Electrochemical Behavior of Benzo[c]cinnoline and Its Bromo Derivatives

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The electrochemical behavior of benzo[c]cinnoline and some of its bromo derivatives was studied. Two discrete 2-electron reduction waves in acidic and only one wave in basic media in ethyl alcohol-BR buffer system (l:5 v/v) were observed. A mechanism for the electrode reaction is proposed. Diffusion coefficients, formal potentials for and the derivatives, the number of electrons transferred were determined by using sampled current polarography, cyclic voltammetry, chronoamperometry, chronocoulometry and constant potential coulometry. Adsorption of the molecules on the surface of the mercury drop was analyzed and this phenomena was exploited to calculate the formal potentials and the diffusion coefficients of benzo[c]cinnolines.

Key Words: Electrochemistry, Benzo[c]cinnolines, Adsorption

Introduction

The electrochemical behavior of benzo[c]cinnolines is worth investigating due to their mutagenic, antirheumatic and carcinogenic activity as well as usage in dye chemistry and pharmaceuticals[1−3].

The polarographic behavior of benzo[c]cinnoline in acetonitrile in the presence of various proton donors such as water, phenol, benzoic acid and perchloric acid was reported[4]. The reduction of benzo[c]cinnoline in DMF with 0.1 M $(CH_3)_4NClO_4$ as a supporting electrolyte was used to produce radicals that were detected by ESR[5] The cyclic voltammetric behavior of benzo[c]cinnoline on smooth platinum was studied in liquid ammonia and two reversible reduction peaks were observed[6]. The polarographic reduction of benzo[c]cinnoline on a mercury electrode was reported to be irreversible with a single 2-electron transfer in 80% aqueous alcohol[7]. The electroreduction of benzo[c]cinnolines in the presence of nonreducible electrophiles in DMF

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was studied to synthesize various cyclic compounds[8]. In another report benzo[c]cinnolines were used as model molecules in a study to find out the general expression for the kinetics of (e, H$^+$) transfer reactions[9]. The adsorption characteristics and the surface coverage ratio of benzo[c]cinnolines were also studied[10]. Mono and dicarboxylated derivatives of benzo[c]cinnoline were prepared by the electroreduction of this compound in acetonitrile using a mercury pool cathode in the presence of methyl chloroformate[11]. Benzo[c]cinnoline was reduced in Stafford buffer and showed two discrete 2-electron diffusion controlled waves[12].

Our study concerns the reduction mechanism of benzo[c]cinnoline (I) and its bromo derivatives, namely 1-bromobenzo[c]cinnoline (II), 3-bromobenzo-[c]cinnoline (III) and 4-bromobenzo[c]cinnoline (IV) in an ethanol/water (1:5 v/v) mixture. The diffusion coefficients, formal potentials, number of electrons transferred and number of protons involved in the rate determining step (rds) of the electrode reaction were determined employing electrochemical techniques such as sampled current polarography, cyclic voltammetry, chronoamperometry, chronocoulometry and constant potential coulometry with dropping and hanging mercury electrodes and Pt ultramicro disk electrode (UME). A mechanism for the electrode reaction is proposed. To elucidate the electrode reaction mechanism, macroscale electrolyses were performed to analyze the final reduction products.

Experimental

Reagents

Benzo[c]cinnoline, 1-bromobenzo[c]cinnoline, 3-bromobenzo[c]cinnoline and 4-bromobenzo[c]cinnoline were prepared as described in the literature[13]. The compounds were purified by using column chromatography and crystallized from methanol. The structure of the resulting compounds was elucidated by using UV, IR, ^{1}H-NMR, molecular weight determination and elemental analysis. Acetic acid (BDH, analar), phosphoric acid (Merck), boric acid (Riedel), ammonium metavanadate (Merck), sodium hydroxide (Merck) were used without further purification. Water was distilled and deionized by ELGASTAT water purification system and was used for the preparation of solutions and solvent systems.

Apparatus

The polarographic measurements were carried out on a BAS100B Electrochemical Analyzer equipped with a BAS 100B Cell Stand, and a PAR 303A Static mercury drop electrode. The BAS 100B system was connected to a computer and the data was processed with the BAS100W.EXE program. The auxillary and reference electrodes were a platinium wire and a Ag/AgCl/KCl$_{(sat)}$. 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 ORION 720A pH-meter with a combined glass electrode and Ag/AgCl reference electrode. Nitrogen gas was deoxygenated by passing through a solution of vanadous chloride, concentrated HCl and amalgamated zinc. The Ultramicro electrode (UME) was a BAS MF-2150 model Pt disk electrode with a radius of 5.0×10^{-3} cm.

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. Two reduction waves in the acidic region and a single reduction wave in the basic region at the potential window of solvent-electrode system were observed (Figure 1). The figure indicates one sharp and one broad cathodic peaks at low pH values (pH 8) appear at -450 mV and –830 mV respectively without any anodic counterpart. The first peak moves to more cathodic potentials and merges with the second peak at higher pH values (pH 8). There also appears an anodic peak in basic media. This verifies that the reaction stops at the dihydrogenation step in basic media while it goes to the tetrahydro product in basic media giving a second 2 electron transfer. The reaction scheme is given in the results and discussion. Both waves gave a linear shift towards cathodic potentials with increasing pH values. The number of protons exchanged in the rate determining step of the electrode reaction was calculated by the use of the slope of $E_{1/2}$-pH plot[14]. The number of protons involved for the first peak in the electrode reaction was calculated to be 2 for all derivatives. The current values were almost independent of pH for all derivatives.
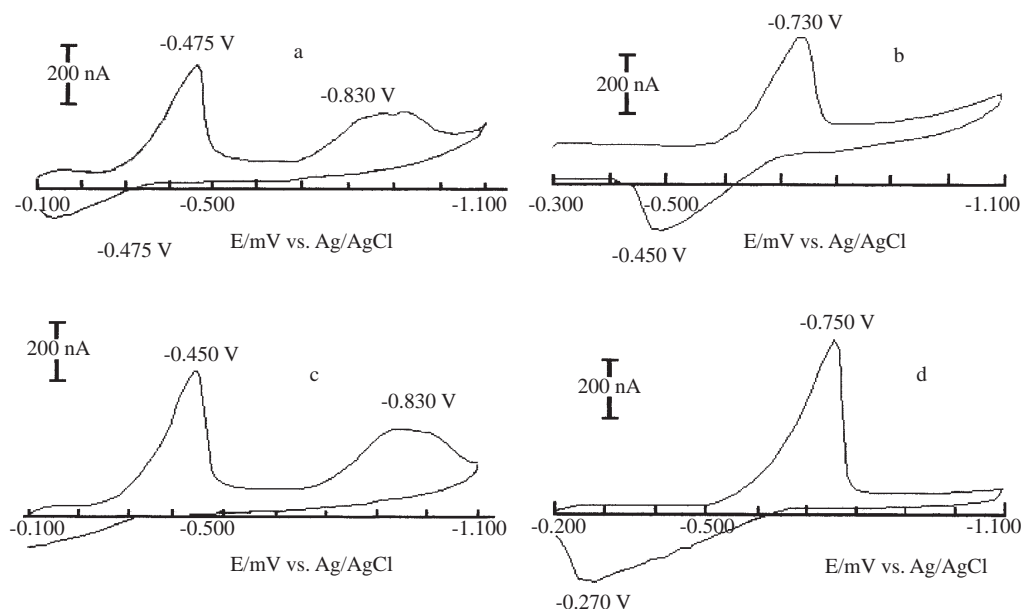

Figure 1. Cyclic voltammograms of benzo[c]cinnoline (I) and 1-bromobenzo-[c]cinnoline (II) on HMDE vs Ag/AgCl. a) I, pH = 3.0, b) I, pH = 8.0, c) II, pH = 3.0 , d) II, pH = 8.0 (1:5 v/v ethanol:BR buffer, scan rate = 100 mV s^{-1}).

The number of electrons transferred in both waves and the diffusion coefficients of the compounds were determined using a chronoamperometric Cottrell equation with a hanging mercury drop electrode,

$$i_t = \frac{nFAC^*D^{1/2}}{\pi^{1/2}t^{1/2}} \tag{1}$$

and the steady state current (i_{ss}) with ultramicro Pt disk electrode[15]:

$$i_{ss} = 4rnFC^*D \tag{2}$$

where r is the radius of the ultramicro electrode (5×10^{-3}cm). When i_t was plotted against $t^{-1/2}$, the Cottrell slope S_{cott} was obtained as

$$S_{\text{cot}} = \frac{nFAC^*D^{1/2}}{\pi^{1/2}} \tag{3}$$

When equations (2) and (3) are combined, the number of electrons transferred is found to be

$$n = \frac{4\pi r S_{\text{cot}\,t}^2}{A^2 F C^* i_{ss}} \tag{4}$$

Here, C^* is the bulk concentration of the compound (mole/cm^3), A is the electrode surface area (cm^2), and the other terms have their usual meanings.

The experimental Cottrell slope was determined from the chronoamperometric i_t 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 cm^2 was employed. Then cyclic voltammetric scans were taken within a suitable potential range using the ultramicro Pt disk electrode to obtain the steady state diffusion-limited current (i_{ss}). Cathodic and anodic portions of the cyclic voltammogram were found to be close to overlapping and independent from the scan rate as expected from Equation (2).

D and n values were calculated for both waves at acidic and basic pH values from equations 3 and 4 respectively, and the results are listed in Table 1. The relatively higher values of n, especially in basic pH ranges, may be attributed to the absorption that is not considered in equations 1 through 4.

Table 1. The chronoamperometric (on HMDE) and cyclic voltammetric (on ultramicro Pt disk electrode) data of the benzo[c]cinnoline and its bromo derivatives.

Comp	Wave	pH	C (mole/L)	i_{ss} (A)	S_{cott}	n	D (cm^2/s)
	First	3.02	1.7×10^{-5}	2.98×10^{-8}	6.15×10^{-7}	2.23	5.67×10^{-4}
I	First	8.31	1.7×10^{-5}	1.92×10^{-9}	1.77×10^{-7}	2.43	4.20×10^{-5}
	Second	3.02	1.7×10^{-5}	ill defd.	ill defd.	—-	—-
	First	2.96	1.7×10^{-5}	3.81×10^{-9}	2.05×10^{-7}	1.94	5.64×10^{-5}
II	First	8.36	1.7×10^{-5}	6.15×10^{-9}	2.64×10^{-7}	1.99	9.35×10^{-5}
	Second	2.96	1.7×10^{-5}	8.09×10^{-9}	4.22×10^{-7}	1.84	—-
	First	2.98	1.7×10^{-5}	3.07×10^{-9}	1.79×10^{-7}	1.85	4.29×10^{-5}
III	First	8.33	1.7×10^{-5}	4.15×10^{-9}	2.40×10^{-7}	2.45	7.72×10^{-5}
	Second	2.98	1.7×10^{-5}	8.78×10^{-9}	4.40×10^{-7}	2.03	—-
	First	3.02	1.7×10^{-5}	4.61×10^{-9}	2.58×10^{-7}	2.55	8.93×10^{-5}
IV	First	8.34	1.7×10^{-5}	9.25×10^{-9}	1.18×10^{-7}	2.65	1.86×10^{-5}
	Second	3.02	1.7×10^{-5}	ill defd.	ill defd.	—-	—-

The number of electrons found by constant potential coulometry was also 2 for the first and the second waves. 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%.

The first wave is a 2-electron reduction of the N=N double bond. This wave is irreversible. There is a second wave for the acidic media corresponding to the reduction of dihydrobenzocinnoline to a tetrahydro product. This wave is also irreversible. However, the situation changes in basic media where both these waves merge giving a a small anodic peak. This behavior is quasi reversible. The difference between cathodic

and anodic peak potentials was found to be dependent upon the scan rate, showing that the behavior is nearly irreversible.
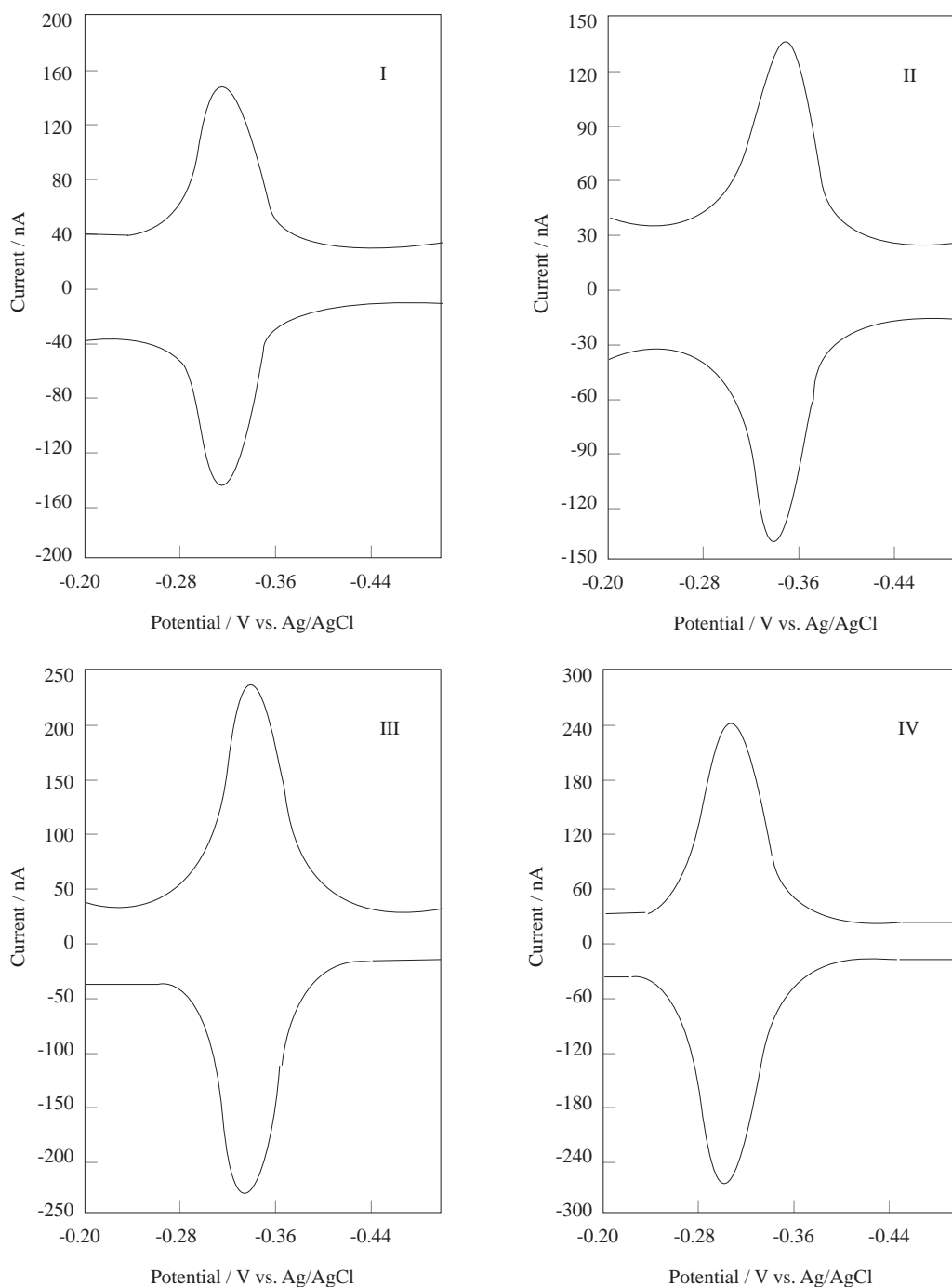

Figure 2. Cyclic voltammograms of benzo[c]cinnoline and its bromo derivatives at slow scan rates. Scan rate = 100 mV s^{-1}, c = 1.67 × 10^{-7} M, 1:5 ethanol+BR buffer. Benzo[c]- cinnoline(I), 1-Bromobenzo[c]cinnoline(II), 3-Bromobenzo[c]cinnoline(III), 4-Bromo-benzo[c]cinnoline(IV),

Adsorptional characteristics

At slow scan rates the cathodic and anodic cyclic voltammetric peaks are symmetric with respect to both the potential and current axis (Figure 2). This type of symmetric current-potential curve in cyclic voltammetry is a characteristic indication of adsorption phenomena[16]. Moreover, the adsorption of benzo[c]cinnoline and its bromo derivatives on the mercury surface was clearly observed when the scan rate was increased or concentration decreased[17]. The adsorption phenomena was also indicated by the increase of $i_p/C\sqrt{v}$ and by the insignificant decrease of i_p/Cv with increasing scan rate as shown in Figure 4. The cyclic voltammograms of the derivatives at high scan rates and at low concentrations exhibited a post peak to the normal cyclic voltammetric peak indicating the adsorption of the reactant, that is, benzo[c]cinnolines[17].

Assuming that a non-compact film of adsorbed molecules on the mercury surface was formed during the negative sweep and the adsorption was of Langmiur type, the following expression derived by Garrido et al.[16] at 25°C was exploited to calculate the diffusion coefficients of the benzo[c]cinnoline and its derivatives:

$$i_p = 1.06 \times 10^6 n^2 ACvD^{1/2}t_p^{1/2} \tag{5}$$

where t_p is the adsorption time from the beginning of the life of the drop until E_p is reached. This equation also predicts that i_p varies linearly with scan rate. This prediction was justified by the log i_p vs log v plot with a slope of about 0.8 for every molecule. Diffusion coefficients calculated from the equation (5) are given in Table 2. The values, calculated using the theoretical equation for adsorption controlled current were more realistic and very close to the literature values which are 4.26×10^{-67} and 7.65×10^{-6} cm^2/s[16]. Diffusion coefficients were also calculated using the Cottrell equation assuming that the electrode reaction was purely diffusion controlled. The higher values calculated for the purely diffusion case are almost certainly due to the omission of adsorption phenomena. These results clearly show that the adsorption phonemena should not be disregarded when one wants to find the diffusion coefficients of organic molecules.
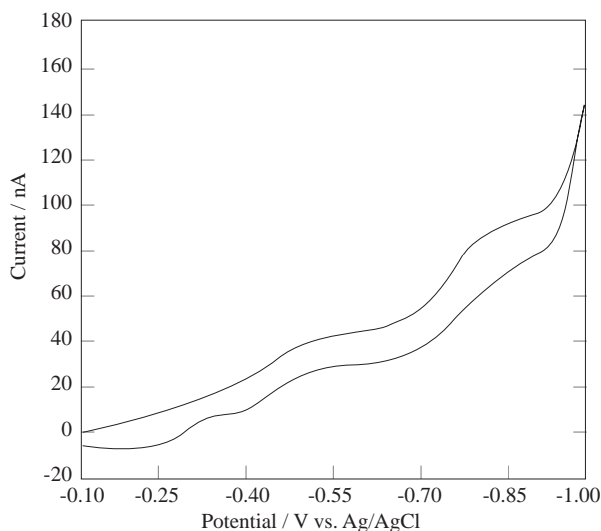

Figure 3. UME voltammogram of of benzo[c]cinnoline Scan rate = 100 mV s^{-1}, c = 1.67×10^{-7} M, 1:5 ethanol+BR buffer.

For slow scan rates, the reduction and oxidation peaks had almost symmetrical shapes with respect to the peak maxima. Under these conditions, the cathodic and anodic peak potentials E_p^c and E_p^a were nearly

equal to $E^{o'}$ for each derivative as shown in Figure 3[17]. The formal potentials found from these symmetric cyclic voltammograms for benzo[c]cinnoline and its bromo derivatives are given in Table 2.
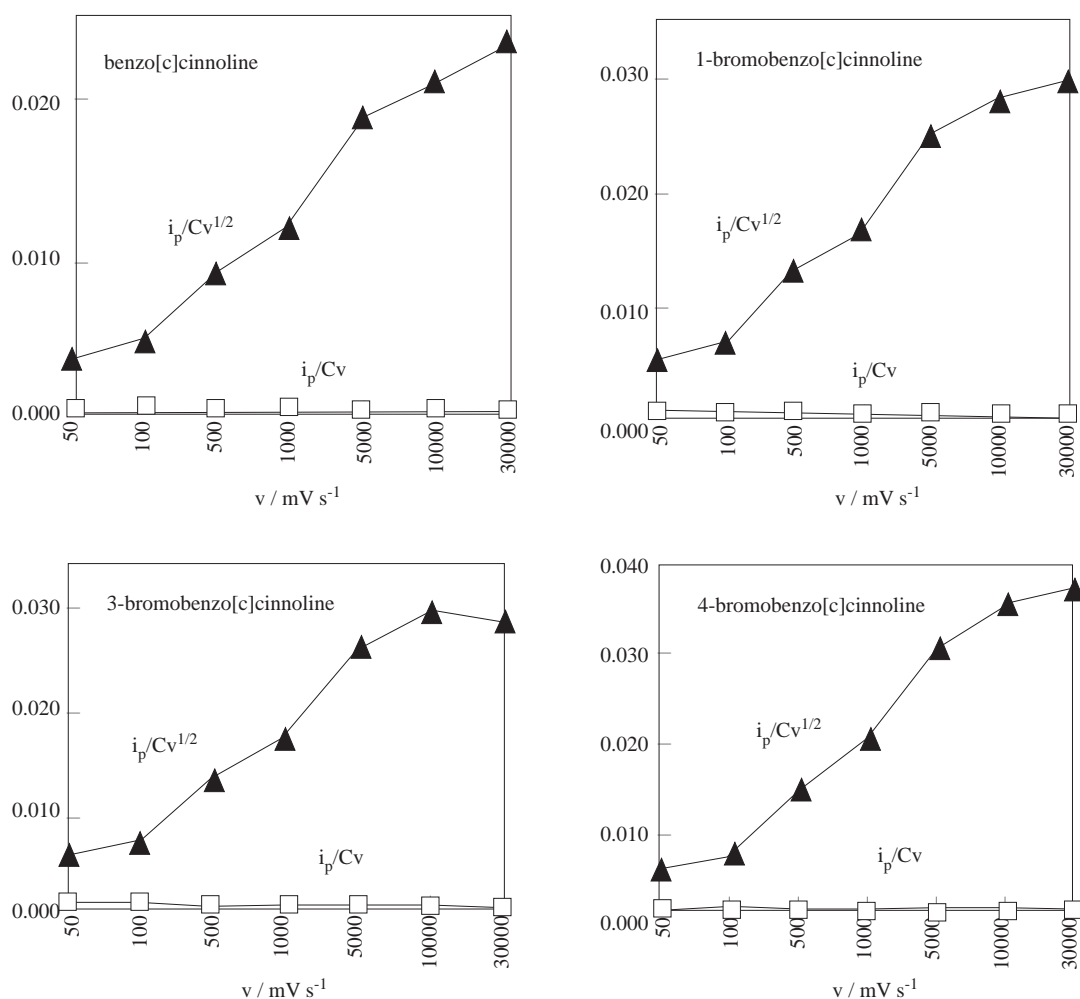

Figure 4. Adsorption of benzo[c]cinnoline and its bromo derivatives are indicated by the variation of $i_p/C\sqrt{v}$ (□) and i_p/Cv (□) functions with the scan rate.

As can be deduced from Table 2, the formal potentials of benzo[c]cinnoline derivatives vary as expected from the inductive and mesomeric effects of the substituents on the aromatic ring in acidic media. Bromo substituents in positions 1 and 4 attract electrons from the azo ring more easily than in position 3, leaving the azo ring more electron deficient. This is reflected in the less negative formal potentials for 1-Br and 4-Br derivatives compared to the parent molecule and 3-Br derivative. The benzo[c]-cinnoline itself has the most negative formal potential, indicating that the inductive effect of the substituents is operative and affects the reducibility of the reaction center in acidic media. When the resonance hybrid forms are considered, the mesomeric effect of the substituents is in the order of 1, 4, and 3, as can be seen from Table 2. These results are in accordance with our experimental results. No regular relation between the formal potentials was observed for benzo[c]-cinnoline derivatives in basic media. In basic medium the azo ring becomes more electron-rich, because of the presence of the unshared electrons on the nitrogen atoms, causing the inductive and mesomeric effects of the substituents to become less operative.

Table 2. Diffusion coefficients, formal potentials and adsorptional characteristics of benzo[c]-cinnolines and its bromo derivatives. $c = 1.67 \times 10^{-5}$ M, 1:5 ethanol + BR buffer.

Comp	pH	D (cm^2/s)	E^o(mV)^a	pH	Γ (mole/cm^2)
	2.89	3.01×10^{-6}	-409.85±0.58	4.58	4.45×10^{-11}
I	11.36	3.45×10^{-6}	-919.70±0.48	9.96	4.93×10^{-11}
	2.61	7.76×10^{-6}	-348.15±0.99	4.81	7.38×10^{-11}
II	11.48	1.90×10^{-5}	-921.85±1.76	9.81	1.19×10^{-11}
	2.60	7.42×10^{-6}	-387.40±0.76	4.75	2.42×10^{-11}
III	11.48	8.14×10^{-6}	-940.40±2.36	9.96	2.64×10^{-11}
	2.76	6.97×10^{-6}	-365.80±0.76	4.80	1.37×10^{-11}
IV	11.40	1.74×10^{-5}	-917.28±1.78	10.01	4.94×10^{-11}

a) Confidence limits with 90% probability levels.

Surface concentration measurements

The surface concentrations of the adsorbed molecules of benzo[c]cinnoline and its bromo derivatives were 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 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:

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

where 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[18]. The details of chronocoulometric measurements of the amount of adsorbed species were given elsewhere[18,19]. The amounts of reactants adsorbed on the mercury surface (Γ, mol/cm^2) are given in Table 2. No noticable differences were observed in the adsorbed amount for the compounds studied.

Mechanism of the electrode reaction

Two entirely different mechanistic schemes for the reduction of benzo[c]-cinnoline in aqueous media were proposed[4,12].

According to Millefiori, benzo[c]cinnoline in acetonitrile in the presence of water or other proton donors is reduced in two 2-electron waves and the most probable final reduction product on a mercury electrode is 2,2$^{'}$-diaminobiphenyl[4]. The first wave represents the reduction of the molecule to the dihydro compound. The second 2-electron wave is claimed to be due to the -N-N- bond breakage forming 2,2$^{'}$-diaminobiphenyl. No experiments to identify the final product were reported. His inference is based on the fact that a) all *ortho*-diazines suffer the electrochemical reductive cleavage of the N=N bond, b) the chemical reduction of benzo[c]-cinnoline gives 2,2$^{'}$-diaminobiphenyl, and c) the assumption of the impossibility of any alternative reduction of biphenyl moiety due to the presence of electron donating NH substituents[4].

Alternatively, Gupta and Raina claim the reduction of biphenyl moiety to 2,7,9,10-tetrahydrodiazaphenanthrene in acidic pH ranges of Stafford buffer containing 20% ethanol[12]. Their inference is based on a) the analogy of reduction of 9,10-dihydrophenantrene to 1,4,9,10-tetrahydrophenantrene, and b) 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 parent molecule respectively. These authors contend that benzo[c]cinnoline is not reduced in basic pH values in Stafford buffer[12].

Our experimental observations reveal that benzo[c]cinnoline and its bromo derivatives are reducible with two 2-electron waves in an extensive pH range from 2 to 12 in universal BR buffer, which is almost identical to Gupta and Raina's working medium. The UME results (Figure 3) reveal two waves corresponding to a 2 electron transfer each. Our experiments indicate that the mechanism proposed by Gupta and Raina is plausible. That is, the first wave is the reduction of benzo[c]cinnoline to dihydrobenzo[c]cinnoline with a quasi-reversible behavior. The second irreversible wave is due to the reduction of dihydrobenzo[c]cinnoline to tetrahydro product:
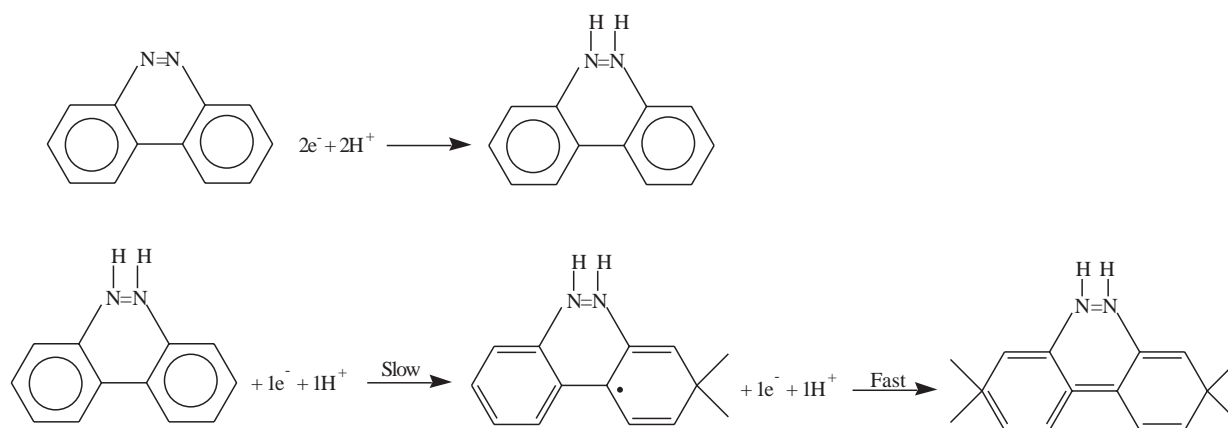
The fact that the compounds undergo only one 2-electron reduction in basic media shows that the reduction stops at the dihydrogenated step.

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 cm^2. A few mg's of solid product was obtained. In the IR spectra of this product (KBr disk) there were no characteristic -NH$_2$ bands observed on the spectrum of 2,2$'$-diaminobiphenyl, ca. 3387 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 and 2876 cm^{-1} are present, indicating that the final product is much more likely to be 2,7,9,10-tetrahydrodiaza-phenantrene.

Acknowledgment

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