# COMMUNICATIONS

## LETTERS

# Electrochemical Formation of the Dianion-Salt of Nitrobenzene in Aprotic Solvent.

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During the past two decades the electrochemical reduction of nitrobenzene in aprotic solvent such as acetonitrile and dimethylformamide has received considerable attention.[1-6] In previous papers[7,8] we reported studies on the reduction mechanism of nitrobenzene at a lead electrode in ethanol-water mixture solvent. Based on kinetic evidence, $C_6H_5N(OH)_2$ was proposed as an intermediate in the first reduction step of the reaction in which nitrobenzene is reduced to nitrosobenzene. To support the assumption of $C_6H_5N(OH)_2$ as an intermediate the reduction on nitrobenzene was carried out in dry $CH_3CN$ with excess $NaClO_4$ as electrolyte. A reddish brown salt was produced, whose formular seems to be $C_6H_5N(ONa)_2$.

Although existence of radical anion and dianion of nitrobenzene have been assumed,[9,10] the radical anion is
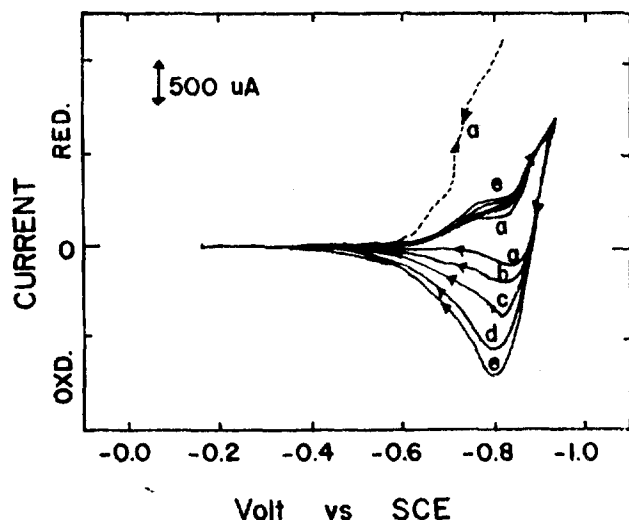


**Figure 1.** Cyclic voltammograms of $10^{-3}M$ $C_6H_5NO_2$ in unstirred (solid line) and stirred (dashed line) solution. Scan rates were 5 mV/sec.(a), 10 mV/sec.(b), 20 mV/sec.(c), 50 mV/sec. (d) and 100 mV/sec. (e). Electrolyte/Solvent: $0.1M$ $Et_4NCl/CH_3CN$
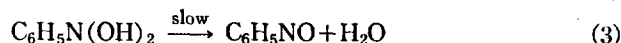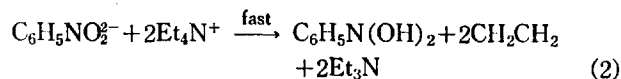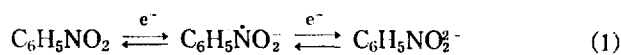
confirmed to be stable in aprotic solvents by the combined experiments of electron spin resonance spectroscopy and polarography.

In this paper, we report more evidences for the dianion $(C_6H_5NO_2^{2-})$ and its salt $(C_6H_5N(ONa)_2)$. The evidences were obtained from cyclic voltammetry with platinum wire or mesh as working electrode and from various analytical data.

The cyclic voltammograms of nitrobenzene in $0.1M$ $Et_4NCl\text{-}CH_3CN$ were obtained with various scan rates and are shown in Figure 1.

There are two waves in the reduction side in both stirred and unstirred solutions, while a single oxidation wave was obtained in the unstirred solution only. The two reduction waves are due to two consecutive reduction steps.

If $C_6H_5NO_2^{2-}$ is produced by reversible charge transfer reactions such as equation (1), which is followed by chemical reactions (2) and (3), anodic peak current in cyclic voltammogram is expected to decrease with decreasing scan rate since the oxidizable $C_6H_5N(OH)_2$ is consumed by the chemical step (3), while cathodic peak current is hardly changed as in Figure 1.

$$C_6H_5NO_2 \xrightleftharpoons{e^-} C_6H_5\dot{N}O_2^- \xrightleftharpoons{e^-} C_6H_5NO_2^{2-} \qquad (1)$$

$$C_6H_5NO_2^{2-}+2Et_4N^+ \xrightarrow{fast} C_6H_5N(OH)_2+2CH_2CH_2 +2Et_3N \qquad (2)$$

$$C_6H_5N(OH)_2 \xrightarrow{slow} C_6H_5NO+H_2O \qquad (3)$$

The dianion of nitrobenzene is beleived to be basic species strong enough to substract hydrogens from the ethyl groups in $Et_4NCl$ to produce ethylene gas.[11] If $H_2O$ is produced by reaction (3) during electrolysis, acetonitrile is presumably decomposed through equation (4).

$$CH_3CN \xrightarrow{H_2O} CH_3\overset{\overset{\displaystyle O}{\|}}{C}NH_2 \xrightarrow{H_2O} CH_3COOH+NH_3 \qquad (4)$$
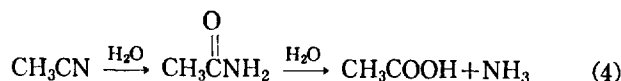
In fact, among the gases which evolved during electrolysis at the potential region of the second reduction wave, $NH_3$

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and $C_2H_4$ were detected. The ammonia thus liberated was converted into ammonium chloride in HCl solution and was identified by IR spectrum of the salt and its melting point. However, these were not detected at the potential region of the first reduction wave.

When $Na^+$ ions were present in excess instead of $Et_4N^+$, nitrobenzene could be reduced and isolated as a disodium salt rather than $C_6H_5N(OH)_2$ via dianion formation (equation (1)) followed by reaction (5).

$$C_6H_5NO_2^{2-} + 2Na^+ \rightleftharpoons C_6H_5N(ONa)_2 \qquad (5)$$
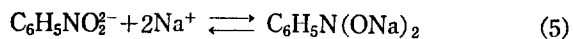
Both $C_6H_5NO_2^{2-}$ and $C_6H_5N(ONa)_2$ are supposed to be oxidizable species but disodium salt ($C_6H_5N(ONa)_2$) could be easily separated, without further reduction or reoxidation back to nitrobenzene, due to its small solubility.

The cyclic voltammograms of nitrobenzene in the stirred solution of $0.1M$ $NaClO_4/CH_3CN$ are given in Figure 2. Two waves in both the reduction and oxidation sides were obtained only when the potential was scanned downward to the second reduction step.

Furthermore, reduction product of nitrobenzene in $1M$ $NaClO_4/CH_3CN$ was isolated as a reddish brown solid, whose conductivity in DMSO solution was larger than that of pure DMSO by a factor fo $10^3$ when the concentration was about $0.1g/ml$. The product decomposed at about $300°C$, was soluble in water and insoluble in organic solvents such as $CH_3CN$, DMF, THF, alcohol and ether. After a small amount of the product was dissolved in air-saturated water, the UV-spectrum of the solution was similar that of nitrobenzene. And the ratio of Na to $C_6H_5NO_2$ in the solution was analyzed to be 1.92.

Therefore the chemical formular of the product seems to be $C_6H_5N(ONa)_2$, which could be oxidized by oxygen through equation (6).

$$C_6H_5N(ONa)_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow C_6H_5NO_2 + 2NaOH$$
$$(6)$$
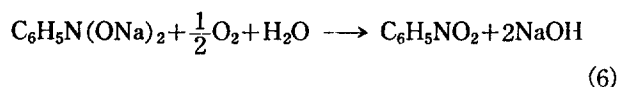
When a large amount of the product was dissolved in oxy-
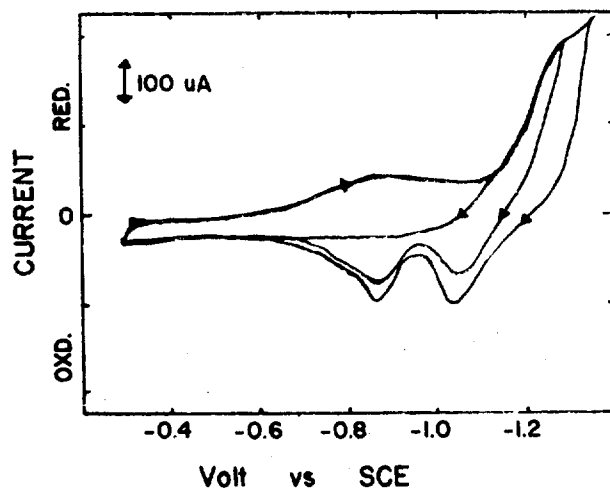


**Figure 2.** Cyclic voltammogram of $10^{-3}M$ $C_6H_5NO_2$ in stirred solution. Scan rate: 20 mV/sec., Electrolyte/Solvent: $0.1M$ $NaClO_4/CH_3CH$

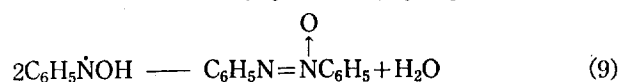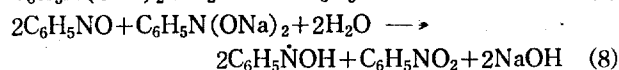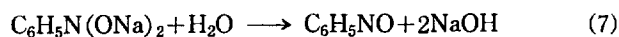**TABLE 1: Mass Spectral Data of $C_6H_5NO_2$ and its Reduction Product ($C_6H_5N(ONa)_2$)**

| M/e | Probable Fragment | Relative Intensity | | |
|---|---|---|---|---|
| | | $C_6H_5NO_2$ | Reduction Product | |
| | | | Fresh | Aged Sample |
| 17, 18 | OH, $H_2O$ | * | * | ** |
| 28 | $N_2$ | * | ** | |
| 30 | NO | 10 | ≠ | ≠ |
| 51 | $C_4H_3$ | 45 | | |
| 65 | $C_5H_5$ | 14 | 50 | 7 |
| 77 | $C_6H_5$ | 100 | 26 | 20 |
| 93 | $C_6H_5O$ | 17 | 100 | 100 |
| 107 | $C_6H_5NO$ | 5 | 10 | 21 |
| 123 | $C_6H_5NO_2$ | 55 | | 13 |
| 134 | | | | 12 |
| 169 | | | | 13 |
| 170 | | | | 9 |
| 182 | Azobenzene | | | 12 |
| 198 | Azoxybenzene | | | 14 |

*background, **much higher than background, ≠complex spectra at the of M/e=30–60

gen-free water, solid azoxy benzene and oily nitrobenzene were readily separated from water solution, while only nitrobenzene is separated in air-saturated water. Based on the above facts, it is seen that $C_6H_5N(ONa)_2$ in oxygen-free water is changed to $C_6H_5NO$ through equation (7).

If $C_6H_5NO_2^{2-}$ and $C_6H_5N(ONa)_2$ are more oxidizable species than $C_6H_5NO$, $C_6H_5NO$ could be reduced to $C_6H_5\dot{N}OH$ by $C_6H_5N(ONa)_2$ (equation(8) ).

And the reduced radical, $C_6H_5\dot{N}OH$, seems to be easily coupled by equation (9).

$$C_6H_5N(ONa)_2 + H_2O \longrightarrow C_6H_5NO + 2NaOH \qquad (7)$$
$$2C_6H_5NO + C_6H_5N(ONa)_2 + 2H_2O \longrightarrow$$
$$2C_6H_5\dot{N}OH + C_6H_5NO_2 + 2NaOH \qquad (8)$$
$$2C_6H_5\dot{N}OH \overset{O}{\underset{\uparrow}{\rule{2cm}{0.4pt}}} C_6H_5N = NC_6H_5 + H_2O \qquad (9)$$

When $KClO_4$ was used instead of $NaClO_4$ as the supporting electrolyte, $C_6H_5N(OK)_2$ was produced whose chemical behaviour was observed to be similar to the of $C_6H_5N(ONa)_2$ mentioned above. A reduction product of p-$CH_3O(C_6H_4)$-$NO_2$, had similar reactivity toward water and oxygen.

The mass spectral data of nitrobenzene and its reduction product are compared in Table 1. To confirm the existence of $C_6H_5(ONa)_2$ and its reactions a portion of the reduction product was removed from the cell and was immediately placed in the sample chamber of mass spectrometer. Another portion was put under the same condition of the mass spectrometer after being aged in a dessicator for two days. The data presented in Table 1, suggest that the reduction product $C_6H_5N(ONa)_2$ readily changes to nitrobenzene and a coupled compound such as azo-or azoxy-benzene.

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