

Studies in Chronopotentiometric Behaviour of Nitrobenzene

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The chronopotentiometric study of nitrobenzene in citrate buffer of varying pH (3.80-5.05) has shown that the initial reduction product is β -phenylhydroxylamine. The reduction characteristics of this compound is pH dependent. While further reduction of this product occurs readily at lower pH value, it becomes more difficult as the pH increases. The current reversal chronopotentiometry shows the oxidation step of β -phenylhydroxylamine and thus provides a method of identifying the compound near the electrode surface. It is noticed that the value of $t_0\tau^{1/2}/c$ of the second reduction step decreases, when the transition time of the first wave is below a particular value, the time depending on the pH. At pH 4.52 it is 20 sec. An explanation is offered to account for these observations.

It is well established that nitrobenzene gets reduced at a mercury electrode surface by an initial step of four electrons at all pH values giving β -phenylhydroxylamine and it is further reduced in acid solutions (pH < 4) by a second step involving two electrons to give aniline¹. Nitrosobenzene gets reduced by an initial step of two electrons at pH in the range 1-9. In acid solutions, this also gets reduced further by a two electron step, the products being identical with that of nitrobenzene^{2,3}. Direct determination of the polarographic behaviour of β -phenylhydroxylamine confirm these findings in general^{2,4-6}. β -Phenylhydroxylamine can be oxidized to nitrosobenzene over a wide range pH values. In acid medium, it can be reduced to aniline.

The reducibility of β -phenylhydroxylamine in acid medium is generally attributed to the formation of salt $\text{PhN}^+\text{H}_2\text{OH}^7$. The pK value of the salt is given by various authors as 3.2⁸, 4.5⁴, 2.25⁵ and 1.86⁶. The variation of the half-wave potentials of the reduction step with pH has been explained severally. While Heyrovsky *et al.*⁵ suggest the formation of $\text{PhN}^+\text{H}_2\text{OH}_2^+$, Darchan *et al.*⁶ point out the variation in the reduction characteristics in different buffers of the same pH and explain this as due to the surface activity of the buffer components.

The dc polarogram of nitrobenzene in acetate buffer (pH 4.7) does not show the second step. But the electrolysis of this solution at a constant potential of -0.6 V (vs SCE) takes up four electrons and this reduced solution is further reducible as shown¹ by the second polarographic wave at about -0.8 V. Further electrolysis of the solution at -0.9 V uses up two more electrons for the reduction. Electrolysis of the nitrobenzene solution at a constant potential of -0.9 V directly takes up six electrons and yields a product which is not further reducible¹.

In order to understand this peculiar behaviour of the second reduction step extensive study of the oxidation and reduction characteristics of β -phenyl-

hydroxylamine is not very convenient because of the low stability of the compound. A study of the reduction properties of the product formed during the constant current reduction of nitrobenzene making use of direct and current reversal chronopotentiometry has now been undertaken and the results are presented in this paper.

Materials and Methods

Apparatus—The manual set-up used for the dc polarograms is described earlier¹. A set-up for the direct and current reversal chronopotentiometry, essentially similar to that described by Gaske⁹, was employed and is described below.

A constant current source consisted of a 90 V Eveready battery No. 700 D having in series a set of high resistances (22 K Ω to 1 M Ω), a selector switch and a milli/microammeter. The current used varied from 2 mA to 90 μ A. A cell was connected in series with the ammeter through a DPDT switch to facilitate current reversal in the cell during electrolysis without disturbing the current in other parts of the circuit. The cell consisted of a cylindrical tube of uniform internal diameter (2 cm), siliconized to prevent wetting of the surface and creeping of the solution between the wall of the tube and the mercury pool. A layer of mercury at the bottom of the tube served as the working electrode. A platinum plate electrode served as the counter electrode. SCE connected to the cell through an agar bridge was used as the reference electrode. An inlet tube facilitated bubbling of inert gas and also served to add mercury. A water seal served as pressure release while separating the test solution from outside. The constant current source was connected between the mercury pool and platinum plate electrode. The potential of mercury pool w.r.t. SCE was monitored continuously on a high impedance x - y recorder (Carl Zeiss).

The sample solution in the cell (fitted with electrodes, inlet tubes and water seal) was deaerated with an inert gas; pure and dry mercury was

added *in situ* before the chronopotentiogram was recorded.

All the measurements were made in a thermostat at $30 \pm 0.1^\circ$.

Solutions — Nitrobenzene was purified by distillation and fraction distilling at $202^\circ/680$ mm was used. A stock solution of 25 mM was prepared in ethanol purified as described earlier¹. A stock solution of citrate buffer was prepared having a final concentration of total citric acid 0.5M and the requisite quantity of sodium hydroxide solution. This stock buffer was diluted $2\frac{1}{2}$ times with water and the pH measured. This is the nominal pH. The electrolytic experiments were carried out in solutions prepared by mixing 40% of this buffer, 50% ethanol and requisite volumes of depolarizer and sodium perchlorate stock solutions.

Results

Chronopotentiograms of nitrobenzene at various current densities — Chronopotentiograms were obtained with varying transition times (4-60 sec) by choosing suitable current densities. In favourable cases a second step was noticed. The results are presented in Table 1. In all the cases, the value of $i_0\tau_1^{1/2}/c$ for the first step was found to be a constant, the average value being $7.95 \text{ mA mole}^{-1} \text{ sec}^{-1/2}$. The calculated value on the basis of Sands equation using $D=5.6 \times 10^{-6} \text{ cm}^2/\text{sec}$ (from McBain-Dawson cell method¹) is 7.90 ± 0.22 . The potential corresponding to $\tau_1/4$ is reasonably constant.

In cases where the second step appears, the transition time (τ_{sec})¹⁰ for the second step, if it were not preceded by any other reduction step¹⁰, has been calculated from experimental results and the values are recorded in Table 1. For a two electron process the value of $i_0\tau_{\text{sec}}^{1/2}/c$ should be

$3.95 \approx 4$. In solutions of pH 4.2 and over, the second wave was observed in chronopotentiogram traced with all current densities and the transition time for this step corresponded to two-electron reduction. At pH 4.52, the second step appeared in all the cases. When the experimental conditions were so chosen as to give large transition time, this step corresponded to two electrons. When transition times were small, the second step was less than that expected for a two-electron step. Fig. 1 shows that $i_0\tau_{\text{sec}}^{1/2}/c$ falls off for $\tau_1 < 22.1$ sec. At pH 4.73, the transition times corresponding to the second step (τ_{sec}) was invariably less than that expected for a two-electron step. At pH 5.05 the second step does not appear at all over a wide range of variation of τ_1 values (from $\tau_1=4.5$ to 90 sec). In other buffers of pH value 4.4 to 4.7 the behaviour was found to be similar to that in

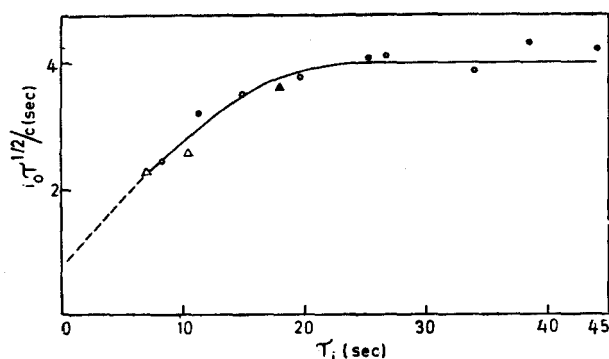


Fig. 1 — Plot of $i_0\tau_{\text{sec}}^{1/2}/c$ vs τ_1 from chronopotentiograms of nitrobenzene in citrate buffer of pH 4.52 at different concentrations and current densities [Concentration of nitrobenzene: 1.488 mM (closed circles); 0.975 mM (open circles); 0.812 mM (open triangles); and 0.487 mM (closed triangles)]

TABLE 1 — CHRONOPOTENTIOMETRIC CHARACTERISTICS OF NITROBENZENE SOLUTIONS

[Citrate buffer — pH range 3.5 to 5.0; ethanol conc. 50%; ionic strength 0.5M (NaClO₄)]

pH	Conc. of PhNO ₂ (mM)	i_0 (A dm ⁻²)	τ_1 (sec)	$i_0\tau_1^{1/2}/c$ (mA mol ⁻¹ sec ^{1/2})	($E_{\tau/4}$) (V vs SCE)	τ_{sec} (sec)	$i_0\tau_{\text{sec}}^{1/2}/c$ (mA cm sec ^{1/2} mol ⁻¹)	($E_{\tau/4}$) ₂ (V vs SCE)
4.20	0.992	1.21	41.67	7.85	-0.60	10.74	3.98	-0.94
4.20	0.992	1.56	27.56	7.92	-0.62	6.55	3.86	-0.96
4.20	0.992	1.63	20.26	7.42	-0.63	6.01	4.04	-0.96
4.52	1.488	1.81	43.97	8.06	-0.61	12.10	4.23	-0.95
4.52	1.488	3.30	11.37	7.47	-0.62	2.12	3.22	-0.98
4.52	0.975	1.57	26.76	8.34	-0.62	6.54	4.12	-0.95
4.52	0.975	2.05	14.92	8.11	-0.62	2.83	3.53	-0.98
4.52	0.975	2.58	8.16	7.57	-0.62	0.86	2.46	-0.97
4.52	0.812	2.08	10.41	8.23	-0.59	1.02	2.58	-0.95
4.52	0.812	2.39	6.98	7.78	-0.62	0.56	2.21	-0.97
4.52	0.487	0.88	17.94	7.68	-0.59	3.97	3.61	-0.95
4.67	0.992	1.02	59.66	7.96	-0.63	15.74	4.09	-0.96
4.67	0.992	1.22	43.29	8.07	-0.62	6.51	3.15	-0.98
4.67	0.992	1.55	23.84	7.63	-0.62	3.59	2.96	-0.96
5.05	0.992	0.83	95.13	8.19	-0.60			
5.05	0.992	1.03	59.90	8.02	-0.62			
5.05	0.992	1.33	35.37	7.99	-0.62			
5.05	0.992	1.41	31.81	8.03	-0.62			
5.05	0.992	1.72	21.08	7.98	-0.63			
5.05	0.992	2.05	15.45	8.11	-0.64			
5.05	0.992	2.95	7.23	8.00	-0.66			
5.05	0.992	3.41	4.46	7.26	-0.67			

Second wave is not defined at pH 5.05

TABLE 2 — EFFECT OF THE TRANSITION TIME OF THE FIRST WAVE ON THE VALUE OF $i_0\tau_{sec}^{1/2}/c$ FOR THE SECOND WAVE

pH	$i_0\tau_{sec}^{1/2}/c = 4$ for	pH	$i_0\tau_{sec}^{1/2}/c = 4$ for
3.80	All values of τ_1	4.67	$\tau_1 > 55$ sec
4.20	do	4.73	$\tau_1 > 68$ sec
4.47	$\tau_1 > 11$ sec	5.05	Second wave does not appear for any value
4.52	$\tau_1 > 22.1$ sec		$\tau_1 < 60$ sec

solution of pH 4.52. Curves similar to that shown in Fig. 1 were drawn in three other buffer solutions and the results are given in Table 2.

Current reversal chronopotentiograms of nitrobenzene at various current densities — In the current reversal experiments, only one oxidation step was noticed and this corresponded to the oxidation of β -phenylhydroxylamine to nitrosobenzene. In no case the oxidation of aniline was noticed. When the current was reversed at the last stages of second reduction, no oxidation was noticed showing that no β -phenylhydroxylamine was still left near the electrode. When the current was reversed at the beginning of the reduction step, the oxidation wave indicated that some β -phenylhydroxylamine was still present near the electrode. When the current was reversed at any stage of the first reduction step, the oxidation step was observed. Typical results for the reoxidation case are shown in Table 3.

Discussion

Nature of the reduction process — The values of $i_0\tau_1^{1/2}/c$ in the pH range 4.2-5.05 indicate that the

first reduction step represents diffusion-controlled four-electron reduction, corresponding to the reduction $-\text{NO}_2 \rightarrow -\text{NHOH}$. When the current is reversed at an intermediate point on the first wave of the chronopotentiogram, the transition time for the reverse step is 1/8th of the forward step¹⁰ indicating that phenylhydroxylamine is oxidized to nitrosobenzene (Table 3). The position of the oxidation step confirms the same. Table 3 also shows that the β -phenylhydroxylamine is available for reoxidation in a solution of pH 5 for as long as 85 sec.

The dc polarographic work has identified the first step as a four-electron reduction to β -phenylhydroxylamine. The ratio of the height of the second wave to first wave varies from 0.4 to practically zero in the pH range 2 to 5. It is quite likely that there might be two species of β -phenylhydroxylamine formed in equilibrium with each other at the electrode surface, the proportion of the two varying with $\text{pH}^{2,4,7}$. However, coulometric analysis with mercury pool cathode indicates that the second step uses two electrons possibly due to the fact that the mercury pool electrode where the time of electrolysis is large (30 min to 1 hr as compared to about 4 sec in the d.m.e.) affords enough time for the transformation and thus the second reduction also goes to completion¹. This explains the lower values of $i_0\tau_{sec}^{1/2}/c$ which in turn further indicate that part of β -phenylhydroxylamine is not in a reducible form and escapes reduction.

The current reversal chronopotentiometric experiments corresponding to the first wave indicate that the ratio of τ_b/τ_f is nearly 0.125 indicating that the β -phenylhydroxylamine is completely oxidized in one-step, whatever the time of electrolysis and no indication is available for two forms of the

TABLE 3 — EFFECT OF CURRENT REVERSAL AT DIFFERENT STAGES OF REDUCTION IN THE CASE OF THE FIRST CHRONOPOTENTIOMETRIC WAVE

pH	Conc. of [PhNO ₂] (mM)	i_0 (A dm ⁻²)	τ_f^* (sec)	τ_b (sec)	τ_b/τ_f	E_{ox} (V vs SCE)
5.05	0.992	0.93	85.76	11.28	0.1315	+0.01
5.05	0.992	0.93	55.84	7.04	0.1260	+0.01
4.73	0.446	1.195	14.22	1.80	0.1266	+0.05
4.73	0.446	1.195	10.80	1.24	0.1148	+0.05
4.52	0.992	1.216	52.52	5.58	0.1061	+0.025
4.52	0.992	1.216	41.22	4.51	0.1094	+0.021
4.52	0.992	1.216	32.03	3.32	0.1035	+0.024
4.52	0.992	1.56	31.02	3.22	0.1038	+0.021
4.52	0.992	1.56	22.99	2.68	0.1166	+0.022
4.52	0.992	2.07	21.20	2.19	0.103	+0.036
4.52	0.992	2.07	17.01	2.22	0.1305	+0.025
4.52	0.992	2.97	10.48	1.27	0.121	+0.049
4.52	0.992	2.97	4.83	0.62	0.128	+0.06
4.52	0.992	3.70	2.30	0.29	0.132	+0.06
4.52	0.992	4.61	3.70	0.40	0.109	+0.05
4.52	0.794	1.57	19.42	2.4	0.124	+0.03
4.52	0.794	2.07	6.35	0.82	0.129	+0.04
3.76	0.992	0.82	96.45	12.99	0.135	+0.10
3.76	0.992	1.06	90.35	10.26	0.114	+0.10
3.76	0.992	1.46	24.32	3.00	0.123	+0.11
3.76	0.992	2.20	16.78	1.98	0.118	+0.12

*Current was reversed interrupting the first reduction step.

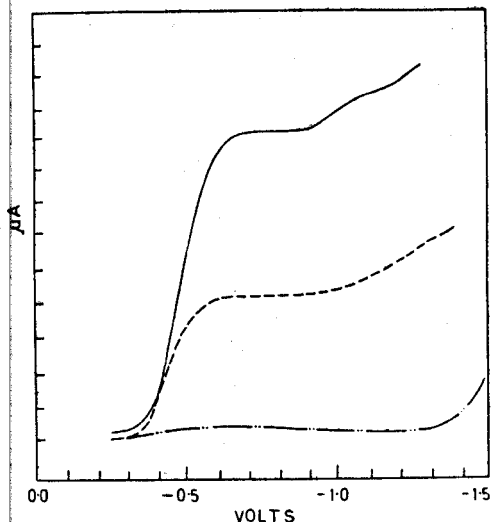
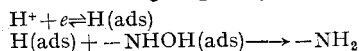


Fig. 2 — Polarograms of nitrobenzene in citrate buffer of pH 4.52 [Conc. of nitrobenzene: 1.488 mM (continuous curve), scale 5.9 div/ μ A; 0.1984 mM (dashed curve), scale 25.4 div/ μ A; and blank (dot dashed curve)]

compound. It is quite likely that one possible explanation of this anomaly is that the two processes, namely oxidation to nitrosobenzene and reduction to aniline follow two different mechanisms. As Pearson⁷ has pointed out, the primary electrode reaction is the reversible deposition of the hydrogen ions on the cathode. These atoms take part in the reduction and as these are removed in the reaction, fresh hydrogen atoms are formed by the electrode reaction. It is quite possible that in addition to the conversion to a more easily reducible form, one has to take into consideration the proper orientation of $-NHOH$ at the electrode surface. The reduction of $-NHOH$ group may be proceeding as:



At higher pH values $H(ads)$ is quite small so that reaction hardly takes place. In the intermediate pH range, possibly proper orientation is needed

and this is time dependent. This explains why at intermediate pH range the value of $i_0 \tau_{sec}^{1/2}/c$ decreases at high current densities, as there is not enough time for proper orientation at the electrode surface to make reduction possible.

Heyrovsky⁵ employing fast current reversals using Kalousek switch established that the oxidation never took place whatever the frequency indicating the irreversibility of the second step. Current reversal chronopotentiometry being reported presently also does not give any indication of oxidation.

The polarograms of nitrobenzene (Fig. 2) taken at two concentrations of nitrobenzene (0.1984 mM and 1.483 mM) in citrate buffers of the same pH indicate that the diffusion current constant of the second wave is higher in 1.483 mM solutions than in 0.1984 mM solutions. It therefore appears that the concentration of the depolarizer might also have something to do with the magnitude of the second polarographic wave representing the reduction of β -phenylhydroxylamine to aniline.

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