solutions (pH greater than 10) esr studies\(^{18,20}\) showed the presence of a short-lived intermediate corresponding to the nitrobenzene radical anion. In nonaqueous solvents\(^{21-23}\) such as acetonitrile and dimethylformamide the nitrobenzene radical anion is reported to be very stable.

The mechanism of the electrochemical and chemical coupling reaction between two nitrobenzene derivatives to yield azoxy, azo- or hydrazobenzene has also been studied\(^{14-18}\). As a result of these studies the coupling reactions were either assumed to take place via a self-condensation reaction of a hypothetical intermediate, nitrosobenzene, in aqueous media, or via condensation of a nitrosobenzene molecule with a phenylhydroxylamine molecule in acidic and neutral aqueous solutions. However, the exact mechanism remains unresolved.

Fleischman, et al.\(^{17}\) proposed that nitrobenzene is reduced directly to phenylhydroxylamine on mercury electrode in aqueous sulfuric acid solutions, and nitrosobenzene is not an intermediate in this reduction. But phenylhydroxylamine reduced from nitrosobenzene were said to condense with remaining nitrosobenzene.

In the present investigation kinetic measurements of the electrochemical reduction of nitrobenzene and its derivatives on lead cathodes were made in order to elucidate the mechanism of the reduction reactions.

**EXPERIMENTAL**

Chemicals and Materials. Reagent grade nitrobenzene (Eastman Kodak) was purified by means of vacuum distillation\(^{19}\). Phenylhydroxylamine\(^{25}\) was prepared by reduction of nitrobenzene with zinc metal in the presence of ammonium chloride. Nitrosobenzene\(^{26}\) was prepared by oxidation of phenylhydroxylamine using sodium dichromate. The crude products were purified by recrystallization from ethyl alcohol.

Reagent grade tetraethylammonium chloride (Aldrich), sodium hydroxide(Baker), lithium chloride(Baker), and sulfuric acid(Baker) were used as supporting electrolyte without further purification. All electrolytic solutions were prepared from reagent grade absolute ethyl alcohol (Malinkrodt) and doubly distilled water(80 percent by volume in alcohol) with tetraethylammonium chloride (or lithium chloride) and sodium hydroxide as the electrolyte for basic solutions and sulfuric acid for acidic solutions.

A smooth electroplated lead wire was used as the working electrode. Lead was electroplated on platinum wire or platinum mesh, on which copper was previously electroplated, in a fluorobate bath\(^{27}\). These electrodes were chemically
polished in a solution of 80% glacial acetic acid and 20% hydrogen peroxide for a few seconds\(^2\). After the electrodes were withdrawn from the bath, they were immediately degreased by washing with isopropyl alcohol followed by washing with a stream of doubly distilled water.

**Apparatus and Measurements.** The cell used for the electrochemical reactions was a 3-compartment pyrex glass cell. The working electrode compartment was separated from the counter electrode compartment by a fritted glass disc and connected to the reference electrode compartment by a Luggin capillary. The general construction of the cell was similar to the one described elsewhere\(^2\).

All electrochemical measurements were performed with a Beckman Model Electroscan-30 electrochemistry system and an electrometer (Keithley 610C). All the potential data given here are referred to the saturated calomel electrode (SCE).

The electrolytes of pH 8.50 or greater were buffer mixtures of tetraethylammonium chloride and sodium hydroxide solutions whose pH's were measured with a glass electrodes.

After desired period of electrolysis, the products were identified by TLC technique and spectrophotometry from an aliquot portion of sample removed quickly from the solution being electrolyzed. Kieselgel GF\(_{254}\) (Merck) and chloroform were used for the fixed phase and eluent, respectively, in the TLC. The spectrophotometric identification was made by comparing the spectra obtained with a Beckman DK-2A spectrophotometer with the standard spectral data in the literature\(^3\).

Stationary state current-voltage curves (Tafel 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.

**RESULTS**

**Polarization Curve and Reaction Order.** The steady state polarization (i~v) curves obtained for the reduction of nitrobenzene in the solutions of varying pH by galvanostatic method are presented in Fig. 1. The polarization curves with increasing current were close to those with decreasing current.

The current (i) at a fixed potential was observed to be independent of concentration of nitrobenzene (\(\phi\text{NO}_2\)) in each solution down to the lowest concentration used, that is,

\[
\frac{\partial \log i}{\partial \log (\phi\text{NO}_2)}|_{E, \theta} = 0
\]

![Fig 1. Steady-state Polarization curve. The Tafel slopes are indicated in mV.](image)

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The Tafel slopes, \(-\frac{\partial E}{\partial \log i}\) are varied as indicated in mV in the figure.

\textbf{pH Dependence.} Figs. 1 and 2 show that the polarization curves are varied in various pH ranges. As presented in Fig. 2 the pH dependence of current at constant potential, \((\log i/\partial \text{pH})_E\), was observed to be -2 in basic solution and was zero in acidic solution. The pH's of the electrolyte solutions were measured before and after each experiment and were found to be unaltered by the electrolysis for those solutions presented in Fig. 2.

\textbf{Reduction Kinetics of Nitrobenzene Derivatives.} The steady state current-voltage (i vs. v) curves of nitrobenzene and the chemically synthesized nitrosobenzene and phenylhydroxylamine are shown in Fig. 3 and 4. In basic solutions the Tafel slope for the reduction of nitrosobenzene was obtained to be 60 mV, and was similar to that for the second step in reduction of nitrobenzene. In acidic solutions the Tafel slope is 110 mV for phenylhydroxylamine and 280 mV for nitrosobenzene.

\textbf{Analyses of Products.} Products obtained at various potential and pH were analyzed by TLC technique and spectrophotometric method. Unambiguous identification was mostly possible by matching positions of the TLC spots against those of known reference materials. Confirmation was also made by comparing the uv spectra with the standard spectra in the literature.

The uv absorption at the characteristic wave length for each compound (\(\phi\text{NO}_2: 260 \text{ nm}, \phi\text{NO}:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Steady state polarization curves of 10^{-3}M \phi\text{NO}_2 solutions.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Steady state polarization curves for the derivatives of nitrobenzene in acidic solution of pH 1.90. \(\bigcirc: 10^{-3}M \phi\text{NO}_2\), \(\triangle: 10^{-4}M \phi\text{NO}\), \(\times: 10^{-4}M \phi\text{NH}_2\).}
\end{figure}
305 nm,  \( \phi \text{NHOH} \): 237 nm, \( \phi \text{NH}_2 \): 286 nm) was measured to determine the concentration. Yields of the product compounds (as the mole ratio of the products to nitrobenzene) were calculated from the spectrophotometrically determined concentrations.

In acidic solutions reduction products of nitrobenzene were phenylhydroxylamine and aniline; no nitrosobenzene was found in the solution. When solutions of nitrosobenzene or phenylhydroxylamine were reduced aniline was produced in the Tafel region of each solution (see Fig. 3).

Under the chemical\(^6\) or electrochemical\(^1,16,18\) reaction conditions that have been reported in the literature, nitrosobenzene could not be obtained by direct reduction of nitrobenzene.

**Table 1.** Yield\(^*\) of products in reduction of \( \phi \text{NO}_2 \) in 0.036 M \( \text{H}_2\text{SO}_4 \) %.

<table>
<thead>
<tr>
<th>Product</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi \text{N}^+\text{H}_2\text{OH} )</td>
<td>-800 mV</td>
</tr>
<tr>
<td>( \phi \text{N}^+\text{H}_3^+ )</td>
<td>26</td>
</tr>
</tbody>
</table>

\( * \) Percentage to total products and reactant.

\( * , ** \) In strongly acidic solutions, \( \phi \text{NHOH} \) and \( \phi \text{NH}_2 \) exist in the form of \( \phi \text{N}^+\text{H}_2\text{OH} \) and \( \phi \text{N}^+\text{H}_3^+ \).

**Table 2.** Yield for production of nitrosobenzene with current Density, 15.4 μA/cm\(^2\).

<table>
<thead>
<tr>
<th>pH</th>
<th>11.55</th>
<th>10.60</th>
<th>9.65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield(%)</td>
<td>41</td>
<td>38</td>
<td>71</td>
</tr>
</tbody>
</table>

Vink, et al.\(^32\) and Peterson, et al.\(^33\) found that nitrobenzene is directly reduced to nitrosobenzene by photochemical method. However, in this experiment nitrosobenzene was produced in basic solutions in the Tafel region. Coupling products such as azobenzene and hydrazobenzene were formed with hydrogen evolution at potentials more negative than -1.5 volts.

In basic solutions the products were determined when the total charge passed was 4 faradays for one mole of nitrobenzene. The yields for the production of nitrosobenzene at various pH values with the current density of 15.4 μA/cm\(^2\) are shown in Table 2. The higher yield was obtained with the lower current density. The yield of product \( \phi \text{NO} \) was larger at lower pH.

**DISCUSSIONS**

**Reaction Mechanism in Acidic Solution.**

The Tafel slope for the reduction of nitrobenzene, 139±10 mV as shown in Fig. 1, suggests a single electron transfer in the rate determining step. In Fig. 2 the pH-dependence seems to be absent, therefore, protons are not involved in the rate determining step. A full coverage of the electrode by adsorbed species can be reason-
ably assumed.

The following mechanism is assumed:

\[ \phi \text{NO}_2 \text{soln} + 2H^+ = \phi \text{N(OH)}_2^{2+} \text{soln} \]
\[ \implies \phi \text{N(OH)}_2^{2+} \text{soln} \]
\[ \phi \text{N(OH)}_2^{2+} \text{soln} + e^- + \phi \text{NO}_2 \text{ads} \]
\[ \implies \phi \text{N(OH)}_2^{2+} \text{ads} \]
\[ \phi \text{N(OH)}_2^{2+} \text{ads} + 3e^- + 3H^+ \]
\[ \implies \phi \text{N}^+ \text{H}_2\text{O} \text{ads} \]
\[ \phi \text{N}^+ \text{H}_2\text{O} \text{ads} \implies \phi \text{N}^+ \text{H}_2\text{O} \text{soln} \]

Sadie, et al. 34 found that the pKa of \( \phi \text{NO}_2 \text{H}_2^{2+} \)
is 5.6 by polarographic experiments. Thus, if pH of the solution is lower than 2.8, \( \phi \text{NO}_2 \text{H}_2^{2+} \) is probably dominant over \( \phi \text{NO}_2 \).

Writing the rate of step (3), \( R_3 = k_3 \theta \exp(-\alpha_3 \phi \text{FE}/RT) \), the current due to the sequence of the above steps becomes

\[ i = 4Rk_3 \theta \exp \left( -\frac{\alpha_3 \phi \text{FE}}{RT} \right) \]

where \( \theta \) is the coverage by \( \phi \text{N(OH)}_2^{2+} \), \( \alpha_3 \) is the transfer coefficient of reaction (3), and \( F \) is the Faraday constant. If \( \theta = 1 \) and \( \alpha_3 \) is considered to be about \( \frac{1}{2} \) as usual, the Tafel slope from equation (5) will be 120 mV, which is close to the observed 130 \( \pm \) 10 mV.

From Fig. 3 and Table 1 the reduction of phenylhydroxylamine seems to go to aniline by an irreversible one electron transfer as the rate determining step.

The fact that no nitroso benzene was found in the solution after the electrolysis of nitrobenzene solution and that the rate of reduction of nitrobenzene is slower than that of nitrobenzene (Fig. 3) indicates that nitrobenzene is not an intermediate in the reduction of nitrobenzene in an acidic solution. Fleishman, et al. 11 also proposed that the intermediate is \( \phi \text{N}^+ \text{O} \) as in the present reaction scheme.

**Reaction Mechanism in Basic Solutions.**

In a basic solution unprotonated species \( \phi \text{NO}_2 \) is probably dominant over the protonated species. Since the rate is independent of \( \phi \text{NO}_2 \) concentration (eqn (1)), the electrode reaction can be reasonably assumed to take place through a strongly adsorbed species \( \phi \text{NO}_2 \text{ads} \).

If the unprotonated species acquire one or two electrons, the reduced species can be immediately protonated. Tafel slope, 30 mV as shown in Fig. 1 (curve III) suggests a reversible two electron transfer. The following mechanism is thus assumed:

\[ [\phi \text{NO}_2] \text{ads} + 2e^- + 2H^+ \]
\[ \implies [\phi \text{N(OH)}_2] \text{ads} + 2OH^- \]
\[ [\phi \text{N(OH)}_2] \text{ads} \rightarrow [\phi \text{NO}] \text{ads} + \text{H}_2\text{O} \]
\[ [\phi \text{NO}] \text{ads} \implies [\phi \text{N}^+ \text{H}_2\text{O}] \text{ads} \]
\[ [\phi \text{N}^+ \text{H}_2\text{O}] \text{ads} \rightarrow \text{further reduction} \rightarrow [\phi \text{NHOH}] \text{ads} \]

The reactions of (7) and (8) are consecutive steps. Since the combined steps (6) and (7) are more strongly potential-dependent than step (8), it may be assumed that at more negative potentials the production of \( \phi \text{NO} \) is faster than its further reduction while at less negative potentials \( \phi \text{NO} \) is immediately converted to \( \phi \text{NHOH} \) as soon as it is produced.

In Fig. 4, curve (I) corresponds to reactions (6) and (7); curve (II) to reaction (8). It is to be noted that the two curves merge at more negative potentials. At less negative potentials than the crossed point between curve (I) and (II) in Fig. 4 phenylhydroxylamine was the main product.

The following relations are obtained from equations (6) and (7):

\[ \theta_{\phi \text{N(OH)}_2} = k_2 \theta_{\phi \text{NO}_2} \frac{1}{(\text{OH})^2} \exp \left( -\frac{2FE}{RT} \right) \]

\[ R_3 = k_3 \theta_{\phi \text{N(OH)}_2} \]
\[ = k_3 \theta_{\phi \text{NO}_2} \frac{1}{(\text{OH})^2} \exp \left( -\frac{2FE}{RT} \right) \]
Results of adsorption studies on various metal electrodes by Bockris, et al. indicate that the adsorption of organic molecules is more favorable than water near the potential of zero charge. If $\theta_{NCO}=1$ and $\theta_{SOH}=0$, equation (10) is

$$R_1=K_2\frac{1}{(OH)^+2} \exp \left\{ -\frac{2FE}{RT} \right\}$$

Thus, the current for the production of $\phi$NO is

$$i=2FK_2k_2\frac{1}{(OH)^+2} \exp \left\{ -\frac{2FE}{RT} \right\}$$  \tag{11}

With $T=298^\circ K$, equation (11) is rewritten in the logarithmic form

$$\log i = \log(\text{const.}) - 2\text{pH} - \frac{2}{0.0592} E$$

The Tafel slope and pH dependence of current, $(\partial\log i/\partial\text{pH})_E$, will be 30 mV and $\sim 2$ respectively. The observed values in Fig. 2 (lower parts of the three curves) are in good agreement with this prediction.

The reduction of nitrosoaniline to phenylhydroxylamine is assumed to take place through the following steps.

$$\phi(NO)_{sb} + e^- + H_2O \rightleftharpoons (\phi$NOH)$_{sb} + OH^-$$  \tag{12}

$$\phi(NOH)$_{sb} + H_2O \rightarrow (\phi$NOH)$_{sb} + OH^-$$  \tag{13}

$$\phi$NOH$_{sb} + (\phi$NOH)$_{sb} \rightarrow (\phi$N=\phi)$_{sb} + H_2O$$  \tag{14}

The reactions (13) and (14) are competitive, but reaction (14) is considered to be prevalent at higher coverage of $(\phi$NOH)$_{sb}$, while at low coverage reaction (13) will be favored. The relation between the relative coverage by $\phi$NO($\theta_{NCO}$) and by $\phi$SOH will be

$$\theta_{NCO} = K_1\frac{1}{(OH)^+} \exp \left\{ -\frac{FE}{RT} \right\}$$  \tag{16}

The rates are then,

$$R_{13} = K_2k_3\frac{1}{(OH)^+} \exp \left\{ -\frac{FE}{RT} \right\}$$  \tag{17}

$$R_{14} = k_4(\theta_{SOH})^2$$  \tag{18}

At moderate potential it may be assumed that $\theta_{NCO}=1$ and $\theta_{SOH}=0$, and unless supply of proton donor is limited $R_{13} \gg R_{14}$. Thus, the current for the production of $\phi$NOH is

$$i=2FK_2k_{13}\frac{1}{(OH)^+} \exp \left\{ -\frac{FE}{RT} \right\}$$

This equation is rewritten in the logarithmic form,

$$\log i = \log(\text{const.}) - \text{pH} - \frac{E}{0.0592}$$

This equation predicts a Tafel slope of 59.2 mV and $(\partial\log i/\partial\text{pH})=-1$. The observed values in Fig. 2 (upper parts of the three curves) are in agreement with this prediction. The coupling reaction (14) occurs at much higher potential beyond the range of Fig. 2, along with the hydrogen evolution reaction. Therefore, the coupling mechanism could not be confirmed in this experiment. However, contrary to the mechanism proposed by Fleischman, direct condensation of $\phi$NO with $\phi$NOH was not observed, either during the reduction of $\phi$NO at potentials in the Tafel region or in the mixture of $\phi$NO and $\phi$NOH in basic solutions with pH $\leq 12$.

**Effect of Substituents.** Some preliminary kinetic measurements for the electrochemical reduction of substituted nitrobenzenes were made and further studies are under way.

The substituted nitrobenzenes are found to be reduced in a similar manner in basic solutions to that for the unsubstituted reactant, but at
different rates. The effect of the substituents seemed to generally follow the Hammett relation with a negative \( \rho \). The negative \( \rho \) indicates that substituted nitrobenzenes also follow the mechanism for the unsubstituted nitrobenzene (reactions (6) and (7)) in basic solution.

The mechanism can be rewritten in a generalized form for the substituted nitrobenzenes,

\[
\begin{align*}
\text{X} + 2e^- + 2H^+ & \rightarrow [\text{X}^-]_\text{ads} \quad \text{(20)} \\
\text{X}^{-} + H_2O & \rightarrow [\text{X}OH]_\text{ads} + H^+ \\
\end{align*}
\]

If reaction (20) is a rate-determining dehydration step it will have a negative \( \rho \) value in the the Hammett equation \( \log\left(\frac{k}{k_0}\right) = \rho \alpha \), while reaction (19) has to hold a positive \( \rho \) value. The observed negative \( \rho \) value supports the assumed mechanism.

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