

Electrochemical Behavior of Benzo[*c*]cinnoline-*N*-oxide at Mercury Electrode

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Electrochemical behavior of benzo[*c*]cinnoline-*N*-oxide was studied. Two discrete 2 and 4 electron reduction waves in acidic media but only one wave in basic media were observed in ethanol-BR buffer system (1:5 v/v). The number of electrons transferred and the diffusion coefficient were determined by using various voltammetric techniques, such as sampled current polarography, cyclic voltammetry, chronoamperometry, chronocoulometry and constant potential coulometry. Adsorption of the molecule on the surface of the mercury drop was analyzed and this phenomenon was exploited to calculate the diffusion coefficient of benzo[*c*]cinnoline-*N*-oxide. A mechanism for the electrode reaction is proposed.

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Electrochemical behavior of benzo[*c*]cinnoline-*N*-oxide appears to be worth investigating due to mutagenic, antirheumatic and carcinogenic activity and usage in dye chemistry and pharmaceuticals.^{1,2}

Half-wave potentials for the polarographic reduction of benzo[*c*]cinnoline-*N*-oxide have been measured in a buffered aqueous solution. The buffer was prepared by dissolving disodium hydrogenphosphatedodecahydrate, citric acid monohydrate and potassium chloride in doubly distilled water. The polarographic reduction of benzo[*c*]cinnoline-*N*-oxide on a mercury electrode was reported with a single 4-electron transfer in buffered aqueous solution.³ Cyclic voltammetric behavior of benzo[*c*]cinnoline-*N*-oxide on a hanging mercury drop electrode was studied in an aqueous alcohol; and a single 4 electron reduction peak was reported.⁴ The polarographic reduction of benzo[*c*]cinnoline-*N*-oxide on a mercury electrode was reported to be irreversible with a single 4-electron transfer in 80% aqueous alcohol.⁵

Our study concerns the reduction mechanism of benzo[*c*]cinnoline-*N*-oxide (I) in ethanol/water (1:5 v/v) mixture. The diffusion coefficients and number of electrons transferred were determined employing electrochemical techniques such as sampled current polarography, cyclic voltammetry, chronoamperometry, chronocoulometry and constant potential. A mechanism for the electrode reaction was proposed. To elucidate the electrode reaction mechanism, multicyclic voltammogram and macroscale electrolysis experiments were performed to analyze the final reduction products.

Experimental

Chemicals

Benzo[*c*]cinnoline-*N*-oxide was prepared as described in the literature.⁶ The compounds were purified by using column chromatography and were crystallized from methanol. The structure of the resulting compound was elucidated by using UV, IR, ¹H-NMR, molecular weight determination and

elemental analysis. Acetic acid (BDH, analar), phosphoric acid (Merck), boric acid (Riedel), ammonium metavanadate (Merck), and sodium hydroxide (Merck) were used without further purification. Water was distilled and deionized by an ELGESTAT water purification system and was used for the preparation of solutions and solvent systems.

Britton-Robinson buffer

Britton-Robinson buffer was constituted as follows: 8 ml of 0.5 M boric acid, 8 ml of 0.5 M phosphoric acid and 8 ml of 0.5 M acetic acid were diluted to 1 l with deionized water. Britton-Robinson buffers of pH 1.81 to 11.98 were prepared by adding sodium hydroxide.

Apparatus

The polarographic measurements were carried out on a BAS100B Electrochemical Analyzer equipped with a BAS 100B Cell Stand, a PARC 303A Static mercury drop electrode, and a Panasonic Model FIG-310 color plotter. BAS 100B was connected to a computer and the data was processed with BAS100W.EXE program. A platinum wire was used as an auxiliary electrode and a Ag|AgCl|KCl_(sat) electrode as a reference electrode. All solutions were deaerated for 5–10 min with pure nitrogen and a nitrogen atmosphere was maintained over the solutions during the electrolysis. The pH values of the solutions were recorded by an ORION 720A pH-meter with a combined glass electrode and Ag/AgCl reference electrode. Nitrogen gas was deoxygenated by scrubbing through a solution of vanadous chloride, concentrated HCl and amalgamated zinc.

Results and Discussion

Characterization of the electrode reaction

The number of waves observed in cyclic voltammetry were found to be closely dependent upon the pH of the medium. We observed two reduction waves in pH = 3.01 and a single reduction wave in pH = 9.85 at the potential window of solvent electrode system (Fig. 1). The more positive wave (the first wave) was observed in both acidic and basic pH values, while

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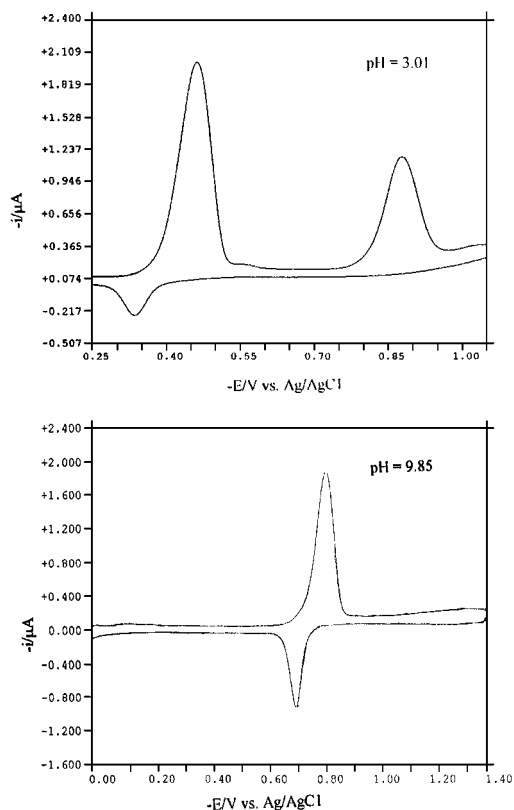


Fig. 1 Cyclic voltammograms of benzo[c]cinnoline-*N*-oxide on HMDE. a) pH = 3.01, b) pH = 9.85, 1:5 v/v ethanol:BR buffer, 1.67×10^{-5} M benzo[c]cinnoline-*N*-oxide solution, scan rate = 0.1 V/s.

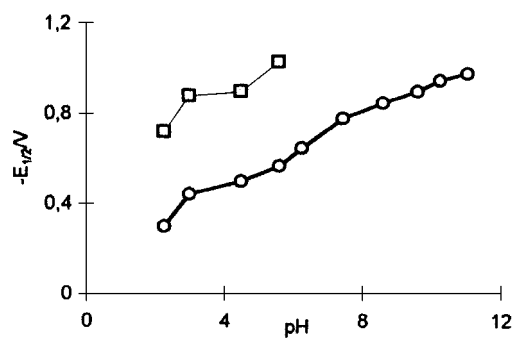


Fig. 2 Effect of pH on the half-wave potentials of 1.67×10^{-5} M benzo[c]cinnoline-*N*-oxide (1:5 v/v ethanol:BR, vs. Ag/AgCl), drop time = 1 s. \circ first wave, \square second wave.

the more negative wave was only seen at acidic pH. The first cathodic peak in CV voltammograms has an anodic counter part while the second peak does not. Both waves were found to show a linear shift towards cathodic potentials with the increasing pH values (Fig. 2). The number of electrons transferred at each polarographic wave was determined by constant potential coulometry. Constant potential coulometric experiments were performed on a mercury pool electrode with an area of 19.6 cm^2 . Electrolysis was continued until the current dropped to about 1%. According to our coulometric study, the number of electrons transferred was 4 and 2 for the first, and second waves respectively (Table 1). The first wave is a 4-electron reduction of N=N-O group. This wave is quasi-reversible; because the difference between the anodic and the

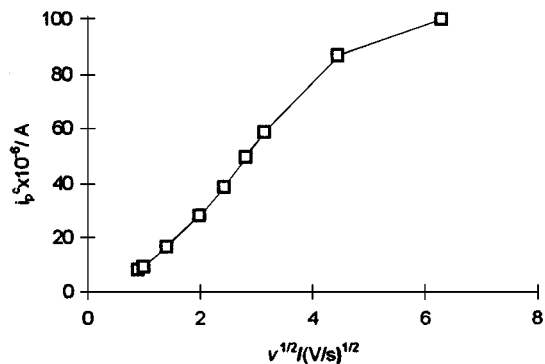


Fig. 3 Variation of cathodic peak current with $v^{1/2}$ for 1.67×10^{-5} M benzo[c]cinnoline-*N*-oxide pH \cong 4.

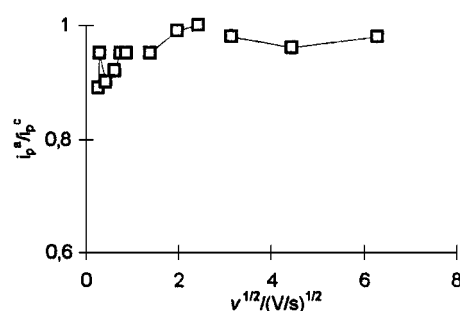


Fig. 4 Variation of i_p^a/i_p^c ratio with $v^{1/2}$ for 1.67×10^{-5} M benzo[c]cinnoline-*N*-oxide. pH \cong 4.

cathodic peak potentials was 0.234 V, which is greater than 0.059/4 V and increased with increasing scan rate (from 0.01 to 50 V s^{-1}). As can be seen from Figs. 3 and 4 the cathodic peak current increased with a increase in $v^{1/2}$. The i_p^a/i_p^c ratio tended to 1.⁷ These results show that the system is not reversible; moreover these results are consistent with a quasi-reversible behavior.⁷

Adsorptional characteristics

Adsorption of benzo[c]cinnoline-*N*-oxide on a mercury surface was clearly observed when the scan rate was increased. The cyclic voltammograms of benzo[c]cinnoline-*N*-oxide at 30 V/s scan rate and at 1.67×10^{-6} M exhibited a prepeak to the normal CV peak, indicating the strong adsorption of the product,⁸ that is benzo[c]cinnoline-*N*-oxide (Fig. 5). Furthermore, chronoamperometric curves could be ascribed to the adsorption. The potential of the HMDE was kept for a definite time at -0.8 V , which is a negative enough value to ensure that no faradaic process occurred. On the chronoamperometric curve the "shoulder" was observed such plateaus on the chronoamperometric curve indicate the adsorption⁹ and such a curve is given in Fig. 6.

The experimental Cottrell slope was determined from the chronoamperometric i vs. $t^{-1/2}$ plot. The constant potential applied was slightly more cathodic than the cyclic voltammetric E_p . A hanging mercury drop electrode with a surface area of $0.0145 \pm 0.002 \text{ cm}^2$ was employed. Assuming that the electron transfer reaction was not complicated by any type of adsorption and was not accompanied by a chemical reaction, diffusion coefficient values were calculated for the first wave at acidic and basic pH values from chronoamperometric cottrell slopes, the results are tabulated in column 4 of Table 1. These

Table 1 Diffusion coefficients, number of electrons transferred, the amount of reactant adsorbed on the mercury surface (Γ , mol/cm²) of 1.67×10⁻⁵ M benzo[c]cinnoline-*N*-oxide, 1:5 ethanol:BR buffer

pH	$\frac{D^a \pm t_s / \sqrt{N}}{\text{cm}^2 \text{ s}^{-1}}$	$\frac{D^b \pm t_s / \sqrt{N}}{\text{cm}^2 \text{ s}^{-1}}$	pH	$\frac{\Gamma \pm t_s / \sqrt{N}}{\text{mol cm}^{-2}}$	Number of electrons transferred (equiv/mol)	
					Peak I	Peak II
3.9	$1.66 \times 10^{-6} \pm 3.30 \times 10^{-7}$	$6.10 \times 10^{-5} \pm 3.03 \times 10^{-5}$	4.2	$2.68 \times 10^{-11} \pm 7.36 \times 10^{-12}$	4.2±0.2	2.03±0.1
9.8	$1.81 \times 10^{-6} \pm 7.78 \times 10^{-7}$	$5.75 \times 10^{-5} \pm 2.14 \times 10^{-5}$	10.3	$2.31 \times 10^{-11} \pm 1.21 \times 10^{-12}$	4.02±0.2	N.D.

a. Calculated from Eq.(1) considering adsorption. b. Calculated from Cottrell slope, ignoring adsorption. t : confidence interval (95%). N : number of experiments. N.D.: not determined.

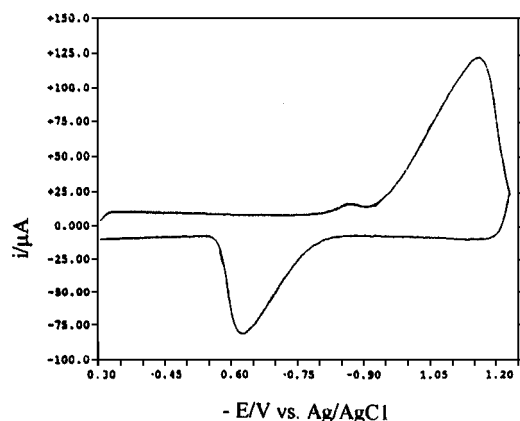


Fig. 5 Cyclic voltammogram of adsorption prepeak for strong adsorption of product (dihydrobenzo[c]cinnoline), 1.67 × 10⁻⁶ M benzo[c]cinnoline-*N*-oxide solution: scan rate = 30 V/s. pH ≅ 10.

diffusion coefficient values were compared with the ones found on the basis of the adsorption to verify the adsorption phenomena. A relatively higher values of diffusion coefficients may be attributed to the first indication of adsorption that is not considered in the cottrell equation.

We assumed that a non compact film of adsorbed molecules on the mercury surface was formed during the negative sweep and the adsorption was langmuir type; The following expression derived by Garrido *et al.*¹⁰ at 25°C was exploited to calculate the diffusion coefficient of the benzo[c]cinnoline-*N*-oxide.

$$i_p = 1.06 \times 10^6 n^2 AC \nu D^{1/2} t_p^{1/2} \quad (1)$$

Here t_p is the adsorption time from the beginning of the life of the drop until E_p is reached. Diffusion coefficients calculated from Eq. (1) is given in Table 1. The values calculated using the theoretical equation for adsorption controlled current were more realistic. Diffusion coefficients were also calculated using the Cottrell equation assuming the electrode reactions was purely diffusion controlled and the values are tabulated in column 4 of Table 1. The higher values calculated for the pure diffusion case are almost certainly due to the omission of adsorption phenomena. These results clearly show that the adsorption phenomena should not be disregarded when one wants to find diffusion coefficients of organic molecules.

Surface concentration measurements

The surface concentration of the adsorbed molecules of benzo[c]cinnoline-*N*-oxide was studied by chronocoulometry. In chronocoulometric experiments, Q vs. $t^{1/2}$ plots were obtained for blank solution and for the solutions that contain electroactive species. From the intercept on the Q axis, total

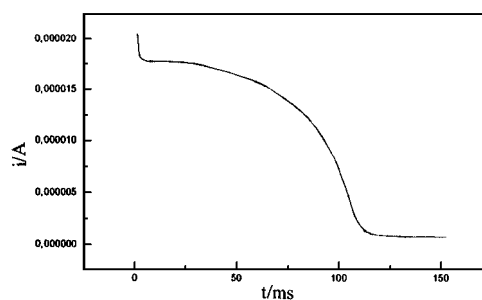


Fig. 6 Current-time curve in 1:5 v/v ethanol:BR buffer, 1.67 × 10⁻⁵ M benzo[c]cinnoline-*N*-oxide solution, potential was stepped from -0.1 V to -0.8 V. pH ≅ 4.

charge and the double layer charge were measured. The difference between these charges was attributed to the charge due to the reduction of adsorbed species which is the last term in the following equation:

$$Q = 2nFAC\sqrt{Dt/\pi} + Q_{dl} + nFA\Gamma$$

Here Q_{dl} is the charge due to the double layer, Γ is the amount of adsorbed reactant and the other symbols have their usual meanings. The details of chronocoulometric measurements of the amount of adsorbed species are given elsewhere.¹¹ The amount of reactant adsorbed on the mercury surface (Γ , mol/cm²) is given in Table 1.

Mechanism of the electrode reactions

According to Ross and Kahan benzo[c]cinnoline-*N*-oxide is studied polarographically at three apparent pH's of 1.9, 5.2 and 13.0 in solutions containing 80% ethanol (by volume). A single wave is obtained for benzo[c]cinnoline-*N*-oxide. Benzo[c]cinnoline-*N*-oxide is reduced to dihydrobenzo[c]cinnoline.

Alternatively, Gupta and Raina claims the reduction of biphenyl moiety to dihydrobenzo[c]cinnoline in acidic pH ranges of stafford buffer containing 20% ethanol. Their inference is based on the analogy reduction of 9,10-dihydrophenanthrene to 1,4,9,10-tetrahydrophenanthrene and the reduction of biphenyl to 1,4-dihydrobiphenyl. The only experimental support of their mechanism is the observation of two spots on TLC with R_f values 0.37 and 0.33 supposed to correspond to dihydro and tetrahydro products of the parent molecule respectively.¹²

Our experimental observations reveal that benzo[c]cinnoline-*N*-oxide is all reducible with 4-electron wave in an extensive pH range from 2 to 12 in universal BR buffer which is almost identical to Ross-Kahan's working medium. Our experiments indicate that the first wave is the reduction of benzo[c]cinnoline-*N*-oxide to dihydrobenzo[c]cinnoline with a quasi-reversible behavior. The second irreversible wave is due to the

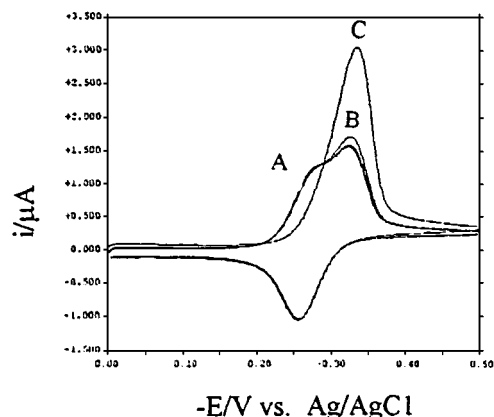


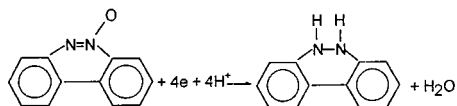
Fig. 7 Multiple scan CV voltammogram of 1.67×10^{-5} M benzo[*c*]cinnoline-*N*-oxide on HMDE, Scan rate: 0.1 V/s, (1:5 v/v ethanol:BR buffer). The number of scans: 9. $\text{pH} \cong 4$.

reduction of dihydrobenzo[*c*]cinnoline to tetrahydro product.

Multiple scan CV experiment was performed. First cathodic cyclic voltammogram (C) indicates the reduction of benzo[*c*]cinnoline-*N*-oxide to dihydrobenzo[*c*]cinnoline. Dihydrobenzo[*c*]cinnoline on the mercury surface is oxidized to benzo[*c*]cinnoline. In the other sweeps whilst benzo[*c*]cinnoline-*N*-oxide is reduced to benzo[*c*]cinnoline (B), benzo[*c*]cinnoline on the mercury surface is reduced to dihydrobenzo[*c*]cinnoline (A) (Fig. 7). Therefore in the first scan cathodic current is greater than that for the other scans.

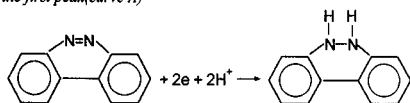
Based on these results, the following mechanism can be proposed:

First cathodic scan (curve C):

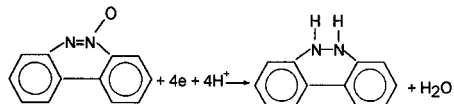


the other scans:

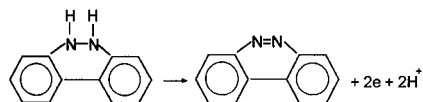
the first peak (curve A)



the second peak (curve B)

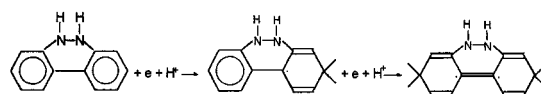


the anodic peak



Dihydrobenzo[*c*]cinnoline is reduced to tetrahydro product. The fact that the compound undergoes only one 4-electron reduction in basic media shows that the reduction stops at the dihydrogenated step.

To elucidate the structure of the product, a macroscale electrolysis at a constant potential was carried out in acidic and basic media on a mercury pool electrode with a surface area of 19.6 cm². In the IR spectra of this product there were no characteristic -NH₂ bands as were observed on the spectrum of 2,2'-diaminobiphenyl, *ca.* 3387 cm⁻¹ and 3364 cm⁻¹. On the other hand, 2,2'-diaminobiphenyl spot was not observed on the TLC of the macroscale electrochemical product. The NH band at 3412 cm⁻¹ and the aliphatic C-H bands at 2953 cm⁻¹ and 2876 cm⁻¹ are present, indicating that the final product is much more likely to be 2,7,9,10-tetrahydrodiazaphenanthrene. The following mechanism can be proposed:



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