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# Electrochemical Oxidation of Benzidine and Hydrazobenzene

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The electrochemistry of benzidine and hydrazobenzene was studied in water-acetonitrile mixed solutions at various pHs and the results are reported. The cyclic voltammetric peak for the oxidation of benzidine shows a pH dependency of −62 mV/pH in the pH range of 0-3.5, no pH dependency between pH values of 3.5 and about 10.5, and of about −50 mV/pH between pH=10.50 and 14.0, indicating that oxidation mechanisms differ depending on the pH of the medium. However, the CV peak for the hydrazobenzene oxidation is shown to be independent of pH of the medium, suggesting that the proton is not involved in the rate limiting step of the electrochemical oxidation of hydrazobenzene to azobenzene. Results of *in situ* spectroelectrochemical experiments indicate that the oxidation products obtained during the oxidation of benzidine and hydrazobenzene depend on the result of dynamic equilibria taking place at various pHs.

## Introduction

The electrochemistry of benzidine and hydrazobenzene is an important component in understanding and controlling electrochemical polymerization reactions of aniline in acidic aqueous media, because various dimers of aniline have been identified during the early stage of the oxidation of aniline at low concentrations.[1-6] These dimers have been shown to proceed to produce polyaniline; some dimers are more important than others.[7] Of three possible dimers produced, a head-to-tail dimer, *p*-aminodiphenylamine (or N-phenyl-*p*-phenylene diamine), would be the most desirable intermediate for preparing polyaniline. Both benzidine and hydrazobenzene have been shown to polymerize to polyaniline,[7] although physical properties of polyanilines prepared from different precursors have not been characterized.

The electrochemistry of benzidine has been studied by several groups of investigators for different reasons. It has been studied as an indicator for redox titrations[8,9] and as a model to study the oxidation mechanisms involved in primary, secondary, and tertiary aromatic amines.[10-12] Only a few studies on the electrochemistry of hydrazobenzene has been reported due to its instability in an acidic medium owing to the benzidine rearrangement reaction.[13,14] The reduction of azobenzene to hydrazobenzene in acidic media,

which was shown to be reversible on polarographic time scale, has been used as a model for studying electrochemical-chemical (EC) reaction mechanisms to develop electrochemical techniques.[15-18] The electrochemically reduced product of azobenzene, *i.e.*, hydrazobenzene, undergoes a benzidine rearrangement reaction[19] and thus served as a model reaction for developing electrochemical techniques for studying EC reactions.

In this study, we have conducted cyclic voltammetric and *in situ* spectroelectrochemical studies on the electrochemistry of benzidine as well as hydrazobenzene in a wide range of pHs and report the results. The results indicate that benzidine undergoes a two electron transfer in acidic solutions to form a deprotonated dication, benzidinequinonediimine. In the medium pH range, it undergoes two one electron step reactions as in nonaqeous solvents. The chemical reversibility of the electrochemical reaction of the hydrazobenzene-azobenzene pair is also demonstrated by *in situ* spectroelectrochemical techniques.

## Experimental

Aldrich's hydrazobenzene and Matheson's benzidine were used after sublimation. Other chemicals of ACS reagent grade were used without further purification. Stock solutions
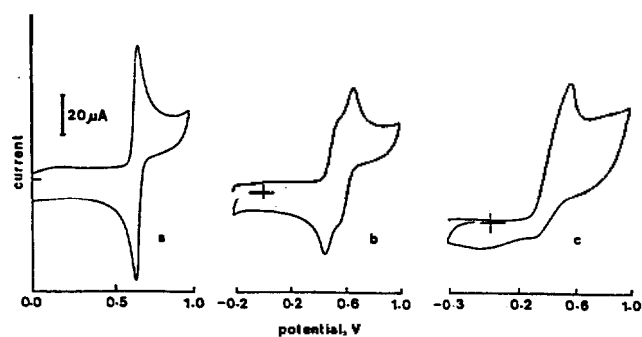
**Figure 1.** Cyclic voltammograms for the oxidation of 1.0 mM benzidine in a 30% acetonitrile and 70% water mixed solvent at pHs of: (a) 0.93, (b) 3.68, and (c) 6.46. The scan rate was 100 mV/s.
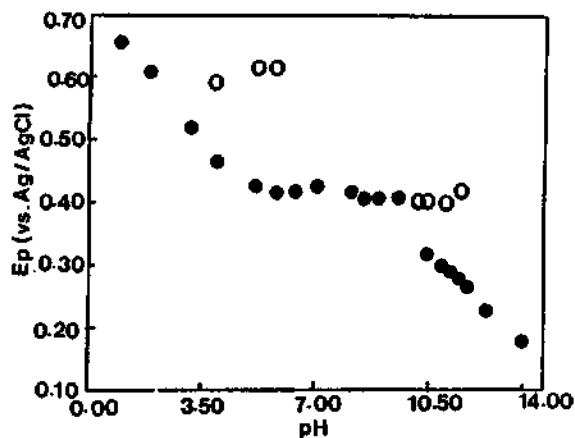


**Figure 2.** Cyclic voltammetric peak potentials for the benzidine oxidation at various pHs.



**Figure 3.** Typical cyclic voltammogram recorded at 100 mV/s for the oxidation of 1.0 mM hydrazobenzene at pH=1.68.

of 0.010 M benzidine and hydra/obenzene were first prepared in acetonitrile and used after appropriated dilution so that the final concentration was 1.0 mM in benzidine or hydrazobenzene in a 30% acetonitrile-70% water mixed solvent with their pHs adjusted to proper values with potassium hydrogen phthalate, hydrochloric acid, and/or sodium hydroxide. The ionic strengths of the solutions were adjusted to 0.20 by adding proper amounts of KCl.

Electrochemical measurements were made with a Princeton Applied Research (PAR) model 173 or PAR 273 potentiostat-galvano-stat. A near normal incidence reflectance spectroelectrochemical setup described elsewhere[20-22] was used to record spectra during electrolysis. A reflective platinum disk electrode (Sargent-Welch catalog number, S-30101-20) with a platinum disk diameter of 6.5 mm was used after polishing with 0.2 μm alumnina slurries. An Ag/AgCl, sat'd. KCl electrode and a platinum spiral wire were used as a reference and counter electrodes, respectively.

## Results and Discussion

Figure 1 shows typical cyclic voltammograms (CVs) recorded during the oxidation of benzidine at pH values of 0.93, 3.68, and 6.46, respectively. In CVs recorded at lower pHs, a small current attributable to the oxidation of hydrazobenzene is noticed at about 0.26 V. The CV in Figure 1(a) shows
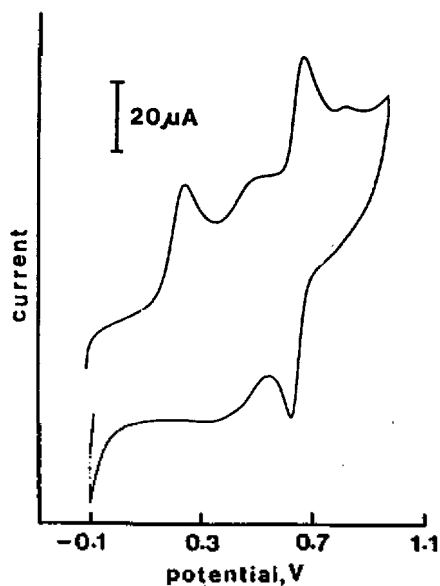
a well defined, reversible two electron wave as can be judged from the $\Delta E_p$-value of about 30 mV at pH=0.93, whereas two consecutive reversible waves are seen in the CV shown in Figure 1(b). The oxidation wave is not reversible any more at pH=6.46 (Figure 1(c)).

The dependency of the peak potential on pH for the benzidine oxidation is shwon in Figure 2. As can be seen in this figure, the pH dependency is very complex. At lower pHs between pH=0 and 4.0, a relation of

$$E_p = 0.722 - 0.062 \ pH \ V \tag{1}$$

is observed indicating that two protons are involved in the reaction as in

$$BZ \rightleftarrows BZ^{2+} + 2H^+ + 2e^- \tag{2}$$
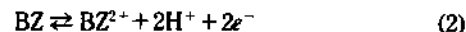
The benzidine dication produced is in resonance with a quinoid structure, benzidinediquinoneimmine (BZDQI), which is protonated in acidic medium.[10] The protonated diquinonediimine, BZDQI·2H⁺, is shown to be very stable in acidic medium. The standard electrode potential would then be 0.694 V, which is in good agreement with the value reported by Oldfield and Bockris (0.723 V) in a sulfuric acid solution.[10] The discrepancy between their and our results might have resulted from the difference in media in which measurements have been made. At pHs higher than 3.5, two CV peaks are observed as shown in Figure 1(b) and the second CV peak potential appearing at about 0.6 V is practically independent of the pH, while the first oxidation peak still shows the same pH dependency up to pH=5.8. This indicates that the proton is not involved in the rate determining step of the oxidation of the second species. We believe that the oxidation of benzidine is a two one-electron process in this pH region and the first electron transfer product is a radical cation according to the reaction,

$$BZ \rightleftarrows BZ^{+\cdot} + e^- \tag{3}$$

followed by

## CV Peak Currents

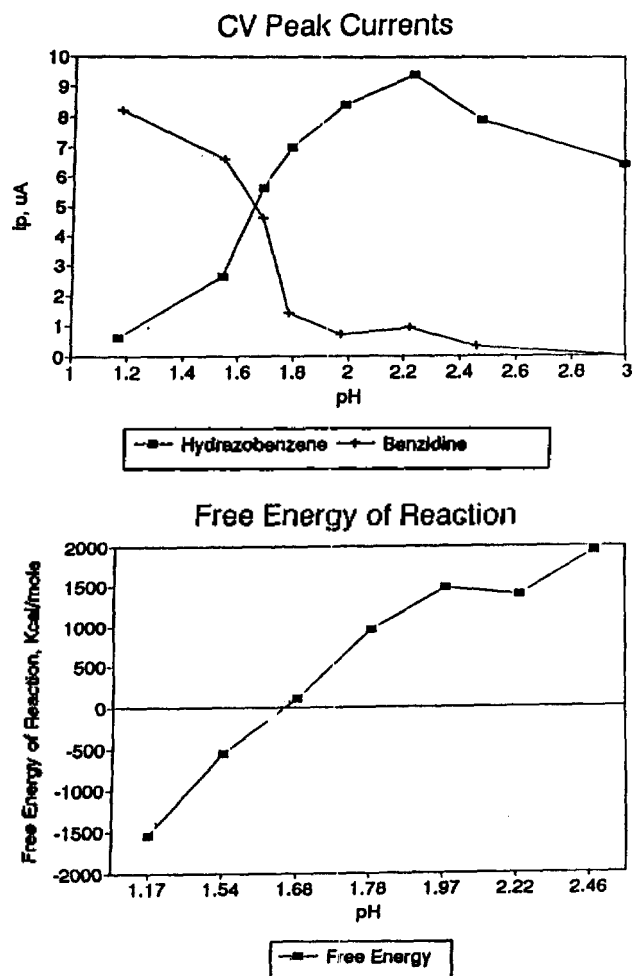

## Free Energy of Reaction



**Figure 4.** (a) Cyclic voltammetric peak currents for oxidations of benzidine and hydrazobenzene at various pHs, and (b) the free energies of reaction [5] for the benzidine rearrangement calculated from respective CV peak currents at various pHs.

$$BZ^{+\cdot} \rightleftarrows BZ^{2+} + e^- \qquad (4)$$

as in nonaqueous solutions. The stability of the radical cation of benzidine has been demonstrated in nonaqueous solutions.[11] Above pH = 10.30 however, another small prepeak is observed at around 0.28 V suggesting that another electroactive compound might have been produced from benzidine. Benzidinequinonediimine undergoes a hydrolysis reaction to a corresponding quinone in an alkaline solution.[10]

Figure 3 shows a typical CV recorded from hydrazobenzene, whose initial concentration is 1.0 mM, in a solution with its pH = 1.68. There are four anodic CV peaks seen in this Figure, *i.e.*, at 0.26, 0.54, 0.70, and 0.85 V. The CV peak at 0.70 V is easily identified as that of benzidine from its peak potential and $\Delta E_p$. The oxidation at 0.26 V arises from oxidation of hydrazobenzene as it is observed in any solutions containing hydrazobenzene. The ones at 0.54 and 0.85 V must be from other rearrangement reaction products including diphenyline. The benzidine rearrangement reaction is

$$\text{hydrazobenzene} \rightleftarrows \text{benzidine} + \text{diphenyline} \qquad (5)$$

with other minor products. Since the major product is benzi-
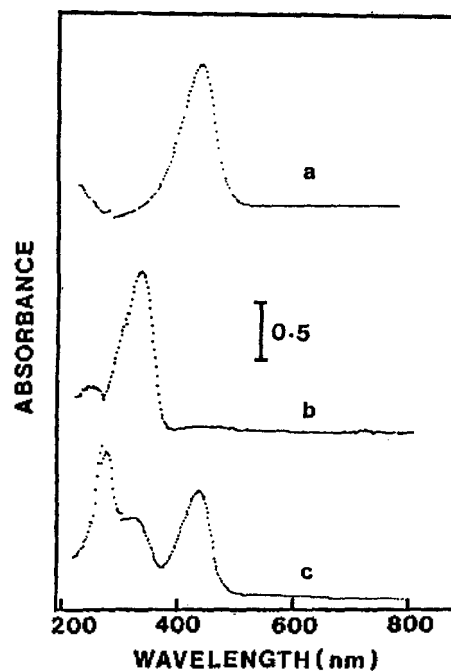


**Figure 5.** Spectra recorded during electrolysis of 1.0 mM hydrazobenzene in: (a) 1.0 M HCl at 0.75 V, (b) at pH = 4.79 at 0.27 V, and (c) at pH = 2.20 at 0.891 V.

dine, we decided to make measurements on CV currents arising from hydrazobenzene and benzidine only. The hydrazobenzene CV wave has been known to undergo a two electron oxidation to azobenzene according to

$$\text{hydrazobenzene} \rightleftarrows \text{azobenzene} + 2H^+ + 2e^-. \qquad (6)$$
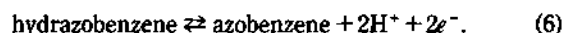
However, the CV peak potential in our study does not show a pH dependency suggesting that the proton is not involved in the rate determining step of the oxidation. This is also shown in CV shapes since no reversal (cathodic) peak is observed for the oxidation of hydrazobenzene. This indicates that the immediate electron transfer product for the hydrazobenzene is not observed during the cathodic scan; an early view that the redox reaction of the azobenzene-hydrazobenzene is polarographically reversible does not appear to be true. Our results indicate that the reaction should be described as a repeated EC (electrochemical-chemical) reaction type, *i.e.*,

$$RH_2 \rightleftarrows RH_2^{+\cdot} + e^- \qquad (7)$$

$$RH_2^{+\cdot} \rightarrow RH\cdot + H^+ \qquad (8)$$

$$RH\cdot \rightleftarrows RH^+ + e^- \qquad (9)$$

$$RH^+ \rightarrow R + H^+ \qquad (10)$$

where $R$ is azobenzene and $RH_2$ is hydrazobenzene with the overall reaction of

$$RH_2 \rightarrow R + 2H^+ + 2e^- \qquad (11)$$

Since the measurements were made at least about 30 minutes after the solution was prepared, the current ratio at various pHs indicate the extent of the equilibrium reached for the benzidine rearrangement reaction. Figure 4 shows their respective current measured at various pHs (a) and

the free energy of the reaction calculated from the respective current ratio (b). It can be seen in Figure 4(b) that hydrazobenzene is more favorable above pH=1.7 in the equilibrium reaction.

The dynamic equilibrium of the benzidine rearrangement reaction was also demonstrated by the results of spectroelectrochemical experiments. When a 1.0 mM hydrazobenzene solution in a 1.0 M HCl is oxidized at 0.75 V, a spectrum shown in Figure 5(a) is obtained. Here the major oxidation product is the quinoid form of benzidine produced from reaction [2], which shows an absorption band at 428 nm, after the benzidine rearrangement reaction [5]. We ran similar experiments on a 1.0 mM benzidine solution in acidic solutions of various pHs, and only one absorption band at 428-430 nm was observed (not shown). Benzidinequinonediimine, which was shown to have at least 50 minutes of the half-life,[9] was reported to absorb at 428 nm.[4,8,9] This spectrum indicates that 100% of hydrazobenzene has been converted to benzidine before electrolysis. When it is oxidized at 0.27 V in a solution of pH=4.7, a spectrum shown in Figure 5(b) is obtained. Here, the only oxidation product is azobenzene with its absorption peak at 322 nm.[8] Note also a band observed at about 420 nm with a low absorbance, which should be from the oxidation product of benzidine, BZDQI. It was demonstrated that this band is the only observed one even at higher electrode potentials (not shown). Also, azobenzene was shown to be the major electrolysis product in solutions of pHs higher than 2.0. When the pH is between 1.54 and 2.48, a spectrum as shown in Figure 5(c) is obtained during the electrolysis at 0.89 V. Four species are seen to be present in this spectrum. Absorption peaks at 264 nm (benzidine), 290 nm (hydrazobenzene), 326 nm (azobenzene), and 426 nm (benzidine diquinone) are all observed. While the two absorption peaks at 264 nm and 290 nm overlap heavily, their oxidation products are very well resolved at 326 nm and 426 nm.

From these observations, we conclude that the following reaction scheme describes the dynamic relations for the electrochemical oxidation of benzidine and hydrazobenzene:

Hydrozobenzne ⇄ Benzidine
　pH≥1.7　　　　pH≤1.7
　　↓　　　　　　　↓
Azobenzene　　Benzidine diquinone
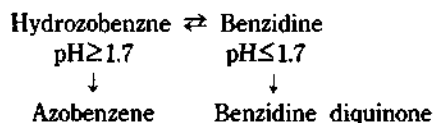
In a medium with its pH higher than 4.0, benzidine appear to undergo a chemically reversible one-electron transfer to form a radical cation first, followed by a further oxidation to the dication. In these cases, the deprotonation of the oxidized species and its conjugation to the quinoid structure may be a rate limiting step. As the pH of the medium becomes higher, the oxidation reaction becomes irreversible as is evidenced by the lack of the reversal, cathodic current in CVs. The reaction shows a pH dependency again at higher pHs indicating that the proton affects the oxidation of benzidine. We have not been able to identify the products produced in alkaline aqueous media.

Hydrazobenzene undergoes a two electron oxidation to azobenzene in nonqueous solutions as well as in alkaline aqueous medium.[24,25] For this reason, we have not investiga-

ted the details of the oxidation of hydrazobenzene in high pH media.

In conclusion, the benzidine rearrangement equilibrium is facile, and the head-to-head dimer, hydrazobenzene, produced during the early stage of the aniline polymerization is shown to undergo a rapid rearrangement to benzidine. When the pH is moderately high, hydrazobenzene may be formed as a dimer. This may explain the poor conductivities of polyaniline prepared in a medium of higher pHs. Both benzidine and hydrazobenzene have been shown to initiate the polymerization reaction of aniline without having to oxidize aniline.

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