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A study of the electrochemical reduction of nitrobenzene to p-aminophenol

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The electrochemical reduction of nitrobenzene has been studied in aqueous organic solvents containing sulphuric acid. It is shown that the yield of *p*-aminophenol and the maximum current density for the reaction is dependent upon the solvent, the cathode metal, the electrode potential, the concentration of acid and the rate of stirring of the catholyte. The changes of products would not be obvious from the *I–E* curves but it is possible to find conditions where the yield of *p*-aminophenol is > 75% at a current density of $150\,\mathrm{mA\,cm^{-2}}$.

1. Introduction

Although the study of the cathodic reduction of aromatic nitrocompounds dates back to the last century [1], these reactions remain of interest for several reasons. Firstly, the electrochemistry of nitrobenzene under various aqueous conditions and including reactions in undivided cells and using pulsed potential control provides possible routes to aniline, nitrosobenzene, phenylhydroxylamine, azoxybenzene, azobenzene, hydrazobenzene, benzidine, *p*-aminophenol and quinone. Several such electrosyntheses have been considered for commercial exploitation and have been the subject of pilot scale studies. Secondly, conclusions concerning reaction mechanisms drawn from electroanalytical experiments are not always consistent with the products of preparative scale electrolyses. Certainly there is no doubt that the products are sensitive to the reaction conditions and the control of the electrolysis to obtain a single product remains a challenge.

In this paper, we report the study of the cathodic reduction of nitrobenzene in acidic aqueous organic media and discuss the effect of various electrolysis parameters of both the *I–E* curves and the products. The objective was to seek conditions where *p*-aminophenol could be isolated in good yield and the electrolysis carried out at high current density.

The literature concerning the reduction of nitrobenzene is extensive but it has been thoroughly reviewed [2–5]. The value of many of the papers, is, however, diminished because the authors did not attempt product analysis or relied on inadequate analytical methods. The most relevant papers to this study are those published by Udupa and co-workers [6, 7] and Rance and Coulson [8].

2. Experimental

2.1. *Instrumentation*

All the electrochemical experiments were carried out with a modified Chemical Electronics Potentiostat. A Chemical Electronics Waveform Generator, type RB1, and a Hewlett-Packard 7015 *x–y* recorder were also used to obtain *I–E* curves. For electrolyses, a home-built electronic integrator was used to measure charge and a Cambridge Instruments ammeter to measure current.

Analysis of products used a Pye 104 gas chromatograph and a Pye Unicam SP600 visible spectrometer. Mass spectra were recorded using an AEI MS 12 or a Kratos MS 30 mass spectrometer.

2.2. *Cells and electrodes*

All experiments were carried out in three electrode cells. To obtain *I–E* curves, the working electrodes were a sitting mercury drop formed on a capillary (the surface area was controlled with a micrometer), a copper wire and a thin strip of lead sheet. For preparative electrolyses, the working electrodes

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were a pool of mercury (area 30 cm^2), a circular copper gauze (area 30 cm^2) or a circular lead foil (area 30 cm^2). The rotating copper electrode had a PTFE sheath. The counter electrodes were platinum wires or gauzes arranged so that as far as possible the working electrodes had equipotential surfaces. The reference electrode was always a Radiometer SCE and it was separated from the working electrodes by a Luggin capillary and tap.

For preparative electrolyses the working electrodes were placed horizontally towards the base of a 250 cm^3 beaker-type cell. The working and counter electrodes were separated by a large area horizontal sinter. The catholyte was stirred with a magnetic stirrer and a stream of nitrogen and it was also protected from the air.

2.3. *Chemicals*

Solutions were prepared directly from organic solvents of the highest purity available but without further purification, distilled water and BDH Ltd Analar sulphuric acid. All solutions were thoroughly degassed with O_2-free nitrogen (BOC Ltd) before the experiment.

Nitrobenzene, aniline, *p*-aminophenol, azoxybenzene were obtained from BDH Ltd.

2.4. *Analysis*

After completion of the electrolysis, the catholyte was neutralized with solid sodium bicarbonate. The sodium sulphate which precipitated was filtered off and washed with ether. The neutral aqueous solution was also extracted three times with ether and the other extracts were combined. Both the aqueous and ether solutions were then analysed by GLC and a colorimetric method.

The GLC analysis was carried out using a 1.5 m OV 17 silicone oil column, temperature programmed between 120 and 240° C. The carrier gas was nitrogen, flow rate 60 cm^3 min^{-1}. The major products were identified and determined by comparison of the retention times and peak areas, respectively, with those of standard solutions of authentic compounds. The identity of major produces was also checked by mass spectroscopy.

The yields of *p*-aminophenol were checked by measuring the absorbance at 400 nm following the formation of the violet complex between *p*-aminophenol and silver [9]. An aliquot of the extract from the electrolysis was added to an excess of silver nitrate and the adsorbance at 400 nm compared to those of a series of standard samples.

3. Results

3.1. *I–E characteristics*

Steady state *I–E* curves were recorded using a point by point technique for solutions of nitrobenzene (50 mM) at a copper cathode in several 50% organic solvent/water mixtures containing sulphuric acid (3 M). In each aqueous organic solution a single reduction wave was obtained; the limiting currents were similar and the half-wave potentials were close to − 0.4 V versus SCE. A typical curve in 50% acetone/water is shown in Fig. 1. The solubility of nitrobenzene in these aqueous organic media varies substantially and in consequence the limiting current densities for saturated solutions of nitrobenzene are markedly solvent-dependent. The solvents used and the maximum limiting current densities are reported in Table 1.

Fig. 1 shows a comparison of the steady state *I–E* curves at copper, lead and mercury cathodes for nitrobenzene (50 mM) in 50% acetone/50%

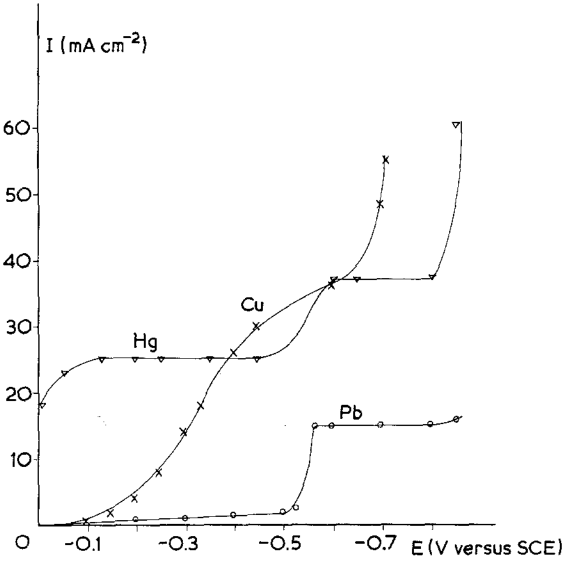


Fig. 1. Steady state *I–E* curves for nitrobenzene (50 mM) in 50% acetone/50% water containing sulphuric acid (3 M) at Cu, Hg, and Pb cathodes.

Table 1. Limiting currents for the reduction of saturated nitrobenzene in 50% organic solvent/50% water mixtures containing sulphuric acid (3 M); copper cathode

	I_L (mA cm^{-2})		I_L (mA cm^{-2})
Acetic acid	560	1,2-ethanediol	110
Acetone	250	Ethanol	320
1,2-dimethoxyethane	470	Methanol	280
Dimethylsulphoxide	160	1-Propanol	800
Dioxan	400		

water containing sulphuric acid. Single reduction processes are observed at copper, $E_{1/2} = -0.38$ V, and at lead, $E_{1/2} = -0.55$ V, but at a mercury cathode the reduction of nitrobenzene occurs in two steps, $E_{1/2} > 0$ and -0.53 V. The limiting currents for the two steps are approximately in the ratio 2 : 1 and the total limiting current is close to that for the single process at copper. Results presented later would lead one to expect that the limiting current density at lead should be the same as that at copper but over most of the potential range the lead surface will be covered with a layer of lead sulphate which may diminish the rate of reduction.

The reaction at copper was studied in more detail. It was shown that the steady state current is proportional to the concentration of nitrobenzene (10^{-2}–5×10^{-1} M) and when the I–E data were replotted as log I versus E, well-defined linear regions with slopes of (170 mV)$^{-1}$ were obtained. Cyclic voltammograms were run for several concentrations of nitrobenzene (1–5 mM) in sulphuric acid (0.1–10 M) and over a range of potential scan rates (0.03–3 V s^{-1}). In all cases a single irreversible reduction peak was observed and under no circumstances was it possible to see oxidation or further reduction peaks for intermediates in the reduction of nitrobenzene although the potential range is restricted by copper dissolution (0.0 V) and hydrogen evolution (− 0.8 V). With more than 1 M sulphuric acid, the peak current and peak potential are independent of the acidity although with less proton the peak potential is shifted to more negative potentials. The peak currents are proportional to the nitrobenzene concentration and to the square root of the potential scan rate and assuming that $n = 6$

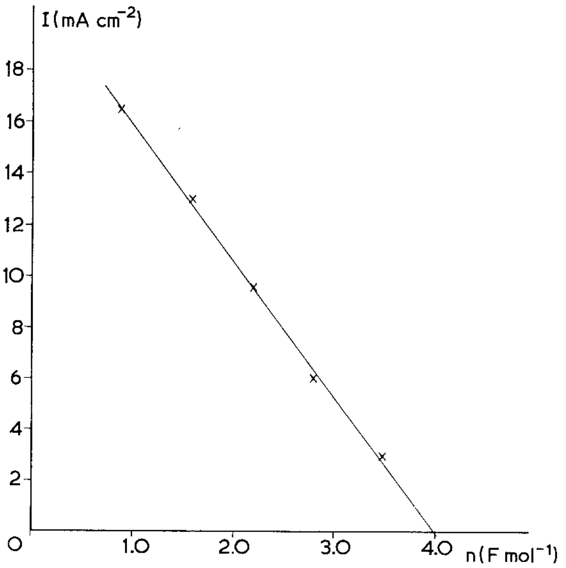


Fig. 2. I–Q plot for the reduction of nitrobenzene (80 mM) in 50% acetone/50% water containing sulphuric acid (3 M); $E = -0.33$ V versus SCE.

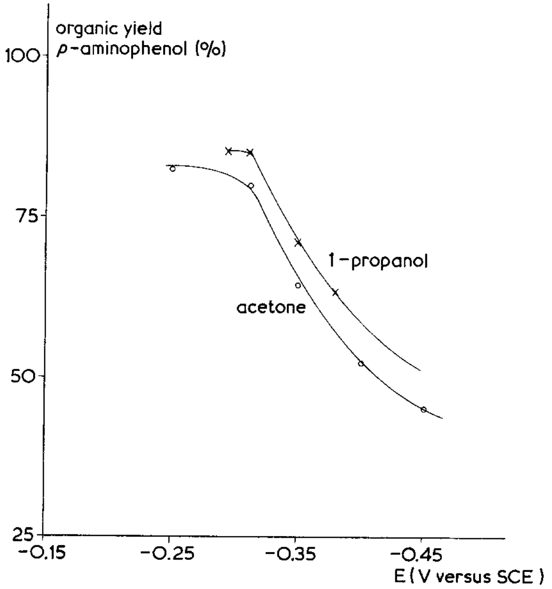


Fig. 3. Yield of p-aminophenol as a function of electrolysis potential. Nitrobenzene (40 mM) in 50% organic solvent/50% water containing sulphuric acid (3 M). × 1-propanol, ○ acetone.

Table 2. Reduction of nitrobenzene (80 mM) in 50% acetone/50% water containing sulphuric acid (3 M). Effect of cathode metal

Cathode	*Potential*	*n*	*Products* (% of $C_6H_5NO_2$ added)		
			p-aminophenol	*Aniline*	*Azoxybenzene*
Cu	−0.30	3.9	81	14	5
	−0.40	4.6	46	29	21
Pb	−0.60	5.3	16	60	16
	−0.85	5.7	15	76	5
Hg	−0.20	4.2	39	29	10
	−0.80	5.7	0	78	13

(see later) the value of the diffusion coefficient calculated from the current function ($I_p/v^{1/2}CA$) and the half-peak width, $E_p - E_{p/2} = 75$ mV, was 0.94×10^{-5} cm^2 s^{-1}. Experiments with a rotating copper electrode also confirmed a mass-transport limited plateau region in the I–E curve ($I/\omega^{1/2}$ indepentent of ω) and a value of 0.88×10^{-5} cm^2 s^{-1} was obtained for the diffusion coefficient from these data.

3.2. *Preparative electrolyses*

A series of controlled potential electrolyses was carried out to determine the effect of various parameters on the yield of *p*-aminophenol. In each case the current was monitored as a function of the charge passed during the electrolysis and *n*, the number of electrons involved in the reduction was determined by extrapolating the I–Q data to zero current; generally the I–Q plot was linear and a typical plot is shown in Fig. 2. When the current had decayed to a low value, the catholyte solution was neutralized and the organic materials were then removed by repeated ether extraction. The ether extract was analysed by GLC and the products were identified and analysed by comparison of the retention times and peak areas with those of authentic samples. The yield of *p*-aminophenol was frequently checked colorimetrically by forming a violet complex between the *p*-aminophenol and silver [9].

Table 3. Electrolysis of nitrobenzene (50 mM) in 50% acetone/50% water containing sulphuric acid. Effect of acidity. Cu cathode, electrode potential — 0.3 V

H_2SO_4 (M)	*Products* (% nitrobenzene added)		
	p-aminophenol	*Azoxybenzene*	*Aniline*
0.3	0	43	52
1.0	45	28	27
3.0	80	12	8

Preliminary experiments were carried out in 50% acetone/50% water to identify the dependence of the products on cathode metal, electrode potential, concentration of sulphuric acid, stirring, temperature and oxygen contamination and the results are summarized in Tables 2–4. It can be seen that the selection of several electrolysis parameters is critical and in all further electrolyses copper was used as the cathode, the concentration of acid was fixed at 3 M and the reactions were carried out in a well stirred (by a stream of N_2 gas and a magnetic stirrer) and oxygen-free solution. While it would be advantageous to use a higher temperature, the design of the experimental cell determined the use of ambient temperature. Table 5 shows the effect of the organic solvent on the yield of *p*-aminophenol and in view of these results and the data in Table 1, later experiments were carried out in acetone or propanol.

Figs. 3 and 4 report the results of a further series of electrolyses at various potentials. It can be seen that the yield of *p*-aminophenol and the ratio of *p*-aminophenol to aniline decreases as the potential is made more negative, but the choice of a more positive potential is at the cost of a lower current density. At a potential where the initial current is about a third of the limiting current for the concentration of nitrobenzene used, the organic yield and the current efficiency are both in excess of 80%.

Table 6 shows the yield of *p*-aminophenol in experiments with much increased initial concentrations of nitrobenzene. The electrolyses were carried out in 1-propanol/water and it can be seen

Table 4. Electrolytic reduction of nitrobenzene (80 mM) in 50% acetone/50% water containing sulphuric acid. Effect of stirring, temperature and oxygen contamination

Electrode	*E*	*Products* (% $C_6H_5NO_2$ added)	*Comments*
Hg	−0.20	*p*-aminophenol (39) aniline (29) azoxybenzene (10)	All O_2 removed
Hg	−0.20	Aniline (20) azoxybenzene (76)	With trace O_2
Cu	−0.33	*p*-aminophenol (80) aniline (8)	Well stirred
Cu	−0.33	*p*-aminophenol (45) aniline (45)	No stirring
Cu	−0.33	*p*-aminophenol (87) aniline (4)	Well stirred, 70° C

that a high organic yield and current efficiency is possible even when the concentration of nitrobenzene is 0.6 M (i.e. saturated).

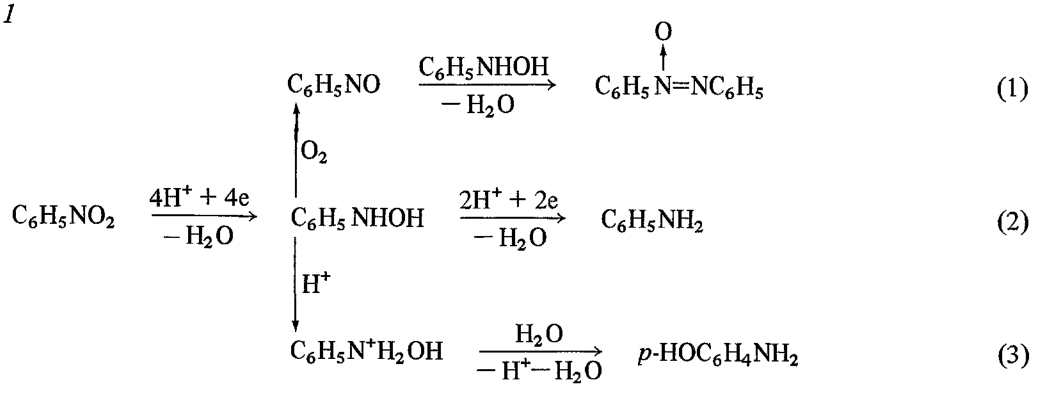
4. Discussion

Many papers have discussed the mechanism of the electrochemical reduction of nitrobenzene in acid solution and, for example, Heyrovsky and coworkers [10, 11] have reported a detailed polarographic investigation of the reaction. The reduction occurs stepwise by successive addition of protons and electrons but under the conditions of this study the reduction is principally a two-step process to phenylhydroxylamine and aniline. When the electrolysis is carried out at a potential where 4e reduction occurs, the products obtained depend on the chemistry of phenylhydroxylamine in the catholyte. In solutions of high acidity the product is *p*-aminophenol formed as a result of nucleophilic attack by water at the *p*-positions of protonated phenylhydroxylamine. The other product normally found is azoxybenzene resulting from partial oxidation of phenylhydroxylamine by trace oxygen in solution or by air during workup.

Certainly the electrolyses carried out during this study have confirmed the necessity of using highly acidic solutions to ensure the protonation of phenylhydroxylamine and to keep the catholyte completely free from oxygen in order to obtain high yields of *p*-aminophenol. It was also noted that an increase in temperature enhanced the yield of *p*-aminophenol presumably by increasing the rate of the rearrangement.

It can be seen from the data reported in Table 2 that there is a strong dependence of the products from the reduction of nitrobenzene on the cathode metal. Surprisingly, the best yield of *p*-aminophenol is obtained at a cathode, copper, where the *I–E* characteristics would indicate a single reduction process and the current in the limiting plateau to be mass-transfer controlled. Moreover, controlled potential electrolysis in the limiting plateau region confirms the transfer of 6 F mol^{-1} and aniline as the product. At potentials in the lower half of the reduction wave, however, *p*-aminophenol is formed with a high efficiency suggesting that although the reduction appears on an *I–E* curve to be a single process, the wave, in fact, consists of two overlying processes, one 4e and one 2e reduction.

Scheme 1



$$\begin{tikzcd}
 & C_6H_5NO \arrow[r, "C_6H_5NHOH", "-H_2O"'] & C_6H_5\overset{O}{\overset{\uparrow}{N}}{=}NC_6H_5 & (1) \\
C_6H_5NO_2 \arrow[r, "4H^+ + 4e", "-H_2O"'] & C_6H_5NHOH \arrow[u, "O_2"'] \arrow[d, "H^+"] \arrow[r, "2H^+ + 2e", "-H_2O"'] & C_6H_5NH_2 & (2) \\
 & C_6H_5N^+H_2OH \arrow[r, "H_2O", "-H^+-H_2O"'] & p\text{-}HOC_6H_4NH_2 & (3)
\end{tikzcd}$$

Table 5. Electrolytic reduction of nitrobenzene (40 mM) in various 50% solvent/50% water mixtures containing sulphuric acid (3 M). Electrolysis at potential where initial current density is 10 mA cm^{-2}, i.e. at approximately 0.33 I_L. Copper cathode

Solvent	*n*	*Yield of p-aminophenol*
Acetone	3.9	81
1-propanol	3.6	85
Dioxan	3.5	52
Acetic acid	3.9	58

The *I–E* curve at mercury clearly shows these two reduction steps well separated on the potential axis but the product spectra are not as simple as was expected. While at the plateau of the more negative wave the product is largely aniline, the electrolysis at the plateau of the first wave is a mixture of aniline, *p*-aminophenol and azoxybenzene and the ratio of *p*-aminophenol to azoxybenzene is not as favourable as at a copper cathode. This latter observation was also noted at a lead electrode and the rate of the rearrangement of phenylhydroxylamine to *p*-aminophenol clearly depends on the cathode material (see also [4]). Hence at least the initial protonation step required for the rearrangement may well occur while the phenylhydroxylamine is absorbed on the electrode surface. On the other hand, the increase in yield of *p*-aminophenol with increased convection would argue that it is favourable to remove from the cathode an intermediate in the rearrangement.

All the above observations are compatible with a competition between routes 1 to 3 for the fate of the phenylhydroxylamine. The yield of *p*-aminophenol was also found to depend on the organic co-solvent and acetone and 1-propanol were found to be the best of those investigated. In later experiments 1-propanol was the preferred solvent because of the higher solubility of nitrobenzene and because less discolouration of the catholyte occurred during electrolysis. In no experiments with 1-propanol was *p*-propoxyaniline found amongst the products. Hence during the rearrangement of phenylhydroxylamine to *p*-aminophenol, the alcohol must be a poor nucleophile compared to water.

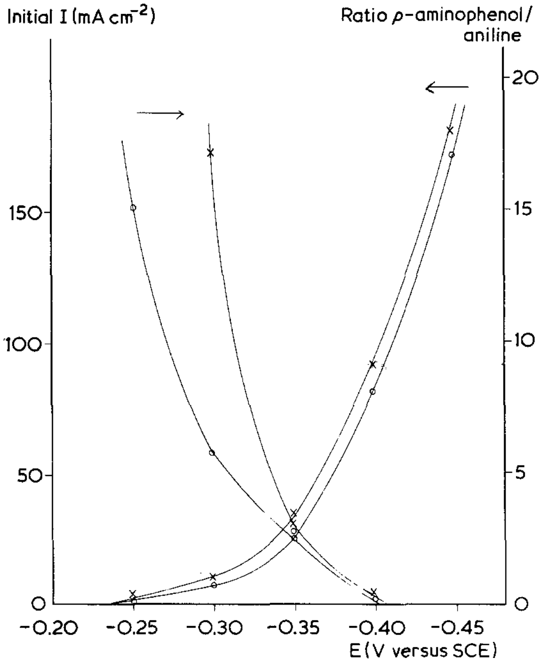


Fig. 4. Ratio of *p*-aminophenol/aniline and initial current density as a function of potential. Nitrobenzene (40 mM) in 50% organic solvent/50% water containing sulphuric acid (3 M). X 1-propanol, o acetone.

Hence it is the conclusion of this work that the best yield of *p*-aminophenol is obtained with a low potential at a copper cathode, using a well-stirred oxygen-free solution in 1-propanol/water containing sulphuric acid (3 M). Indeed, under

Table 6. Electrolytic reduction of nitrobenzene at a copper electrode in 50% 1-propanol/50% water containing sulphuric acid (3 M)

Concentration of nitrobenzene (M)	*E* (V versus SCE)	I_{initial} (mA cm^{-2})	*Yield of p-aminophenol* (%)
0.04	−0.3	10	85
0.4	−0.3	26	82
0.6	−0.4	200	58
	−0.39	150	76
	−0.38	100	82

these conditions the organic yield and current efficiency for *p*-aminophenol compare well with earlier investigations [6–8]. Earlier attempts to exploit this route for the commercial production of *p*-aminophenol have, however, floundered more because of an inadequate current density. Hence the experiments reported in Table 6 were carried out and it can be seen that using a saturated solution of 50% 1-propanol/50% water it was possible to obtain *p*-aminophenol yield of 82% at a current density of 100 mA cm^{-2} and 76% at 150 mA cm^{-2}.

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