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Electrochemical reduction of 2,3′-dinitrobenzidine in buffered aqueous methanol

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2,3′-dinitrobenzidine (2,3′-DNB) gives a single diffusion-limited irreversible polarographic wave in buffered aqueous methanol. Microcoulometric experiments indicate a transfer of ten electrons in the reduction and cyclic voltammetric studies show direct proof for the existence of a nitroso intermediate. Based on the results obtained, a suitable mechanism is proposed for the reduction of 2,3′-DNB in buffered methanolic solutions.

1. Introduction

The reduction of the nitro group can either proceed to the hydroxylamine or to the amine stage depending upon the experimental conditions. The reduction mechanism is influenced by a variety of factors such as the electrode material, the nature of the substitutent, the solvent employed etc. The papers available on the electrochemical reduction of nitrobiphenyls, nitrophenylamines and related compounds in protic media [1–12] have given the mechanistic evidence for the presence of intermediates formed during the reduction. In continuation of our earlier work, we report here the electrochemical behaviour of 2,3′-dinitrobenzidine (2,3′-DNB) in buffered aqueous methanolic solutions. The electrochemical behaviour of 2-nitrobenzidine (2-NB) and 2,3′-DNB in *N*, *N*-dimethyl-formamide (DMF) have already been reported by us [13, 14].

2. Experimental details

2,3′-DNB was prepared according to the literature procedure [15]. The purification of the solvent, supporting electrolyte and the buffers used are similar to those described earlier [6]. The capillary characteristics of the dme are: $m = 0.8814\,\mathrm{mg\,s^{-1}}$, $t = 7.0\,\mathrm{s}$ at a mercury column height of 55 cm (uncorrected) under open circuit conditions. Polarographic measurements and microcoulometric experiments were carried out as described previously [6, 16]. A micro-type hanging mercury drop electrode (hmde, Metrohm EA 290) with an area of $2.20 \times 10^{-6}\,\mathrm{m^2}$ was used as the working electrode in cyclic voltammetric (CV) experiments. Cyclic voltammograms were recorded with PAR 173, 179 and 175 units (Princeton Applied Research Corporation, U.S.A.) in conjunction with an x-y recorder (Digital Electronics, Bombay).

3. Results and discussion

2,3′-DNB gives a single diffusion-limited irreversible polarographic wave at various compositions of methanol (50–80% v/v) and pH (2.5–12). Figure 1 shows the typical polarograms obtained in buffered 50% (v/v) methanol–water mixtures. Microscale controlled-potential electrolysis experiments carried out at the limiting region of the polarographic wave of 2,3′-DNB gave a total of ten electrons ($n_{\mathrm{app}} = 10$) in acidic, neutral and alkaline solutions. The coulometric data are presented in Table 1.

The CV of 2,3′-DNB obtained in alkaline media in 50% (v/v) methanol at $0.1\,\mathrm{V\,s^{-1}}$ sweep rate are shown in Figs 2–4. A single diffusion-limited cathodic peak which corresponds to the d.c. step is seen in the pH range 2.5–12. The CV of 2,3′-DNB taken in strong acid solutions (0.1 M HCl, Fig. 2A) again shows a single cathodic peak (b) in the forward scan. The peak is found to be irreversible on the basis of the usual criteria. It is also seen from Fig. 2A that a small peak, (a), appears before the main cathodic peak (b) as a shoulder in the first cycle but is clearer in the continuous cycle. The peak (a) arises from the reduction of the nitro group present in the 3′-position (*ortho*- to the amino group) in 2,3′-DNB since the hydrogen bonded nitro group is reduced at a more positive potential than the non-hydrogen bonded nitro group [17]. The closeness of the peak potentials of the cathodic peaks, (a) and (b), may be the reason for observing a single wave in the polarographic experiments. It may be mentioned that the CV results of 2,3′-DNB at pH 4.63 (Fig. 2B) are identical with those obtained in 0.1 M HCl. The CV of 2,3′-DNB in neutral (pH 6.36) solutions (Fig. 3A) shows the same two cathodic peaks, (a) and (b), during the forward scan. During the reverse sweep, a new 'redox couple', (c′–c), is seen at more positive potentials (Fig. 3A). The peak separ-

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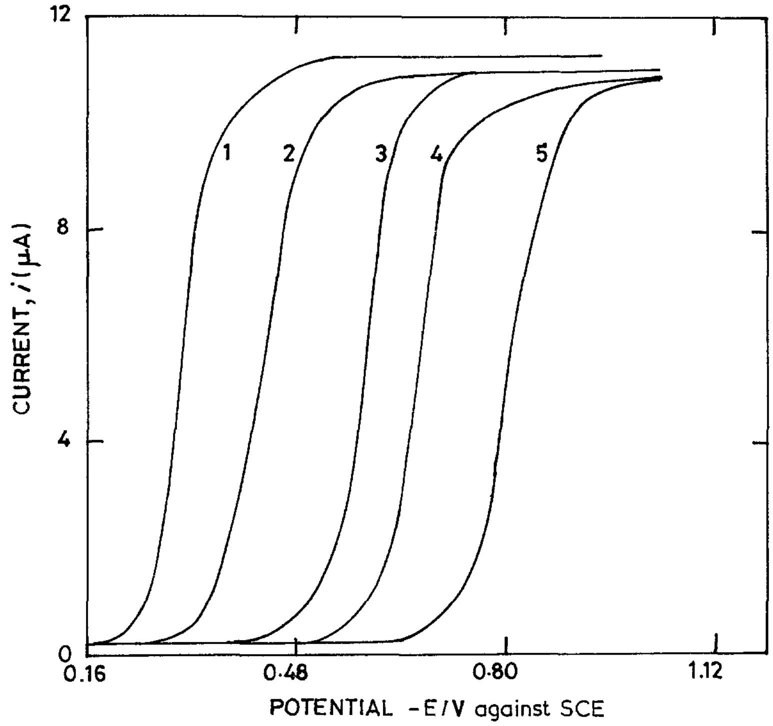


Fig. 1. D.c. polarograms of 2,3′-DNB (5.0 × 10^4 M) in buffered 50% (v/v) methanol–water mixture containing 0.1 M KCl supporting electrolyte at various pH values. Curve 1, pH 2.47; Curve 2, pH 4.2; Curve 3, pH 6.8; Curve 4, pH 8.35; Curve 5, pH 11.88.

ation of the new 'redox couple' ($\Delta E_p = 0.035$ V) corresponds to a two-electron process. A potential hold at the main cathodic peak (b) enhances the peak heights of the new 'redox couple'. It may be pointed out here that a similar 'redox couple' was also observed in the case of 2-NB [18] which clearly indicates that the nitro group in the 2-position of 2,3′-DNB undergoes reduction in the same ways as that in 2-NB. A possible reason for not observing the 'redox couple' (c′–c) in acidic solutions (pH < 5.50) is that in these solutions (Fig. 2) it is quite likely that the 'redox couple' might occur at more positive potentials than 0.0 V vs SCE. In view of the possible oxidation of mercury in the chloride supporting electrolyte, sweep experiments were not extended to positive potential scales.

The CV of 2,3′-DNB in buffered (pH 9.67) alkaline solutions (Fig. 3B) shows a single cathodic peak (b) in the forward scan and an adsorption pre-peak, (d), which disappears during the continuous cycle. In the reverse scan, in addition to the 'redox couple', (c′–c), seen earlier in neutral solutions, one more 'redox couple' (e′–e) is observed at more positive potentials (Fig. 3B). The peak separation (ΔE_p) of 0.03 V between (e′) and (e) suggests a two-electron process. The CV of 2,3′-DNB taken in 0.1 M NaOH shows two well-defined cathodic peaks, (a) and (b), in the forward scan (Fig. 4). The cathodic peaks are separated by about 0.07 V and are sharp when compared to the peaks obtained in 0.1 M HCl. It is seen from Fig. 4 that during the reverse scan, in addition to the 'redox couples' (c′–c) and (e′–e), a further pair of peaks,

Table 1. Microcoulometric data for 2,3′-DNB (5.0 × 10^{-4} M) in buffered 50% (v/v) methanol solutions

pH	n_{app} ± *0.10*
0.1 M HCl	9.95
4.83	9.80
7.50	9.70
9.43	9.80
0.1 M NaOH	9.90

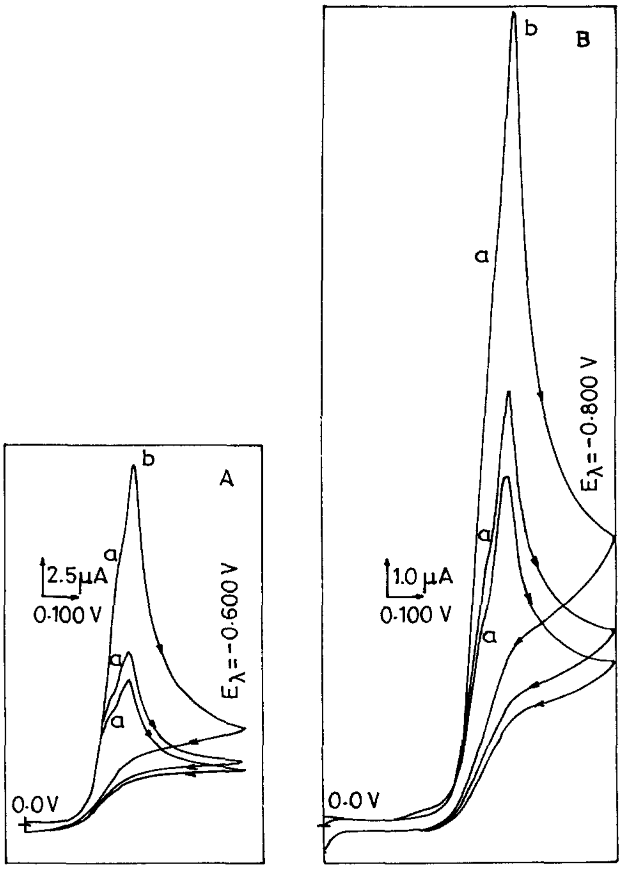


Fig. 2. Cyclic voltammograms of 2,3′-DNB (5.0 × 10^{-4} M) in buffered 50% (v/v) methanol–water mixture containing 0.1 M KCl supporting electrolyte in 0.1 M HCl (A) and pH 4.63 (B) (switching potentials, E_λ, and starting voltages are indicated in the figures; sweep rate, $v = 0.100$ V s^{-1} in both cases).

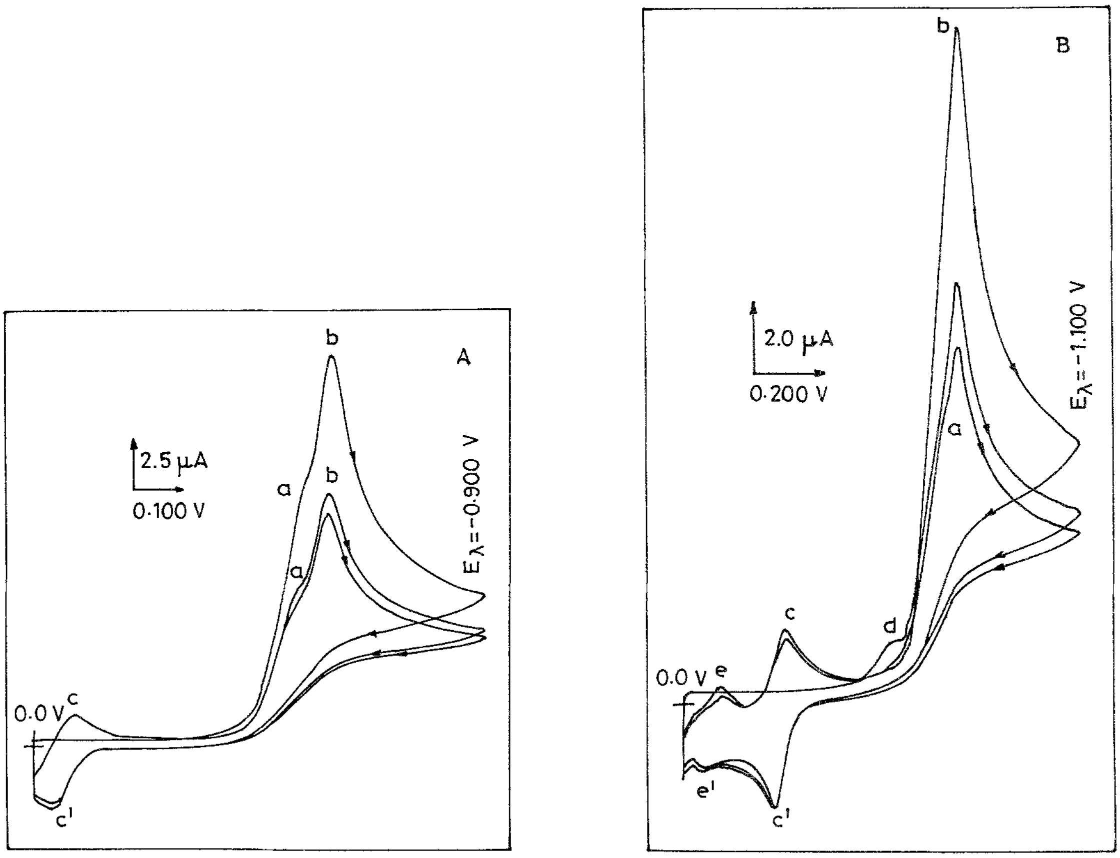
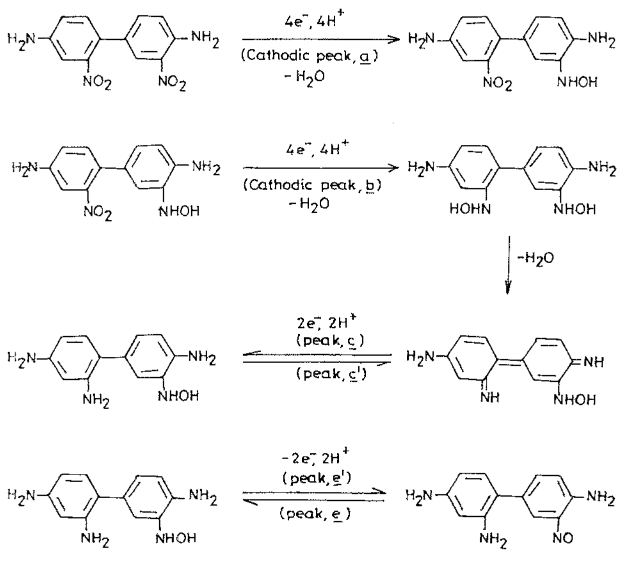


Fig. 3. Cyclic voltammograms of 2,3′-DNB (5.0×10^{-4} M) in buffered 50% (v/v) methanol-water mixture containing 0.1 M KCl supporting electrolyte at pH 6.36 (A) and 9.67 (B) (switching potentials, E_λ, and starting voltages are indicated in the figures; sweep rate, v = 0.100 V s^{-1} in both cases).

(f′-f), is observed at a more positive potential with a peak separation (ΔE_p) of 0.01 V. These peaks may be due to the adsorption-desorption of the product since ΔE_p is characteristic of such processes [19]. The 'redox couples', (c′-c) and (e′-e), observed in buffered media are also seen in unbuffered methanolic solutions, indicating that a similar mechanism is operating in both cases.

Based on the results obtained from polarography, cyclic voltammetry and microcoulometry, the following mechanism is suggested for the reduction of 2,3′-DNB in buffered methanolic solutions:



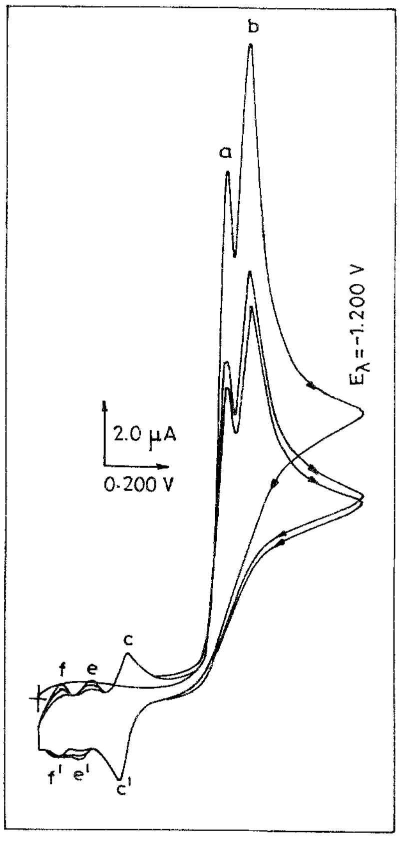
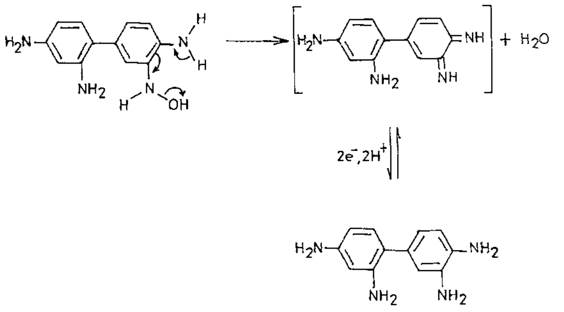


Fig. 4. Cyclic voltammograms of 2,3′-DNB (5.0×10^{-4} M) in 50% (v/v) methanol-water mixture containing 0.1 M NaOH at sweep rate, v = 0.100 V s^{-1} (starting voltage = −0.200 V; switching potential, E_λ, is indicated in the figure).

It is seen from the above mechanism that the nitro group in the 2-position of 2,3′-DNB undergoes reduction in the same way as that in 2-NB [18]. Since the total number of electrons transferred in the reduction of 2,3′-DNB is ten ($n_{\mathrm{app}} = 10$, Table 1), it is clear that the nitro group in the 2-position is reduced to the amine by an uptake of six electrons. This is further confirmed by the fact that the potentials at which the new 'redox couple', (c′–c), appear in the reduction of 2,3′-DNB (Fig. 3A) are comparable to those of the diphenoquinonediimine intermediate seen in the case of 2-NB reduction [18]. It has been reported [20] that hydrogen bonded nitro groups are reduced only to $-\mathrm{N{=}O}$ or $-\mathrm{NHOH}$ depending on the conditions since the intermediates in the reduction are stabilized by hydrogen bonding. In a similar way in the present study, the reduction of the hydrogen bonded nitro group in the 3′-position of 2,3′-DNB stops at the hydroxylamino stage.

Two pathways can be envisaged for the existence of the 'redox couple', (e′–e), at more positive potentials: (i) Elimination of water from the hydroxylamino group formed by the reduction of the nitro group at the 3′-position leading to an *o*-quinoid structure which subsequently undergoes a reversible two-electron reduction at more positive potentials according to the following scheme:



(ii) Oxidation of the hydroxylamino to the nitroso derivative during the reverse sweep; the nitroso group is then reversibly reduced during the subsequent forward scan thus setting up a 'redox couple'. The possibility (i) is not acceptable for the following reasons. Firstly, the microcoulometric results of 2,3′-DNB (Table 1) indicate $n_{\mathrm{app}} = 10$ in the reduction whereas the involvement of a quinoid intermediate (as depicted in the above scheme) would require a total of twelve electrons. Secondly, the 'redox couple', (e′–e), is observed only in alkaline media (pH > 9.67) whereas the reversible reduction of the quinoid intermediate to the amine would be more favoured in acidic and neutral media and hence the redox peaks (e′–e) should also be observable in these solutions. On the other hand, it is known that the reduction of $-\mathrm{N{=}O}$ to $-\mathrm{NHOH}$ is reversible and takes place at more positive potentials than the irreversible reduction of $-\mathrm{NO_2}$ to $-\mathrm{N{=}O}$. Thus, it is reasonable to visualize that the hydroxylamino group formed at the 3′-position of 2,3′-DNB is reversibly oxidized ($-\mathrm{NHOH} \rightleftharpoons -\mathrm{N{=}O}$) to give the 'redox couple', (e′–e). The question then arised as to why (e′–e) is observed only in alkaline solutions (pH > 9.67) unlike the other 'redox couple', (c′–c), seen in acidic and neutral solutions. As we have mentioned earlier, the reversible two-electron reduction of $-\mathrm{N{=}O}$ to $-\mathrm{NHOH}$ occurs at a more positive potential than that of the parent nitro compound. In an environment where there is hydrogen bonding (as in the present case of 2,3′-DNB), the potential for the 'redox couple' is expected to shift further to a more positive value. Since the electrode process, $-\mathrm{N{=}O}$ to $-\mathrm{NHOH}$, is pH dependent (shift of peak potentials to more negative values as the pH is increased), the 'redox couple', (e′–e), would have appeared at more positive potentials in acidic solutions. As the pH is increased, the potential is shifted to more negative values and the 'redox couple' appears within the potential window as has been observed in alkaline media (pH > 9.67). The above observations strongly suggest the existence of a nitroso intermediate and its subsequent reduction at potentials more positive than in polarographic studies.

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