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Original Scientific Paper

Electrochemical Reduction of 2-(2-Thiazolylazo)-*p*-cresol at a Pyrolytic Graphite Electrode

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The electrochemical reduction of 2-(2-thiazolylazo)-*p*-cresol has been studied in phosphate buffers of different pH at a pyrolytic graphite electrode. The reduction of the dye occurred in a single well-defined 4e, $4H^+$ step and the electrode reaction was found as ECE. The reduction products were separated and characterized by m.p., ^{1}H-NMR and mass spectra. The hydrazo intermediate was found to be unstable and undergoes further reaction, the rate of which obeys the equation rate = $r^0 + k_H [H^+] + k_{OH} [OH^-]$.

INTRODUCTION

Azo compounds constitute an interesting class of organic compounds because of their laboratory applications as acid-base, redox and other indicators. They are also well known for their use in the dye industry and pharmacy.[1] As azo compounds have been found to reduce to the corresponding amines in the liver and intestines,[2] the polarographic reduction of azo compounds has been widely studied.[3,4] In general, it is accepted that reduction of azo compounds at d.m.e. occurs in the 2e, $2H^+$ step to give hydrazo product, whereas, in the presence of strong electron donating substituents such as -OH and $-NH_2$, a four electron reduction has been observed.[5–7] The main data concerning the polarographic studies of azo compounds have been summarized in many reviews.[8–10] Inspite of the fact that polarographic studies do not provide information about reverse reactions, very few attempts have

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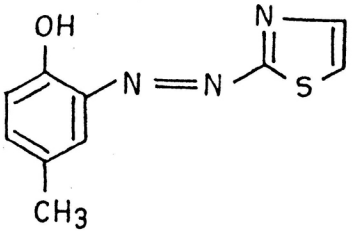
been made to study the redox-reactions of azo compounds at solid electrodes.[11] This paper describes the voltammetric behaviour of an azo dye 2-(2-thiazolylazo)-*p*-cresol (**I**) used for determination of trace metals by the spectrophotometric method,[12] at a pyrolytic graphite electrode. It has been observed that the unstable hydrazo compound formed undergoes further reactions in a first order reaction with respect to hydrogen ion concentration. A reaction mechanism has been suggested on the basis of product characterization.



(**I**)

EXPERIMENTAL

2-(2-thiazolylazo)-*p*-cresol was obtained from Sigma Chemical Co. USA and used as received. All studies were carried out in phosphate buffers[13] of ionic strength 1.0 M, prepared from reagent-grade chemicals. The equipment used for linear and cyclic sweep voltammetry, controlled potential electrolysis and spectral studies were essentially the same as described previously.[14, 15] The pyrolytic graphite electrode (PGE) used was prepared by the method reported in the literature[16] and had an area of 3.1 mm^2.

The stock solution (1mM) of **I** was prepared in methanol (AnalaR). The appropriate volume of the stock solution was then mixed with buffer of desired pH so that the overall percentage of methanol in the mixture became 40%. The pH values reported were determined after the addition of methanol. The solution was then bubbled with nitrogen for 8–10 min and voltammetric curves were recorded. The value of n, the number of electrons involved in the electrode reaction, was determined by the method of Lingane.[17] As the regeneration of the starting material occurred during electroreduction, the controlled potential electrolysis was carried out in a conventional H-cell. The total coulombs were determined only up to the time when the yellow colour of the solution turned colourless.

The kinetic study of disproportionation of the hydrazo intermediate was carried out by reducing the solution of **I** at a potential 100 mV more negative than peak I_a in a conventional H-cell. When the absorbance at λ_{max} was reduced to 50–60%, the potential was turned off and 2.0 mL of the solution was transferred immediately to a 1 cm quartz cell. The change in absorbance with time was monitored at selected wavelengths and the values of k were calculated from log $(A–A_\alpha)$ *versus* time plots.

The products of the electrode reaction were characterized by electrolyzing about 10–12 mg of compound **I** in a buffer of desired pH. The progress of electrolysis was monitored by recording cyclic voltamograms at different time intervals. When the reduction peak 1_c completely disappeared, the electrolysis was stopped and the exhaustively electrolyzed solution was transferred to a 100 mL RB flask and lyophilized. The freeze dried material was dissolved in 1–2 mL of water and passed through a glass column packed with Sephadex G-10 (Sigma, bead size 40–120 μ) using 40% methanol as eluent. The flow rate was adjusted to 0.2 mL/min and the fractions of 5 mL each were collected. The absorbance of each fraction was monitored at 210 nm. The absorbance-volume plot exhibited four prominent peaks between 170–210 mL (P_1); 210–225 (P_2); 270–295 (P_3) and 305–330 mL (P_4). The first two peaks were found to contain phosphate and were therefore discarded. The volumes under the other two peaks were collected separately and lyophilized. The colourless dried materials obtained were characterized by m.p., IR and mass spectra.

RESULTS AND DISCUSSION

Linear sweep voltammetry of compound **I** in the pH range 2.0–11.2 at a sweep rate of 20 mV s^{-1} exhibited one well-defined reduction peak (1_c). The peak potential of peak 1_c was linearly dependent on pH (Figure 1) and the dependence of E_p on pH can be expressed by the relation:

$$-E_p \text{ (pH = 2.0–11.2)} = [25 + 60 \text{ pH}] \text{ mV } \textit{vs.} \text{ SCE}$$

Cyclic sweep voltammetry 0.4 mM solution of thiazolylazo-*p*-cresol exhibited a well-defined reduction peak (1_c) in the entire pH range studied. In the reverse sweep, two oxidation peaks (1_a and 111_a) were observed below pH = 7.0, whereas at pH > 7.0, three anodic peaks were noticed. When the sweep direction was changed again, no new reduction peak was noticed at pH below 7.0. At pH > 7.0, peak 11_c was noticed. Some of the typical cyclic voltamograms of compound **I** are presented in Figure 2. Peak 1_a formed a quasi-reversible couple with peak 1_c in the entire pH range studied and above pH = 7.0, peak 11_a also formed a quasi-reversible couple with peak 11_c, as established by $(E_p)_c - (E_p)_a$ dependence on the sweep rate. At low sweep rates, the peak potentials separation was 15–20 mV and increased to 50 mV at higher sweep rates.

The peak current for the reduction peak 1_c was more or less constant in the entire pH range studied. The ratio of peaks $1_c/1_a$ was also independent of pH and was in the range 1.1 to 1.3. The i_p for peak 1_c increased with increased concentration of compound **I** in the range 0.1 to 1.0 mM. The plot of i_p *versus* concentration was linear (Figure 3) and hence this dye can be safely determined in this concentration range by voltammetry. The ratio of peaks 1_c and 1_a was also more or less constant in the entire concentration range studied and was 1.4–1.6.

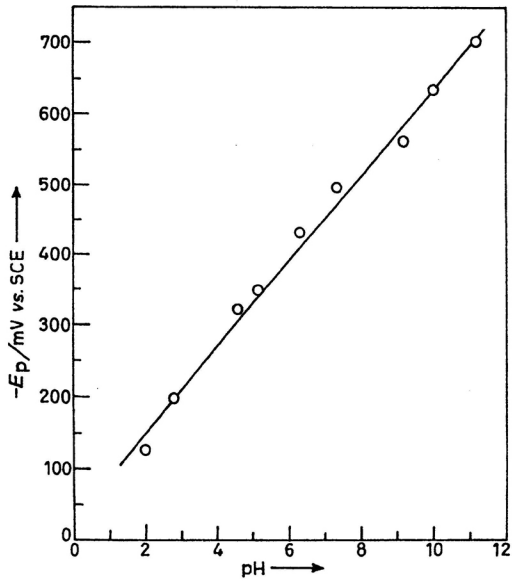


Figure 1. Dependence of E_p on pH for the reduction peak 1_c of 2-(2-thiazolylazo)-*p*--cresol, sweep rate 20 mV s^{-1}.

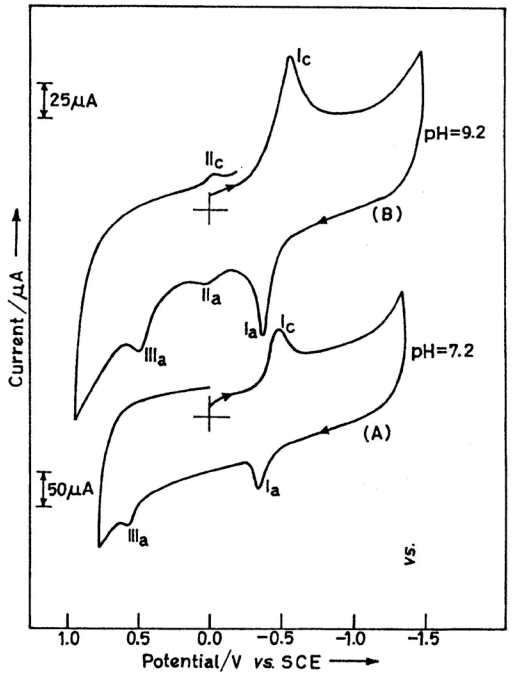


Figure 2. Typical cyclic voltamograms of 0.4 mM 2-(2-thiazolylazo)-*p*-cresol at pH = 7.2 (A) and 9.2 (B), sweep rate 100 mV s^{-1}.

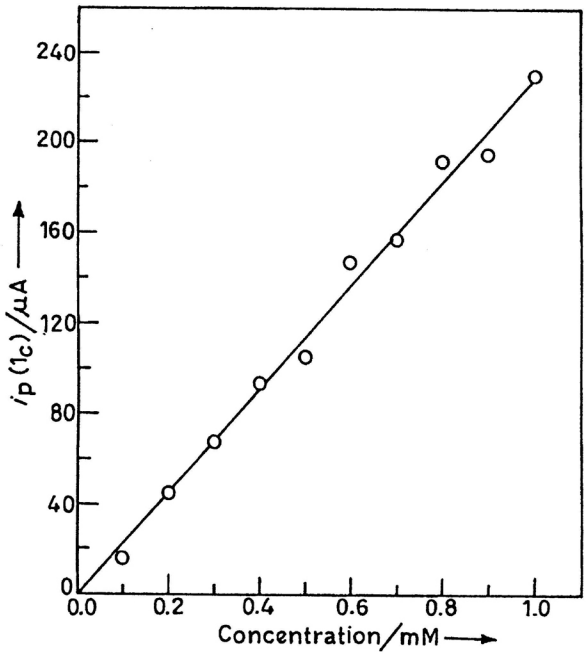


Figure 3. Effect of the 2-(2-thiazolylazo)-*p*-cresol concentration observed on the peak current of peak 1_c.

The effect of the sweep rate in the range 10 mV s^{-1} to 1 V s^{-1} was studied on the peak current of peak 1_c. The value of i_p was found to increase with increased sweep rate (Figure 4) and suggested a weak adsorption of thiazolylazo-*p*-cresol at the surface of PGE.[18] The peak ratio $1_a/1_c$ showed a tendency to reach 1.0 at higher sweep rates (> 1 V s^{-1}) and thus indicated the involvement of chemical follow up steps. To determine the nature of the electrode reaction, analyses were carried out using the criteria suggested by Nicholson and Shain.[19] It was observed that the values of $i_p/\sqrt{v}$ were large at low sweep rates and decreased to a constant value at high sweep rates (Figure 5). The exponential nature of the peak current function *versus* the sweep rate plot indicates the ECE nature of the electrode reaction in which the chemical step is interposed between two electron transfer steps.[20, 21]

Theoritically, it is expected that two distinct peaks should be obtained for an ECE mechanism, however, only one reduction peak (1_c) is observed in the present studies. Such a behaviour is not unusual and has been reported for the reduction of a variety of organic compounds[22] when $(E_P)_2$ is less negative than $(E_P)_1$. Thus, the peak potential of the charge transfer step that follows the chemical reaction is less negative than the initial electrode reaction of compound **I**.

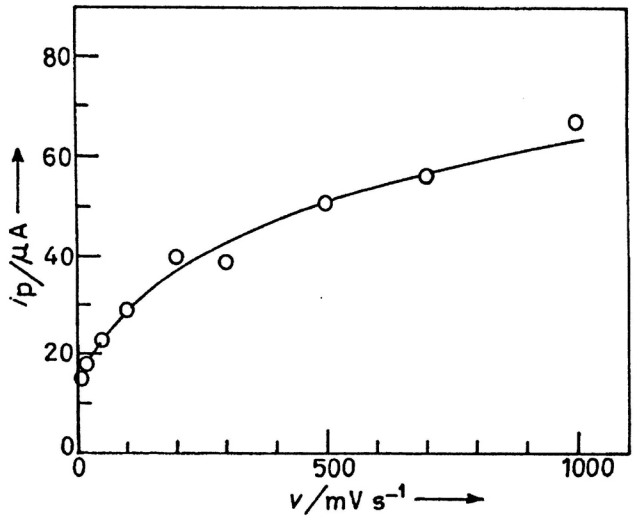


Figure 4. Dependence of the peak current observed on the sweep rate for the reduction peak 1_c, pH = 4.8.

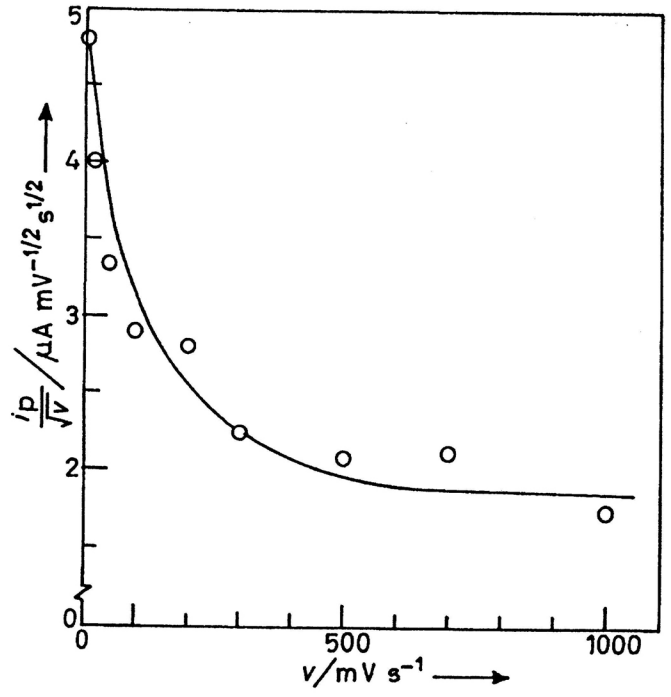


Figure 5. Variation of $i_p/\sqrt{v}$ *versus* v for the reduction peak 1_c at pH = 4.8.

Controlled Potential Electrolysis

Controlled potential electrolysis of 2-(2-thiazolylazo)-*p*-cresol dye was carried out at pH = 2.9, 7.3 and 10.0 to determine the value of n, the number of electrons involved in the reduction. Complete electroreduction of 0.4 mM compound **I** at peak 1_c potentials generally took 3 to 4 h at a large pyrolytic graphite plate (1 × 8 cm). The value of n was found to be 3.8 ± 0.2 at all the three pH (Table I).

TABLE I

Coulometric n-values observed at the PGE for the electroreduction of 2-(2-thiazolylazo)-*p*-cresol

pH	Conc. / mM	Potential mV *vs.* SCE	n*
2.1	0.4	–200	3.7
4.5	0.4	–400	3.8
4.3	0.4	–500	4.0
7.3	0.1	–500	3.8
	0.2	–500	3.9
	0.4	–500	3.8
9.2	0.4	–600	3.6
11.2	0.4	–700	3.8

* Average of at least three replicate determinations.

The progress of electrolysis was monitored by recording cyclic voltamograms at different time intervals. The peak current for peak 1_c systematically decreased with the progress of electrolysis. The plot of log $i_p = f(t)$ was a straight line for the first 20–25 min of electrolysis, after which a deviation from the straight line was observed. This behaviour indicates that the electrode reaction followed a simple path only for the first 20–25 min of reduction, after which chemical reactions played a significant role in the clevage of the initial electrode reaction product.

The cyclic voltammograms recorded during CPE also point to an interesting behaviour. Thus, peak 1_c decreased with the progress of electrolysis (Figure 6, A-C); however, a new oxidation peak 11_a appeared after 1 h of electrolysis even at pH = 2.9. The peak current for peak 11_a and 111_a increased with electrolysis time and finally became constant. The yellow colour of compound **I** turned to colourless after about 2 h of electrolysis. However, a light yellow colour again started to appear at the end of exhaustive electrolysis.

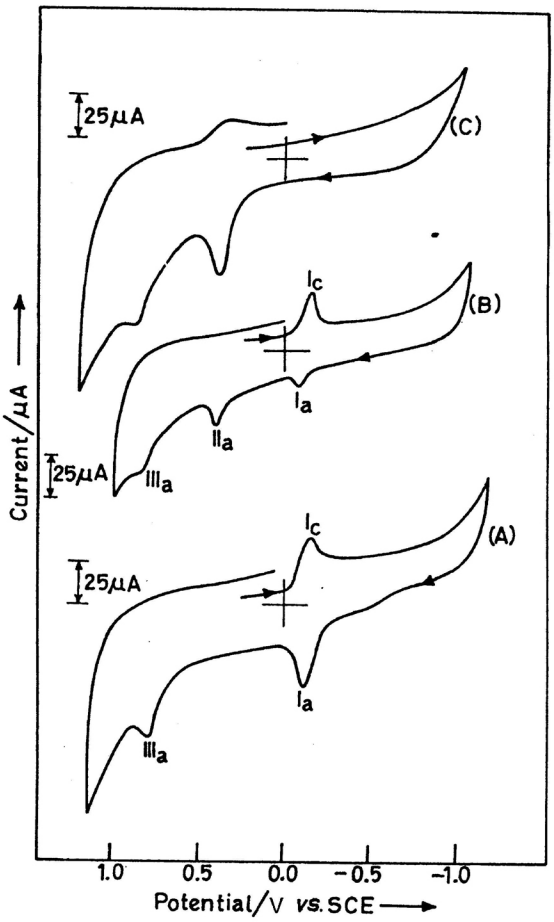
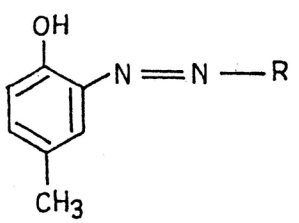


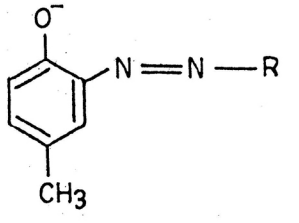
Figure 6. Cyclic voltamograms recorded at different times during the electro-reduction of 2-(2-thiazolylazo)-*p*-cresol at pH = 2.9; curves were recorded at (A) 0; (B) 1 h and (c) 2 h of electrolysis.

Spectral Studies

The UV/Vis spectra of compound **I** were recorded in the pH range 2.0–11.2. In the pH range 2.0–8.0, compound **I** exhibited two well-defined bands at 210 and 375 nm and a shoulder at around 440 nm. However, at pH > 8.0, the shoulder at 440 nm disappeared and a well-defined band was observed at 530 nm. The absorbance at λ_{max} was plotted against pH and showed an inflection at around pH = 8.0, which corresponded to the pK_a of compound **I**. The pK_a represents dissociation of the phenolic proton and, thus, the species existing in the solution are:



below pK_a



above pK_a

UV/Vis spectra of compound **I** were also recorded at pH = 4.5 and 9.2 at different time intervals during controlled potential electrolysis. A typical spectrum of thiazolylazo dye at pH = 4.5 is represented by curve 1 in Figure 7 and exhibits λ_{max} at 210, 375 nm and a shoulder at 440 nm. Upon application of the potential corresponding to peak 1_c, the absorbance in the 300–500 nm region systematically decreases while an increase in absorbance was noticed in the 210–300 nm region (curves 2 to 5). If the potential was turned off after recording curve 3 in Figure 7, an increase in absorbance in the 220–260 and 325–400 nm regions was noticed. An increase in absorbance at the same wavelength as that of the starting compound **I** on turning off the potential clearly suggested that compound **I** was again generated, most likely due to further reactions of the hydrazo intermediate.

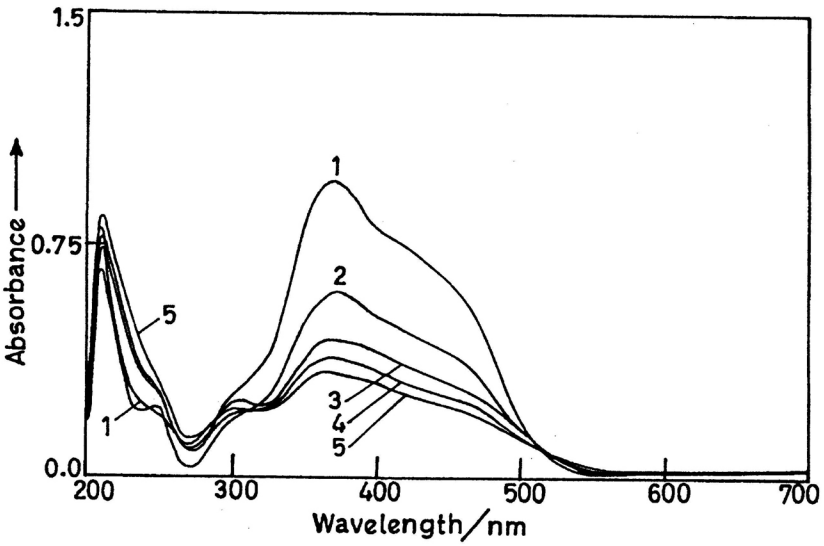


Figure 7. Spectral changes observed during the electro-reduction of 2-(2-thiazolylazo)-*p*-cresol at pH = 4.5, Potential 0.5 V *vs.* SCE. Curves were recorded at (1) 0; (2) 10; (3) 15; (4) 20 and (5) 40 min of electrolysis.

At pH = 9.2, the UV/Vis spectrum of compound **I** exhibited three λ_{max} at 210, 375 and 530 nm (Figure 8, curve 1). When the potential corresponding to peak 1_c was applied, a systematic decrease in absorbance in the 300–600 nm region was noticed (curves 2–8). Curve 9 was recorded after 2 hours of electrolysis and the absorbance at 375 and 530 nm did not decrease further even when electrolysis was carried out for 2 more hours. If the potential was turned off after recording curve 4 in Figure 8, the absorbance in the 300–400 regions showed an increase whereas the absorbance at 530 nm did not change. It is expected that the reduction of compound **I** should be completed in 3 to 4 h, as observed during controlled potential electrolysis. However, curve 10 indicates about 50–60% reduction. This difference in behaviour is due to the electrode potential applied to the reduction. To monitor the spectral changes, a potential similar to peak potential was applied, whereas, for determining the value of n, a much higher negative potential was applied to achieve a faster electroreduction.

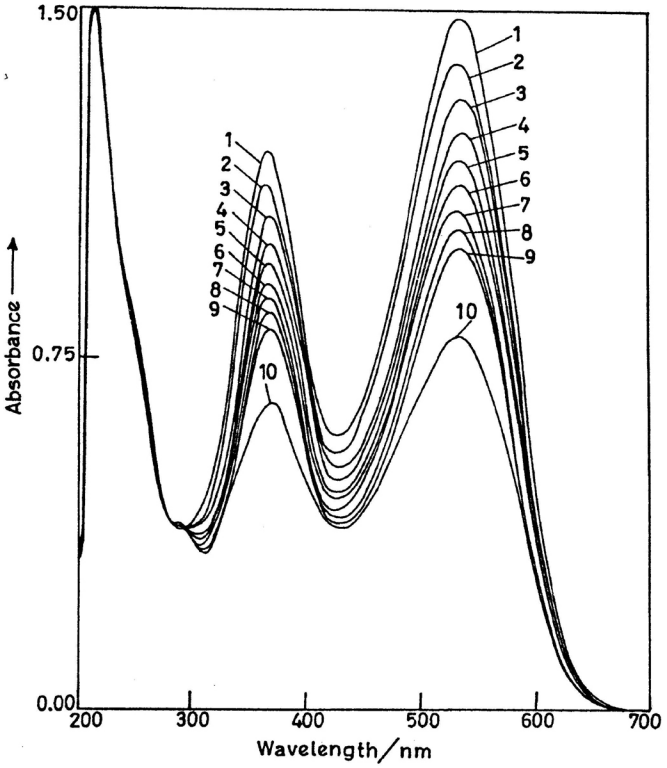
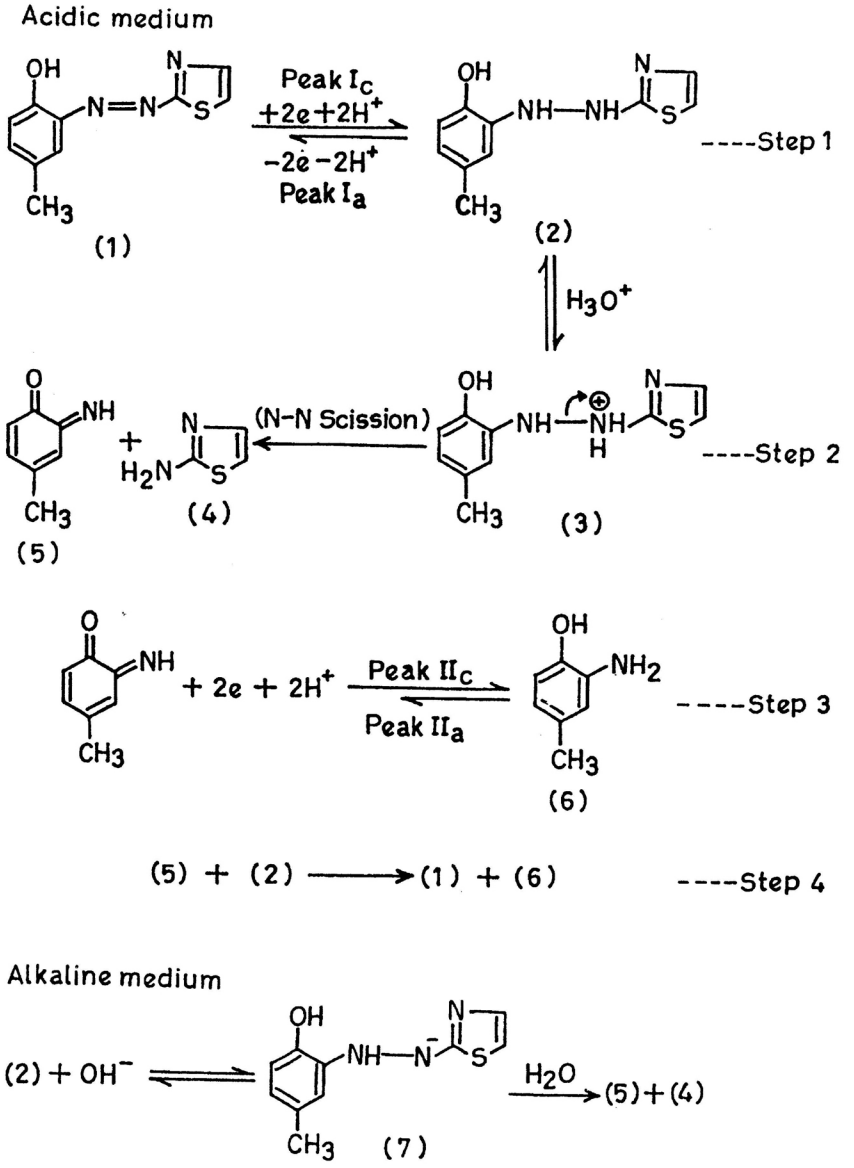


Figure 8. Spectral changes observed during the electro-reduction of 2-(2-thiazolylazo)-*p*-cresol at pH = 9.2. Curves were recorded at (1) 0; (2) 5; (3) 10; (4) 20; (5) 40; (6) 60; (7) 80; (8) 100; (9) 120 and (10) 240 min of electrolysis.



Scheme 1. A tentative mechanism proposed for the electro-reduction of thiazolylazo dye, in acid and alkaline media.

The kinetics of the reaction of the hydrazo intermediate according to step 4 (Scheme 1) was studied in the entire pH range at 250, 305 and 375 nm, where the absorbance increased after turning off the potential. The absorbance *versus* time plots, after turning off the potential at these wavelengths,

showed an exponential increase due to the formation of species **1** (Figure 9). The plot of thereotical dependence of log $[A_\infty / A_\infty - A]$ *vs.* time was a straight line. The rate constants were calculated from the linear plots of log $(A_\alpha - A)$ *versus* time and the values of the rate constant observed at different pH are summarized in Table II. The rate determining step is the reversible chemical reaction of the first or pseudo first order step.

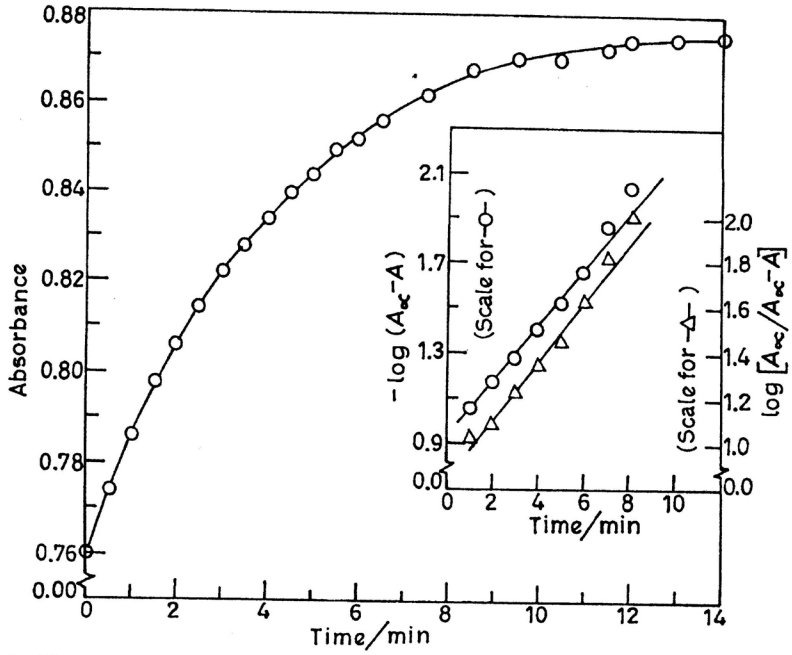


Figure 9. Observed variation in absorbance with time and log $(A_\infty - A)$ with time for the decay of UV-absorbing intermediate at pH = 9.2.

TABLE II

Observed k values for the disproportionation of the hydrazo intermediate generated during electroreduction of 2-(2-thiazolylazo)-*p*-cresol

pH	$k \times 10^3$ s^{-1} *		
	375 nm	305 nm	250 nm
2.1	–	1.1	–
4.5	2.8	3.0	2.8
6.3	2.3	2.4	2.4
7.3	2.1	2.5	2.4
9.2	2.5	2.8	–

* Average of at least three replicate determinations.

Product Characterization

The electrolysis products corresponding to peak 1_c were characterized at pH = 3.0 and 9.0 and were the same at both pH. Chromatographic peaks (P_1 and P_2) obtained in gel-permeation chromatography (see Experimental) were due to the buffer phosphate and hence discarded. The volume under peak P_3 on lyophilization gave a light brown coloured compound having m.p. 91–92 °C. The mass spectrum of the material exhibited a clear molecular ion peak at m/e 100 (100%) and hence the molar mass of the compound was 100. The other high mass peaks observed in the spectrum were at 76 (65.2%); 74 (12.8%); 60 (10.2%); 59 (60.1%); 58 (42.1%). UV spectrum of this compound exhibited a λ_{max} at 254, 432 nm and the product was identified as 2-aminothiazole by comparison with the authentic sample. As 2-aminothiazole has been found to be electroactive in nature,[23] the cyclic voltammograms of the isolated product and authentic 2-aminothiazole were also recorded at different pH. It was interesting to observe that cyclic voltamograms of both compounds were indistinguishable, having an oxidation peak with E_p similar to peak 11_a of compound **I** and hence it was concluded that the product corresponding to peak P_3 was 2-aminothiazole.

The formation of 2-aminothiazole as one of the reduction products of compound **I** suggested that N-N clevage occurred during the electroreduction of compound **I** and hence the other product should be 2-amino-4-methylphenol. The cream coloured material obtained on lyophilization of the volume collected under peak P_4 showed a single spot in TLC ($R_f = 0.32$) and had a m.p. = 135 °C. The mass spectrum of the material gave a clear molecular ion peak at m/e 123 (100%) and ^{1}H-NMR exhibited following signals δ: 2.1 s, -CH_3; 6.1 d, H; 6.3 d, H; 6.4 d, NH_2; 6.5 s, OH; 6.6 s, H.

Thus, the material was identified as 2-amino-4-methylphenol. To further confirm that the product is 2-amino-4-methylphenol, cyclic voltamograms of the authentic material were recorded at different pH. The appearance of peaks 11_a and 11_c at exactly the same potential as observed in the cyclic voltammetry of compound **I** further confirmed that the product was 2-amino--4-methylphenol.

Redox Mechanism

It is clear from the above paragraphs that the electroreduction of compound **I** occurred in a single 4e, $4H^+$ step in the ECE mechanism at a pyrolytic graphite electrode. The appearance of only one reduction peak clearly indicated that the peak potential of the second step was less negative than the first step and hence only one 4e, $4H^+$ peak was observed in the entire pH range. Thus, the ECE reduction of compound **1** involves the first 'E' step as 2e, $2H^+$ reduction to give the corresponding hydrazo derivative **2** (Scheme 1). The first step appears to be quasi-reversible in cyclic voltammetry and

hence peak 1_a represents the conversion of hydrazo derivative to compound **1**. Step 2 then involves scission of N-N bond in hydrazo derivative. The protonation of **2** gives species (**3**) which, on attack of water, gives 2-aminothiazole (**4**) and quinone imine (**5**). The second 'E' step represents the 2e, $2H^+$ reduction of quinone imine (**5**) to give 2-amino-4-methylphenol (**6**) in a quasi-reversible process.

In an alkaline medium, the removal of proton rapidly gives species (**7**), which on N-N scission rapidly forms 2-aminothiazole (**4**) and quinone imine (**5**). The oxidation reduction of amino phenols has been well-documented in the literature.[24] The hydrazo derivative (**2**) can also react with quinone imine (**5**), as it has been reported during reduction of aromatic and heterocyclic azo compounds.[5,6] Thus, the value of k observed at different pH indicates the rate of reaction of the hydrazo intermediate to give 2-amino-4-methylphenol (**6**), and the starting compound (**1**) is more or less the same in the entire pH range. This behaviour indicates the acid and base catalyzed nature of the hydrazo reaction.

The reaction rate of the hydrazo intermediate (**2**) also competes with N-N scission and hence can be represented as rate $= r^0 + k_H\ [H^+] + k_{OH}[OH^-]$, where r^0 is the spontaneous rate due to water catalysis. The influence of H_3PO_4, $H_2PO_4^-$, $H_2PO_4^{2-}$ in the acid base catalysis can be neglected.

In conclusion, it is believed that compound **I** is reduced at PGE in 4e, $4H^+$ step by the ECE mechanism. The first 2e, $2H^+$ reduction gives the hydrazo derivative. The electron attracting thiazolyl group and electron repelling -OH group weakens the NH-NH bond and causes further reaction with (**5**) to give 2-amino-4-methylphenol and 2-aminothiazole as the final products of electroreduction.

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SAŽETAK

Elektrokemijska redukcija 2-(2-tiazolilazo)-*p*-krezola na pirolitičkoj grafitnoj elektrodi

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Elekrokemijska redukcija 2-(2-tiazolilazo)-*p*-krezola na pirolitičkoj grafitnoj elektrodi proučavana je u fosfatnim puferima različitih vrijednosti pH. Redukcija boje odvija se u jednom dobro definiranom četirielektronskom koraku uz sudjelovanje 4 iona H^+. Nađeno je da je mehanizam elektrodne reakcije ECE. Redukcijski produkti odijeljeni su i karakterizirani talištem, ^{1}H-NMR i masenim spektrima. Utvrđeno je da je hidrazo-produkt nepostojan i da podliježe daljnjoj reakciji čija se brzina može opisati jednadžbom: $r = r^0 + k_H[H^+] + k_{OH}[OH^-]$.