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SHORT COMMUNICATION

Electrochemical reduction of *o*-nitrobenzaldehyde in aqueous ethanolic sulphuric acid medium

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1. Introduction

Nitrobenzaldehydes have been extensively studied polarographically in aqueous alcoholic solutions of different pH [1-8]. *o*-, *m*- and *p*-isomers behave differently in media of different pH. The electron-withdrawing nitro-group shifts the reduction potential of the carbonyl group present in the nitrobenzaldehydes to the positive side relative to unsubstituted benzaldehyde.

o-Nitrobenzaldehyde gives four waves on a mercury electrode in pH ranges below nine [8, 9]. The nitro-group is reduced to hydroxylamine in two steps involving four electrons. Hydroxylamine is further reduced to aniline in a third step. The fourth step is the reduction of the aldehyde group to alcohol. At pH 12 (calcium hydroxide-calcium chloride buffer) nitrobenzaldehyde undergoes reduction as follows

$$\text{-NO}_2 \xrightarrow{\text{I}} \text{-NHOH} \xrightarrow{\text{II}} \text{-NH}_2$$

$$\text{-CHO} \xrightarrow{\text{III}} \text{-CHO}^{\overline{\cdot}} \xrightarrow{\text{IV}} \text{-CHO}^{2-}$$

Nitrobenzaldehydes have also been reduced in aprotic media on mercury and platinum electrodes [10-13]. The stable anion radical of the nitro-group has been detected by ESR [10].

o-Nitrobenzaldehyde is reduced in aqueous acidic medium to *o*-aminobenzyl alcohol. This end product is also obtained by the electroreduction of anthranilic acid under similar experimental conditions [14]. *o*-Aminobenzyl alcohol is an important intermediate in dye and pharmaceutical formulations and is also used to prepare many heterocyclic derivatives.

This paper describes a simple method of preparing *o*-aminobenzyl alcohol from *o*-nitrobenzaldehyde. The voltammetric behaviour of *o*-nitrobenzaldehyde in aqueous acidic media is also discussed.

2. Experimental procedure

Electrolytic pure lead (area, 108 cm^2) and copper (108 cm^2) plates were used as cathode materials. The lead electrode was cleaned by etching in concentrated nitric acid and was then thoroughly washed with distilled water and immediately used for electrolysis. The copper electrode was buffed, then degreased with trichloroethylene.

A simple electrolytic cell was used, a glass beaker as the cathode compartment and two ceramic porous cups as anode compartments. *o*-nitrobenzaldehyde (5 g) (Loba chemie) dissolved in 15% (by volume) aqueous sulphuric acid (AR, Glaxo) and ethanol mixture (1 : 1) was used as the catholyte and the same electrolyte, without *o*-nitrobenzaldehyde, as the anolyte. The lead plates were used as anode materials. The electrolyte was stirred thoroughly by a suitable glass stirrer. The temperature of the electrolyte was maintained at 20° C ± 2° C by means of a freezing mixture. Current at various current densities were passed for the reduction process. More than the theoretical current (> 8 F) was always found to be necessary for the maximum product yield. After completion of electrolysis, the catholyte was distilled under reduced pressure to remove the alcohol and the sulphuric acid was neutralized with ammonium carbonate in cold conditions. Some resinous matter formed was removed by filtration. The clean pale yellow solution was extracted thoroughly with chloroform. The organic layer was separated, dried with anhydrous sodium sulphate and then distilled to obtain a solid. This solid was analysed using infrared spectroscopy.

An 'H' type cell, in which the two compartments are separated by a ceramic frit, was used for voltammetric studies. A platinum sheet served as counter-electrode. A micro-electrode of copper (area 0.287 cm^2), used in voltammetric studies, was polished by 4/0 emery paper, washed with double distilled water and degreased with trichloroethylene. A micro-electrode of lead (area 0.197 cm^2) was also mechanically polished, washed with double distilled water and degreased with trichloroethylene. A potential was applied using a potentiostat (Wenking) and a scan generator (Wenking). The current–potential responses were recorded using a x–y/*t* recorder (Rikadenki). Stock solution of *o*-nitrobenzaldehyde was prepared in aqueous alcoholic sulphuric acid solution and diluted to the required strength.

In the voltammetric experiments, the electrode was placed in the cell containing the background electrolyte which was deaerated for 30 min using purified nitrogen. The background current was recorded. After a few cycles, the background current was reproducible. The background current response was highly reproducible on the copper electrode. However, some irreproducibility was observed on the lead electrode. A saturated calomel reference electrode was used.

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All voltammetric measurements were carried out at 25 ± 1° C.

3. Results and discussion

3.1. *Preparative electrolysis*

Electroreduction of *o*-nitrobenzaldehydes in aqueous alcoholic sulphuric acid solution on the lead electrode gave *o*-aminobenzyl alcohol under galvanostatic conditions. It was a brown coloured solid and melted at 83° C (literature m.p. is 82° C). The product was also confirmed by infrared spectral analysis. A broad band at 3500 to 3100 cm^{-1} is due to free –N–H stretching modes. A strong band at 1275 cm^{-1} is due to the C–O stretching vibration of alcohols. The absence of a strong band between 1680 and 1660 cm^{-1} clearly rules out the presence of any C=O functional group in the aldehyde and the absence of any -NO$_2$ functional group frequency in the range of 1661 to 1499 cm^{-1} was also observed. The effect of various current densities on product formation is given in Table 1. At lower current densities the maximum yield of the product was observed; at higher current densities, the current efficiency was low, which may be associated with hydrogen evolution. On the copper electrode, the product yield was low when compared with the lead electrode. Higher temperature may lead to resinification of the product.

3.2. *Voltammetric behaviour of o-nitrobenzaldehyde in 0.1 M H_2SO_4/50% EtOH*

Under voltammetric conditions, the lead electrode gave a reversible well defined peak at around – 0.580 V. The rest potential also changed with time. In sulphuric acid media, the lead electrode underwent some chemical reaction [15], thus complicating the *o*-nitrobenzaldehyde reduction process. Hence detailed voltammetric investigations were not possible.

On the copper electrode, a single irreversible peak at around – 0.285 V was observed for the reduction of *o*-nitrobenzaldehyde in acidic media. The peak current increased with sweep rate (Fig. 1) and concentration (Fig. 2). The peak potential also shifted cathodically with increase in sweep rate (V) and concentration (C). The peak current constant, $i_p/ACV^{1/2}$ (A is the area of the electrode) remained constant in the concentration range 1 to 10 mM and in the sweep rate range 10 to 500 mV s^{-1}. All this evidence suggests

Table 1.

Current density (A dm^{-2})	*Cell voltage (V)*	*Product yield (%)*	*Current efficiency (%)*
1.0	3.73	61.46	30.73
2.5	4.27	53.17	26.58
5.0	5.15	40.00	20.00
7.5	6.00	35.00	17.50

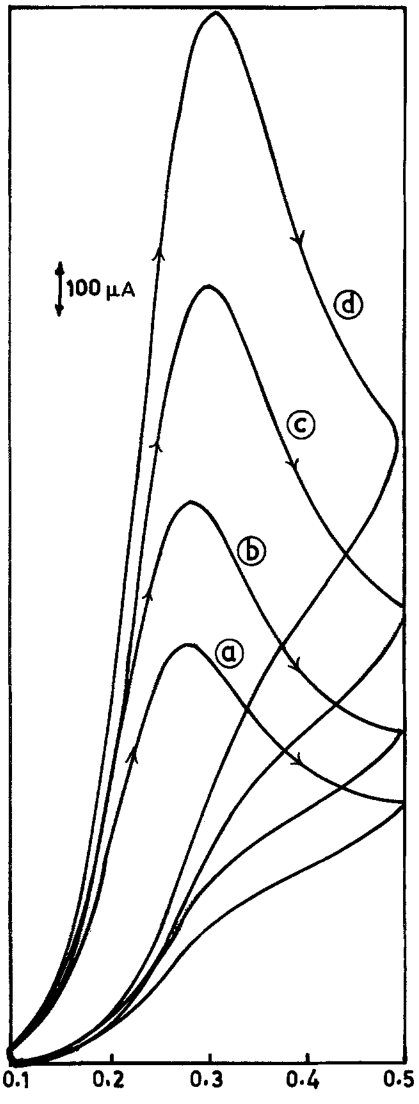

Fig. 1. Cyclic voltammograms for *o*-nitrobenzaldehyde reduction on copper electrode in 0.1 M H_2SO_4/50% EtOH at various sweep rates and [*o*-nitrobenzaldehyde] = 5.3 mM: (a) 20, (b) 40, (c) 80 and (d) 160 mV s^{-1}.

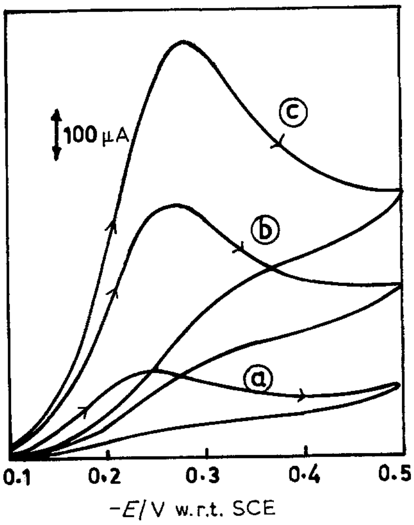

Fig. 2. Cyclic voltammograms for *o*-nitrobenzaldehyde reduction on copper electrode in 0.1 M H_2SO_4/50% EtOH at various concentrations and at a sweep rate of 20 mV s^{-1}. (a) 1.102, (b) 3.242 and (c) 5.30 mM.

an irreversible diffusion controlled process. The value of αn_a is obtained from the peak width (Equation 1) and was found to be 0.8

$$E_\mathrm{p} - E_{\mathrm{p}/2} = \frac{48}{\alpha n_a} \quad (1)$$

The diffusion coefficient (D) for *o*-nitrobenzaldehyde was assumed to be $8.00 \times 10^{-6}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ [16]. By substituting D and αn_a into the equation for an irreversible diffusion controlled process (Equation 2), n was calculated and was found to be approximately four.

$$i_\mathrm{p} = 2.98 \times 10^5\, n(\alpha n_a)^{1/2} A c V^{1/2} D^{1/2} \quad (2)$$

Hence, we conclude that *o*-nitrobenzaldehyde undergoes a four-electron irreversible diffusion controlled process on a copper electrode in aqueous acidic media (Figs 1 and 2). Further reduction processes may merge with the reduction of the background electrolyte.

4. Conclusion

The present investigation indicates that *o*-nitrobenzaldehyde is reduced to *o*-nitrobenzyl alcohol on lead and copper cathodes in an aqueous alcoholic sulphuric acid medium. *o*-nitrobenzaldehyde gives a four-electron irreversible diffusion controlled peak on a copper electrode leading to the formation of phenylhydroxylaminealdehyde and further reduction waves are not clearly observed under the present experimental conditions. Studies of this compound in media of different pH as well as in non-aqueous media may be useful in elucidating the reduction mechanisms.

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