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The polarographic behaviour of benzo[c]cinnoline in acetonitrile in the presence of various proton donors (water, phenol, benzoic acid and perchloric acid) is reported. In aprotic medium benzo[c]cinnoline is reduced in two one-electron waves, followed by one two-electron wave. The most probable final reduction product is 2,2'-diaminobiphenyl. The addition of proton donors causes a shift and/or appearance of new polarographic waves, which can be related to the reduction of various protonated species.

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Benzo[c]cinnoline may be considered to be a model compound for a planar aromatic *cis*-azo structure. It can be prepared from azobenzene by cyclodehydrogenation (1). In spite of structural similarities, the physico-chemical properties of *ortho*-diazines and azo compounds is rather different in many instances, as exemplified by spectroscopic characteristics (2). Important similarities, however, reside in the fact that both series of compounds very probably have positive gas-phase electron affinities (EA). Available experimental data are: pyridazine, EA = 0.317 eV (3); azobenzene, EA = 0.40 eV (4). Accordingly, *ortho*-diazines and aromatic azo compounds should display stable radical anions, which may be observed in cyclic voltammetry, so that the potential determining step is a one-electron diffusion-controlled, reversible process (5-8). Study of the polarographic behavior of acyclic aromatic *cis*-azo compounds may prove difficult owing to the rapid isomerization of the *cis*-azo radical anion to the *trans* form. The present work is intended to study the effects of various proton donors on the electrode reduction of a *cis*-structured azo compound, benzo[c]cinnoline, in acetonitrile solutions.

Results and Discussion.

The polarographic data for the reduction of benzo[c]cinnoline in acetonitrile in the presence of water, phenol, benzoic acid and perchloric acid, as proton donors, are summarized in Figures 1 and 2.

Reduction in aprotic medium.

In anhydrous acetonitrile solutions, benzo[c]cinnoline shows two one-electron waves at half-wave potentials $E_{1/2}$ of -1.554 and -1.863 V, respectively, followed by a two-electron wave with $E_{1/2} = -2.40$ V (curve 1 of Figure 1). The first two waves represent a reduction mechanism similar to that found in *ortho*-diazines (5,8,12) and azo hydrocarbons (6,10,13,14) in aprotic media: the first wave is the reversible step to form the monoanion; the second wave is irreversible owing to fast protonation reactions of

the dianion, and forms the dihydro compound. Wave C very probably corresponds to the reduction of the $-NH-NH-$ bond to give 2,2'-diaminobiphenyl. This inference is based on the fact that: a) all *ortho*-diazines suffer the elec-

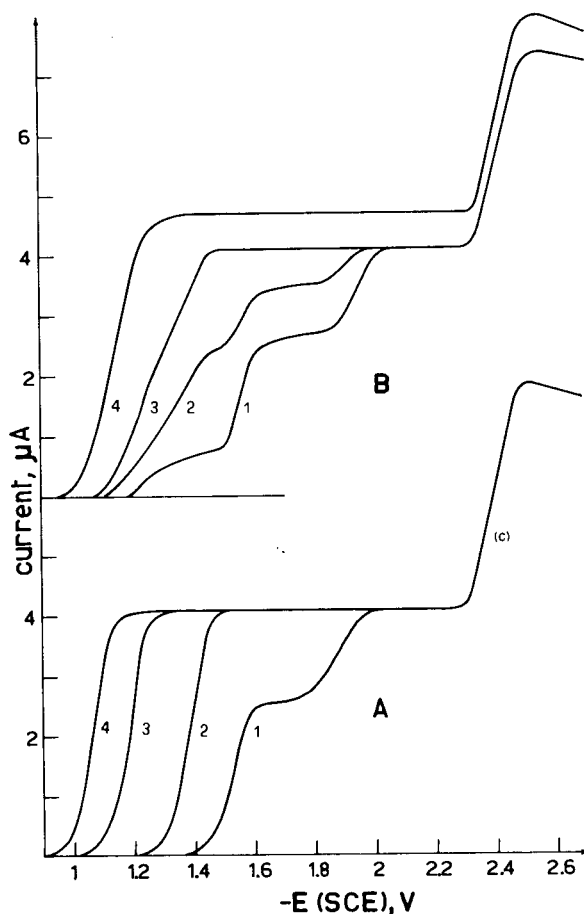


Figure 1. A) Effect of water addition on d.c. polarograms of benzo[c]cinnoline. Water content: (1) 0, (2) 1%, (3) 5%, (4) 10%. B) Effect of phenol addition. Phenol concentration: (1) 10^{-4} , (2) $6 \cdot 10^{-4}$, (3) $1.3 \cdot 10^{-3}$, (4) $6 \cdot 10^{-3} M$.

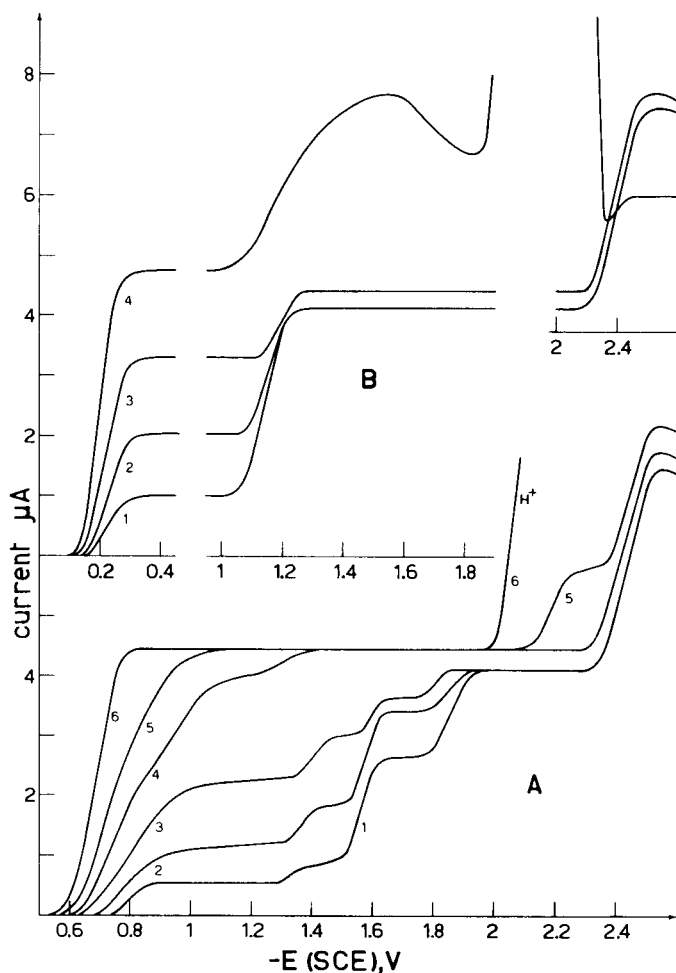
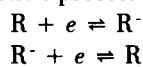
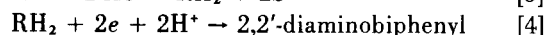
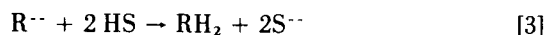


Figure 2. A) Effect of benzoic acid addition on d.c. polarograms of benzo[c]cinnoline. Benzoic acid concentration: (1) 10^{-4} , (2) $3 \cdot 10^{-4}$, (3) $6 \cdot 10^{-4}$ (4) $1.2 \cdot 10^{-3}$, (5) $2 \cdot 10^{-3}$, (6) $5 \cdot 10^{-3} M$. B) Effect of perchloric acid addition. Perchloric acid concentration: (1) $3 \cdot 10^{-4}$, (2) $6 \cdot 10^{-4}$, (3) 10^{-3} , (4) $4.2 \cdot 10^{-3} M$.

trochemical reductive cleavage of the N=N bond (12,15,16); b) the chemical reduction of benzo[c]cinnoline gives 2,2'-diaminobiphenyl (1); and c) the alternative reduction pathway should involve the biphenyl moiety. Biphenyl is indeed reduced to a much more negative potential than $E_{1/2}$ of wave C: in dimethylformamide a single one-electron wave is observed at $E_{1/2} = -2.59$ V (*vs* S.C.E.) (17), the second wave lying beyond the discharge of the supporting electrolyte. In 96% aqueous dioxane it is reduced at $E_{1/2} = -2.8$ V (*vs* S.C.E.) (18). Moreover, the two electron-donor NH groups should make the reduction of biphenyl more difficult. The overall reduction process may be written as follows:



[1]
[2]



It is worth noting the smaller disproportionation energy value for the reaction:



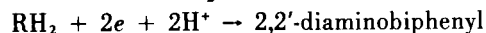
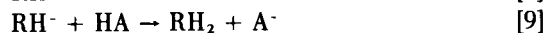
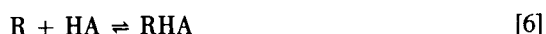
for benzo[c]cinnoline (-0.31 eV) than for azohydrocarbons (*ca.* 0.6 eV) (6,9), as measured by the difference between $E_{1/2}$ (second wave) and $E_{1/2}$ (first wave). This accounts for a greater solvation energy of R^{2-} in *ortho*-diazines than in azo hydrocarbons as a consequence of their greater basicity, and also for a minor stability towards reaction [5] for R^- in *ortho*-diazines than in azo hydrocarbons, which is indicative of a greater delocalization of the extra electron in the latter compounds.

Effect of Water Addition.

Water addition to acetonitrile solutions causes the first wave to grow at the expense of the second wave and to shift to more positive potentials. In 99% acetonitrile the two waves coalesce in a single two-electron wave. Thus, the reduction mechanism is of the e.c.e.c. type as found in the related cinnoline compound (12) and in the azobenzene (6). The water content which causes coalescence is much less than in the case of cinnoline (12) and azobenzene (6), in agreement with the greater basicity of the benzo[c]cinnoline anion as compared with the basicities of the anions of cinnoline and azobenzene. The shift to more positive potentials of the first wave on the addition of water is larger than that expected owing to changes in the dielectric constant of the medium, on the basis of Born theory. Undoubtedly, some specific interactions, such as hydrogen bonding interactions, occur between water molecules and radical anions. Wave C results unaffected by the medium composition.

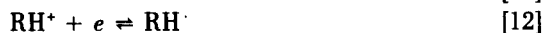
Effect of Phenol Addition.

On adding phenol, a pre-wave is observed at a potential *ca.* 0.25 V more positive than the first wave in acetonitrile. As further acid is added, the height of the first wave increases with respect to the second wave; simultaneously the pre-wave increases at the expense of both waves, until a single two-electron wave is observed when the concentration of the phenol approximately doubles the depolarizer's concentration. This behavior is similar to that shown by many organic compounds (19), including azobenzene (20). The appearance of the pre-wave corresponds to the formation of a hydrogen-bonding type complex between phenol and benzo[c]cinnoline. In fact, intermolecular as well as intramolecular hydrogen-bonding interactions may lead to a decrease of the energy of the lowest unoccupied molecular orbital, hence to a lower reduction potential (21,22). Here again wave C is practically unaffected by the presence of the phenol. The overall electrode reduction may be formulated as follows.



Effect of Benzoic Acid Addition.

The addition of benzoic acid produces marked differences in the electroreduction behavior of benzo[c]cinnoline, with respect to the addition of phenol. Now two pre-waves are observed, the first of which occurs at a potential noticeably more positive (*ca.* 0.8 V) than the first wave. The evolution of these waves is clearly apparent from Figure 2. Since benzoic acid is a much stronger proton donor than phenol, it is very likely that pre-waves are due to the reduction of the protonated benzo[c]cinnoline and of the hydrogen-bonding complex, respectively, through a mechanism somewhat similar to that proposed for the reduction of azobenzene in the presence of acetic acid (20):



followed by reactions [8], [9], and [4].

This mechanism differs from that proposed for the electrode reduction of some nitrogen heterocycles (12,23) in the presence of benzoic acid, which is based on the assumption that $E_{ARHA} > E_{ARH^{\cdot}}$. If this assumption is valid, an intermediate wave would also appear in the polarographic reduction of benzo[c]cinnoline in the presence of perchloric acid since $E_{1/2}(RH^{+}) < E_{1/2}(RHA)$. Actually, no such wave is observed (Figure 2, B), and thus it is reasonable to assume $E_{ARH^{\cdot}} > E_{ARHA}$. Wave C appears to be split when more than $1.2 \times 10^{-3}M$ benzoic acid is added. The total height of the two resulting waves equals the height of the initial wave. The protonated dihydrobenzo[c]cinnoline is therefore the most probably electroactive species.

Effect of Perchloric Acid Addition.

The addition of perchloric acid to 95% aqueous acetonitrile gives rise to a pre-wave at a potential much more positive than the first wave (*ca.* 1 V). The pre-wave increases at the expense of the next wave until a single two-electron wave is obtained, when the perchloric acid concentration doubles the depolarizer's concentration. The pre-wave is associated with the reduction of protonated benzo[c]cinnoline: reactions [10], [12], [13], [8] and

[9]. Wave C is unaffected by a low concentration of perchloric acid. For a perchloric acid concentration greater than $10^{-3}M$, wave C is submerged by the hydrogen wave. In this case the polarographic behavior of benzo[c]cinnoline resembles that observed in buffered aqueous solutions (15).

EXPERIMENTAL

Benzo[c]cinnoline was obtained commercially and was purified by sublimation before use. Spectrograde acetonitrile was dried over neutral alumina and distilled at constant boiling point. Polarographic grade tetraethylammonium perchlorate was used as a supporting electrolyte. It was dried under reduced pressure at 90°.

Direct current polarograms were recorded with a three electrode Amel polarograph model 563. The potentials were referred to a saturated calomel electrode (S.C.E.). The temperature was maintained at $25 \pm 0.5^{\circ}$.

Acknowledgement.

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