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Electrochemical Behavior of Azobenzene-4,4′-disulfonamide at Pyrolytic Graphite Electrode

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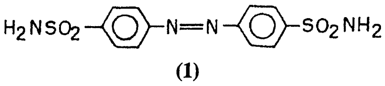
The electrochemical reduction of azobenzene-4,4′-disulfonamide (**1**), an oxidation product of sulfanilamide, has been studied at Pyrolytic graphite electrode, over a wide pH range of 3.0 to 10.6 in the Britton Robinson buffers, by electrochemical and spectroscopic techniques. Under cyclic voltammetric conditions the $2e^-$, $2H^+$ reduction of this compound was found to give hydrazobenzene-4,4′-disulfonamide which has been characterised using IR, mp, mass and NMR spectra. Under controlled potential electrolysis, the presence of two electron withdrawing $-SO_2NH_2$ groups was found to cause the slow disproportionation $[K'=3.29\times10^{-3}\ s^{-1}]$ of the hydrazo compound and sulfanilamide has been found as the major product of reduction. A plausible mechanism for the ECE reduction of **1** is suggested.

The redox chemistry of azo compounds has attracted considerable attention in recent years due to the capability of bacteria in reduction of azo compounds mainly in liver and intestine.[1)] The bacterial azo reduction of water soluble sulfonated azo dyes has been extensively investigated following Brohm and Frohwein work[2)] on decolorization of azo dyes in vitro by lactic acid bacteria. Dieckhues[3)] has comprehensively investigated the bacterial reduction of a number of azo compounds by microorganisms. Daniel has studied the metabolism and excretion of a number of sulfonated azo dyes and found that the azo reduction occurs mostly with the formation of amines and their derivatives when the dyes are orally administered to rabbits.[4)] Amarnath, Ponceau SX and sunset yellow have also been claimed to be reduced by a similar mechanism in rats.[5)] In recent years use of redox reactions in the analysis of azo dyes and their intermediate also attracted considerable attention.[6—8)]

The present paper describes the electrochemical behaviour of azobenzene-4,4′-disulfonamide (**1**), and oxidation product of sulfanilamide which has been claimed to exert bacteriostatic action.[9)] It has been found that $2e^-$, $2H^+$ reduction of compound **1** gives hydrazo compound. The strongly electron attracting $-SO_2NH_2$ group weakens the NH–NH bond and causes disproportionation of the hydrazo intermediate, which proceeds by a base catalysed mechanism and sulfanilamide has been obtained as the major product of electroreduction (Chart 1).



(1)

Chart 1.

Experimental

Azobenzene-4,4′-disulfonamide was synthesized in the laboratory by the method reported in the literature[10)] and its purity was asertained by repeated crystallization, mp, elemental analysis, and TLC. Hydrazobenzene-4,4′-disulfonamide was synthesized by the sodium hydrosulfite reduction of **1** as suggested by Seikel[10)] and had a mp 224°C (lit, 224.5°C).

All voltammetric studies were carried out using Pyrolytic graphite electrode prepared by the method reported in the literature.[11)] Equipments used for the voltammetric and coulometric studies have been described elsewhere.[12)] The spectral studies were carried out using specord (C. Zeiss Zena) spectrophotometer. The kinetic study of disproportionation reaction was studied using Beckman DU-6 spectrophotometer at 10±1°C. FT-IR spectrum of the product was recorded on the Perkin-Elemer 1600 series FT-IR. Mass spectra were recorded using a Peckard 5985 B instrument at an electron beam voltage of 70 eV. ^{1}H NMR spectra were recorded on a Varian XL 300 spectrometer in DMSO-d_6. Thin-layer cell having reticulated vitreous carbon (100 PPI) was prepared in the laboratory for carrying out electrolysis by the method reported in the literature.[13)] Thin layer chromatography was carried out on silica gel G plates with benzene–methanol (80 : 20) as developer. All potentials are referred to a saturated calomel electrode (SCE) at ambient temperature 21±2°C. B.R. buffers were prepared by the reported method.[14)]

For the identification of products, 5—7 mg of azobenzene-4,4′-disulfonamide was electroreduced in B.R. buffer of desired pH at a potential 50mV more negative to the peak potential using three compartment cell. A pyrolytic graphite plate (6×1 cm^2) was used as working electrode and a cylindrical platinum gauze and SCE as the counter and reference electrode respectively. The progress of electrolysis was monitored by recording cyclic voltammograms at different interval of times. When the peak I_c completely disappeared, the electroreduced solution of **1** was removed from the electrolysis cell and was lyopholized. The freeze dried material was dissolved in 1—2 ml of doubly distilled water and passed through a column (3×70 cm) packed with sephadex G-10 (Sigma, bead size 40—120 μm). Doubly distilled water was used as the eluant and fractions of 10 ml each were collected and their absorbance was monitored at 210 nm. The first peak (80—120 ml) emerged out of the column was found to contain phosphate and hence discarded. Fractions corresponding to other peak (175—210 and 220—240 ml) were lyopholized and analyzed by FT-IR, mp, and ^{1}H NMR, mass spectra.

The stock solution (1 mM,1 M=1 mol dm^{-3}) of **1** was prepared in 50% methanol (minimum amount necessary to keep the compound in solution). The solutions for voltammetric studies were prepared by mixing 5 ml of compound **1** with 5 ml of B.R. buffer of desired pH. The solutions were deaerated for 10—15 min and the curves were then recorded.

Result and discussion

Linear sweep voltammetry of **1** at sweep rate 10 mV s^{-1} exhibited a reduction peak (I$_c$) when the sweep was initiated in the negative direction. The peak potential of this peak was dependent on pH and shifted towards more negative potential with increase in pH. The E_p vs. pH plot was linear (Fig. 1) and exhibited a break at around pH 4.0. The dependence of E_p on pH can be expressed by following relations:

$$E_p(0.80-4.1) = (0.16-0.11\ \text{pH})\text{V} \quad (1)$$

$$-E_p(4.1-11.2) = (0.105+0.039\ \text{pH})\text{V} \quad (2)$$

In cyclic sweep voltammetry at a sweep rate of 100 mV s^{-1}, a well defined reduction peak I$_c$ was observed when the sweep was initiated in the negative direction. In the reverse sweep an anodic peak (I$_a$) was observed in the entire pH range 3.0 to 10.6. Some of the typical cyclic voltammograms are presented in Fig. 2. The ratio of peaks I$_a$/I$_c$ was found to be constant and about 0.2 in the entire pH range. The separation of peak potential between peaks I$_c$ and I$_a$ for a reversible charge transfer[15] should be equal to $\frac{59}{n}$ mV. The value of $E_p^c-E_p^a$ observed in the present studies clearly indicated the redox couple as quasireversible in nature. With increase in sweep rate in the range 10—500 mVs^{-1}, the peak currents for peaks I$_c$ and I$_a$ increased but the ratio was again found to be in the range of 0.20—0.25.

The peak current for the reduction peak I$_c$ increased linearly with increase in concentration. The peak current versus concentration plot was practically linear upto 0.08 mM and at higher concentrations the peak current values had a tendency to become constant (Fig. 3). This indicated the adsorption complication[15] associated with reduction of compound **1**. The involvement of adsorption in the electrode reaction was further confirmed by studying the effect of sweep rate on the peak current function. It was observed that the values of $i_P/\text{ACV}^{1/2}$ increased with increase in sweep rate in the range 10 to 500 mV s^{-1} Following equation is expected to hold for reversible case;

$$i_p/\text{ACV}^{1/2} = V^{1/2} + \text{Const.} \quad (3)$$

As the value of $i_p/\text{ACV}^{1/2}$ increased with increase in sweep rate, it was concluded that the redox couple I$_c$, I$_a$ is not reversible and adsorption of the compound **1** at the electrode surface was confirmed. The possibility of coupled chemical reactions was confirmed by the plots of i_a/i_c vs. log V and $\Delta E_{p/2}/\Delta \log V$ versus log V (Fig. 4). The S-shaped curves obtained in both the cases clearly indicated the ECE mechanism for the reduction of **1** as suggested by Nicholson and Shain[16] for the charge transfer followed by an irreversible chemical reaction.

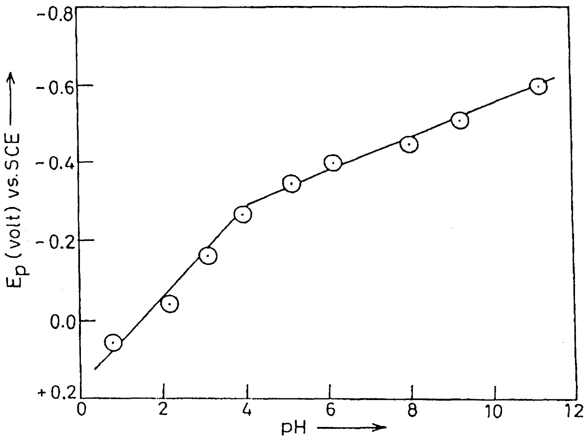


Fig. 1. Dependence of peak Potential on pH for the voltammetric peak of azobenzene-4,4′-disulfonamide at Pyrolytic graphite electrode.

Controlled Potential Electrolysis: Controlled potential electrolysis of 0.5 mM solution of compound **1** was carried out at pH 3.0, 7.1, and 10.0. The progress of electrolysis was monitored by recording the cyclic voltammograms at different time intervals during the electrolysis. It was interesting to observe that peak current of peaks I$_c$/I$_a$ systematically decreased and several new reduction and oxidation peaks started appearing after about two hours of electrolysis. A typical cyclic voltammogram of **1** before electrolysis at pH 9.0 is presented by curve A in Fig. 5. With progress of electrolysis a redox couple (III$_c$/III$_a$) started appearing after 30 min of electrolysis (Curve B), which later on disappeared. An exhaustively electrolyzed solution of compound **1** is presented in Fig. 5d. Peaks I$_c$ and I$_a$ were completely disappeared and an oxidation peak II$_a$ was observed in the cyclic voltammetry. In the reverse sweep two new reduction Peaks IV$_c$-V$_c$ were observed which formed quasi-reversible couples with peaks IV$_a$-V$_a$ observed in the subsequent sweep towards positive potential. Hence, it was concluded that the product of peak I$_c$ reduction is electroactive and undergoes oxidation in Peak II$_a$ reaction and the peak II$_a$ oxidation products exhibit redox couples IV$_a$/IV$_c$ and V$_a$/V$_c$. As peak II$_a$, III$_c$, IV$_a$/IV$_c$ were not observed the cyclic voltammograms of compound **1** recorded at different pH, it was concluded that the products of electroreduction under cyclic voltammetric conditions are different from controlled potential electrolysis.

The value of n, number of electrons involved in electroreduction corresponding to peak I$_c$ was determined using graphical integration of current-time curve as suggested by Lingane et al.[17] For fast electrolysis a thin layer cell as suggested by Norvell and Mamantov[13] was used. The electrolysis in this cell was completed in 10—

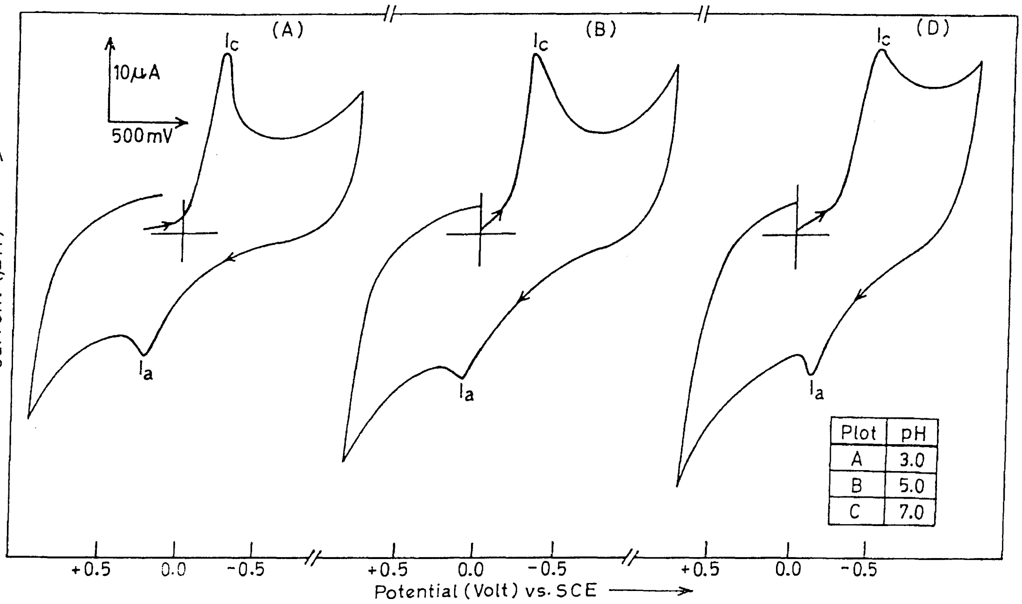


Fig. 2. Typical cyclic voltammograms observed for azobenzene-4,4'-disulfonamide in B.R. buffers of different pH value (sweep rate=100 mV s^{-1}).

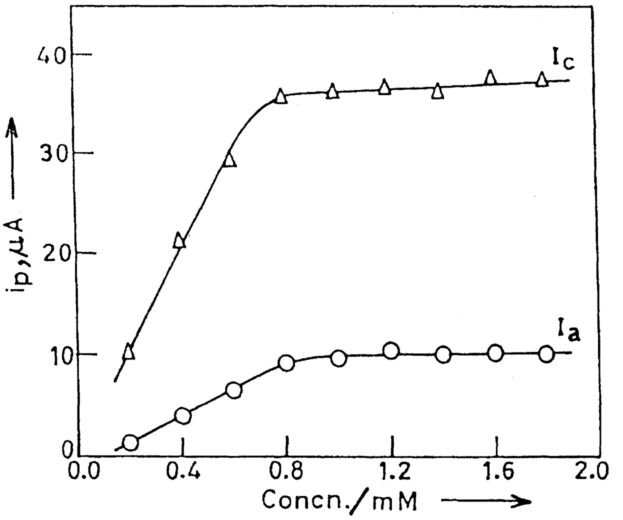


Fig. 3. Variation of peak current with concentration for the voltammetric peaks of azobenzene-4,4'-disulfonamide.

15 min. The plot of log $i_p=f(t)$ for the reduction of **1** was a straight line for the entire period of electrolysis, which indicated that reduction is a single path and no complications due to follow up chemical reactions are involved. The value of n determined at different pH and concentrations was found to be 2.0±0.10. Controlled potential electrolysis of **1** at a large PGE (6×1 cm^2) on the other hand always required more than four hours for complete electroreduction. The plot of log $i_p=f(t)$ was a straight line for first 20—30 min and then indicated a deviation and hence clearly confirmed that electrode reaction followed a single path only for the first 20—30 min and then chemical rections are competing in the bulk clevage of the product. The value of n determined

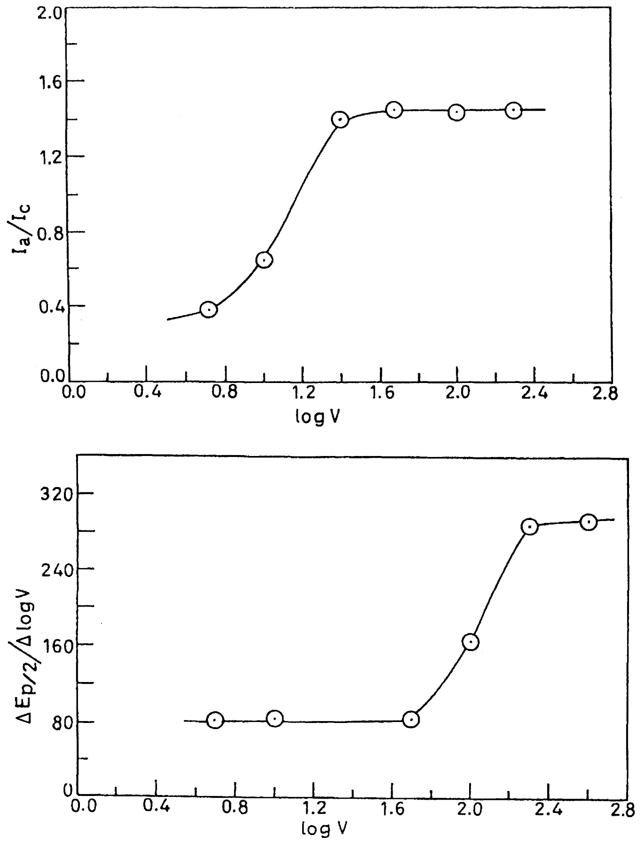


Fig. 4. Observed dependence of I_a/I_c and $\Delta E_{p/2}/\Delta \log V$ on log V for 0.5 mM azobenzene disulfonamide at pH 3.1.

was found as 4.0±0.15 and are presented in Table 1.

Spectral Studies: The UV-vis spectra of compound **1** were recorded in the entire pH range of 3.1 to 10.6 to determine the pK_a value of **1**. It was ob-

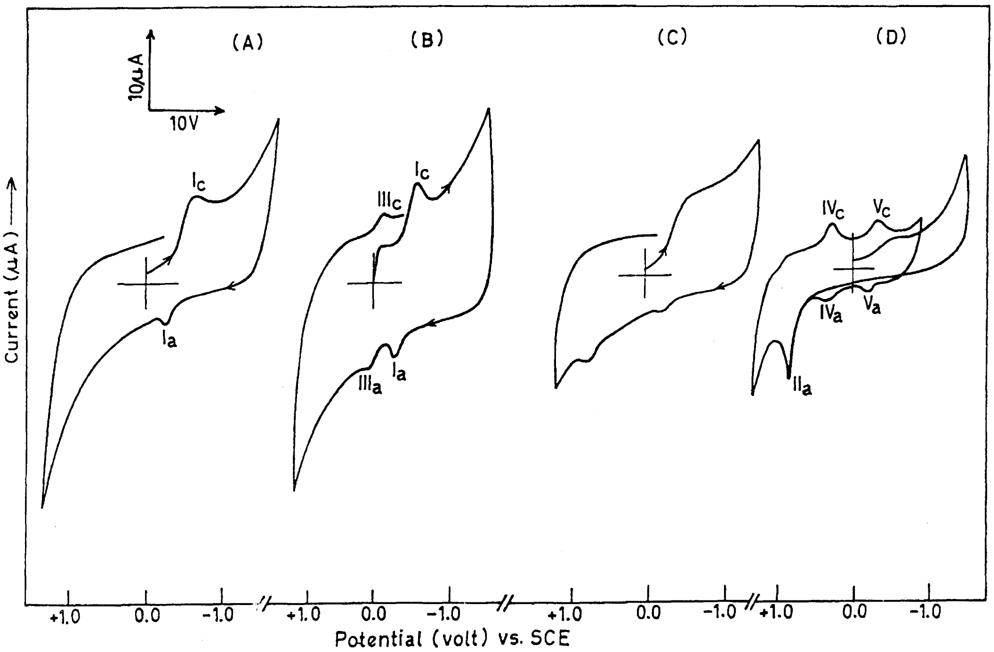


Fig. 5. Cyclic voltammetric changes observed during controlled potential electrolysis of 1 mM of **1** at pH 9.0, Pot. −0.6 V vs. SCE. Curves were recorded at (A) 0, (B) 30, (C) 90, and (D) 240 min of electrolysis.

Table 1. Coulometic n-Values Observed for the Electroreduction of Azobenzene-4,4′-disulfonamide

pH	Concentration mM	Applied potential V (vs. SCE)	Experimental n-value[a)]
3.1	1.0	−0.17	3.85
	0.5	−0.17	4.00
4.1	1.0	−0.27	4.15
	0.5	−0.27	4.10
5.2	1.0	−0.34	3.95
	0.5	−0.34	4.05
6.2	1.0	−0.40	4.00
	0.5	−0.40	3.87
7.1	1.0	−0.44	3.95
	0.5	−0.44	4.10
9.3	1.0	−0.51	4.02
	0.5	−0.51	4.15
11.2	1.0	−0.60	4.00
	0.5	−0.60	3.95

a) Average of at least two replicate determinations.

served that compound **1** exhibits $\lambda_{\max}$ at 323 nm and a shoulder at around 232 nm and at 440nm in the entire pH range studied. The absorbance at 232 and 323 nm were plotted against pH and the resulting dissociation curve gave an inflection point at around pH 4.1. The pK_a of 4.1 observed spectrophotometrically is further supported by the break observed in E_p vs. pH plot and is in the range suggested by Catchpole et al.[18)] Thus, it is concluded that below pH 4.1 compound **1** exists as a protonated species and at pH >4.1 mainly as a neutral molecule. It is reported[19)] that in azo compounds protonation takes place on a distinct N-atom with the formation of an N–H σ bond.[20)] Hence following species must exist in the solution (Chart 2).

The progress of electrolysis of **1** was also monitored by recording the UV-vis spectral changes at different times of electrolysis. The UV-vis spectrum of 0.05 mM of compound **1** before electrolysis at pH 7.1 exhibited a broad maxima at 220 nm and a well defined $\lambda_{\max}$ at 326 nm (Fig. 6 curve-1). Application of potential 50—100 mV more negative to peak I$_c$, leads to the systematic decrease in absorbance at 326 nm whereas absorbance in the region 240—295 nm continuously increased. Absorbance in the region 225—240 nm also systematically decreased. The exhaustively electrolyzed solution of **1** exhibited a maxima at 220 and 276 nm (curve-8) with only one clear isosbestic point at 296 nm. The formation of two scattered isosbestic points at 222 and 242 nm suggested the involvement of competitive chemical reactions.

The above observations lead to the conclusion that the products of electroreduction of **1** absorbs at a shorter wavelength in comparison to compound **1** and hence the π-chromophore system in the product has been decreased. Almost similar spectral changes were observed at pH 3.2 and 10.1 suggesting thereby that

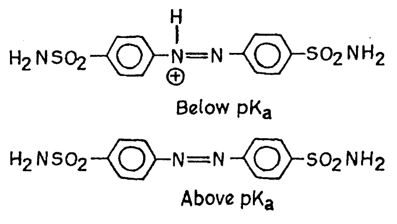


Chart 2.

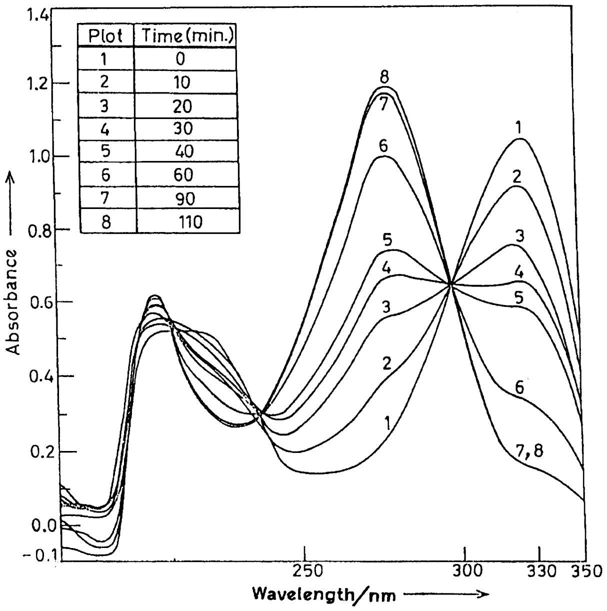


Fig. 6. Observed spectral changes during the reduction of azobenzene-4,4′-disulfonamide at PGE (pH=7.1).

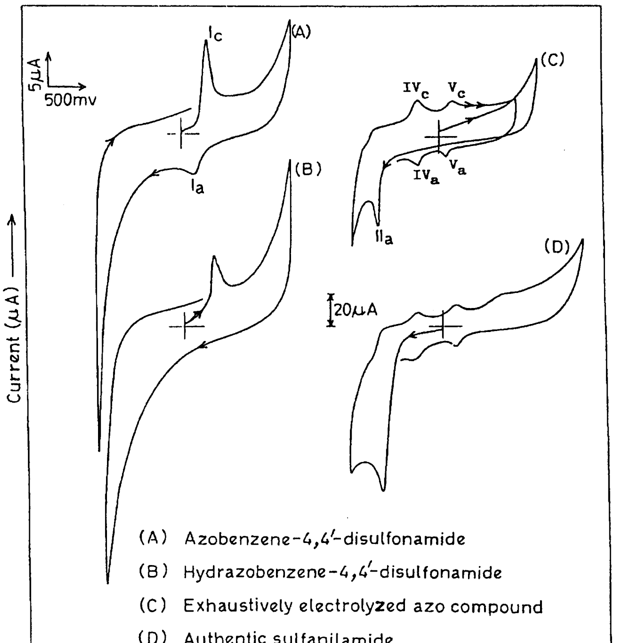


Fig. 7. A comparison of cyclic voltammograms of azo, hydrazodisulfonamides with authentic sulfanilamide at pH 7.1.

the products formed during the electroreduction of **1** at pH 3.2, 7.1, and 10.1 are same. The value of $K'/[H^+]$, where K' is the pseudo first order rate constant for the disproportionation of the hydrazo intermediate is found to be 3.0×10^5 dm^3 mol^{-1} s^{-1}.

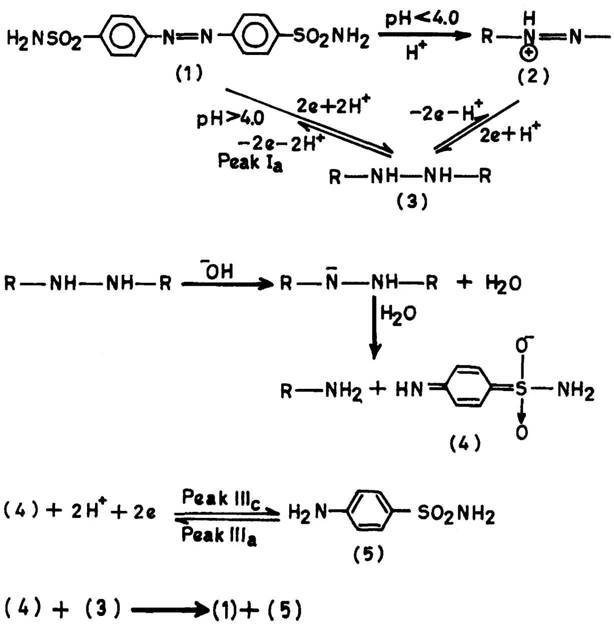
Characterization of the Product: The electroreduction product of azobenzene-4,4′-disulfonamide was characterized at pH 3.1 and 7.1. The exhaustively electrolyzed solution of **1** was lyopholized and passed through sephadex G-10 column (bead size 40—120 μm). The fraction collected between 200—230 ml on lyopholization gave colorless crystals having mp 163°C. The TLC of the material obtained exhibited only one spot (R_f=0.42) indicating thereby that only one product has been formed. The UV spectrum of a dilute solution of this product exhibited a well defined maximum at 275 nm and was similar to that of exhaustively electrolyzed solution of **1** at pH 7.1 (Fig. 6). The mass spectrum of the product gave a clear molecular ion at m/z=172 indicating thereby that the N–N bond in compound **1** has clevaged in the product. Some other high mass peaks observed in the fragmentation pattern were at 168 (8.1%); 167 (9.9%); 166 (100%); 108 (54.2%); 107 (6.9%). The m/z=172 indicated the formation of sulfanilamide as the product. The IR spectrum of the product exhibited absorption bands at 3490, 3400 (-NH, arm.), 3280 (-CH), 1640, 1600 (C=C), 1320, and 1150 ($-SO_2NH_2$) cm^{-1}.

The ^{1}H NMR spectrum of the product supported the product as sulfanilamide as signals at δ=5.78 (S, arm-NH$_2$); 6.6 (d, 2H); 6.90 (S, $-NH_2$) and 7.40 (d, 2H) were clearly observed. A direct comparison indicated that ^{1}H NMR and IR of the product are superimposable and hence clearly indicated that the product of reduction of compound **1** is sulfanilamide. Comparison of cyclic voltammograms of authentic sulfanilamide and exhaustively electrolyzed solution of compound **1** is presented in Fig. 7. It is observed that redox couples IV_a/IV_c and V_a/V_c of exhaustively electrolyzed solution of **1** are practically similar to authentic sulfanilamide and have been assigned to the redox couples of quinone-hydroquinon and azo-hydrazo products. The details of these redox couples have been reported in the literature.[21] Hence, it was concluded that final product of electroreduction of **1** is sulfanilamide.

Identification of sulfanilamide as the product of electroreduction of azobenzene-4,4′-disulfonamide suggested the formation of hydrazo derivative as the intermediate of reaction, which requires the involvement of only 2e$^-$, 2H$^+$. To identify the formation of hydrazo derivative as intermediate cyclic voltammograms of hydrazo derivative were recorded at different pH. It was interesting to observe that reduction of hydrazo derivative occurred at about 50 mV more negative to compound **1** at PGE (Fig. 7). Therefore, with the help of i–t curves an approximate time for 2e$^-$, 2H$^+$ reduction of compound **1** was calculated. The time observed for 2e$^-$, 2H$^+$ transfer for 0.5 mM solution of compound **1** was found close to 1 h at −0.6 V. Hence several solutions of 0.5 mM of **1** were reduced at −0.6 V, 1h and the collected volume was lyopholized. The freeze dried material exhibited two spots in TLC with R_f=0.42 and 0.36 and hence indicated the formation of two products. The volumes collected in column chromatography (see Experimental) on monitoring the absorbance at 210 nm exhibited three peaks. The first peak 80—120 ml was found due to the phosphate and hence discarded. The other two peaks between 175—210 ml (major peak) and 220—240 ml (minor peak) were separately collected and lyopholized. The peak collected between 220—240 ml was broad in shape. The material obtained under volume 220—240 ml had a mp 165°C and its IR and ^{1}H NMR were identical to that of sulfanilamide and hence was characterized as sulfanilamide. The material obtained under volume 175—210 ml (R_f=0.36) was light yellow in color and had a mp 223°C. The FT-IR spectrum of this product did not exhibit peak at 1610 cm^{-1} corresponding to azo group of **1** and hence it was concluded that reduction of **1** occurred in $2e^-$, $2H^+$ process at –N=N– linkage. Peak at 3400 cm^{-1} corresponding to –NH were clearly observed in the IR spectrum. The mass spectrum of the product exhibited a m/z=342 indicating the product as hydrazobenzene-4,4′-disulfonamide.

Redox Mechanism: On the basis of experimental data presented above it can be concluded that azobenzene-4,4′-disulfonamide reduced under cyclic voltammetric conditions in a single $2e^-$, $2H^+$ step to give hydrazo derivative. In controlled potential electrolysis slow disproportionation of the hydrazo product is observed and sulfanilamide, which absorbs at shorter wavelength in comparison to the starting material **1**, was obtained as the final product. The formation of sulfanilamide as the final product of reduction indicated that reduction of **1** involves overall $4e^-$, $4H^+$, at PGE. The rate of disproportionation behavior of the hydrazo derivative can be represented as Rate $=r^\circ+K_{OH}[OH^-]$ where r° is the spontaneous rate due to water catalysis. Hence the following mechanism for the reduction of **1** can be suggested.

As at pH 4.0, the protonated species **2** undergoes reduction, it is concluded that $2e^-$, H^+ reduction of **2** would give hydrazo molecule (**3**) as shown in Scheme 1. Peak I_a represents the oxidation of hydrazobenzene-sulfonamide to azo moeity in a quasi-reversible process. As hydrazobenzene-4,4′-disulfonamide (**3**) possess less extensive π-conjugation than **1**, the λ_{max} during spectral studies shifted to shorter wavelength. UV spectra of the authentic hydrazobenzene-4,4′-disulfonamide and sulfanilamide were also recorded to get an idea about the formation of **3** during spectral studies, however, both the compounds exhibited a λ_{max} at 270 and 275 nm (pH 7.0) respectively and hence a continuous increase in absorbance in the region 240—295 nm was observed during spectral studies. The hydrazo moiety **3** then undergoes slow disproportionation to give sulfanilamide **5** and imine species **4**, which on further $2e^-$, $2H^+$ reduction gives sulfanilamide as the final product of electroreduction. The reduction of imine species **4** was clearly observed in the redox couple III_c/III_a in cyclic voltammetric changes during controlled potential electrolysis. It is also possible that moiety **3** and **4** may combine remote from the electrode or in homogeneous solution to give sulfanilamide (**5**) and azomolecule (**1**). Disproportionation behavior of several hydrazo derivatives has been studied by Florence et al.[22] It has been found that hydrazo compounds with electron donating group exhibit acid catalyzed disproportionation. Azo molecules with heterocyclic moiety on one side of azo group and electron releasing group on the other side have also been reported[23] to undergo acid or base catalyzed disproportionation. However, in the present studies $-SO_2NH_2$ group is present at the para position on both the sides of azo benzene and hence the base catalyzed disproportionation of the hydrazo moiety was observed to give amine as the final product of reduction.



Scheme 1. Tentative mechanism proposed for the electroreduction of azobenzene-4,4′-disulfonamide.

The electrochemical investigation of azobenzene-4,4′-disulfonamide indicates that compound **1** is electro active in nature and readily undergoes electroreduction in a single $2e^-$, $2H^+$ process to give hydrazo derivative under cyclic voltammetric conditions. Under controlled potential electrolysis, the slow disproportionation of the hydrazo moiety ($K'/[H^+]=3.0\times10^5$ $dm^3\,mol^{-1}\,s^{-1}$) was observed to give sulfanilamide as the final product. Thus, it appears that the electron withdrawing $-SO_2NH_2$ groups present in compound **1** facilitates cleavage of –NH–NH– and sulfanilamide is formed.

Burton,[24] Mayer,[25] and others[26] have proposed that oxidation products of sulfonamides may partly be responsible for their antibacterial activity. Thus, it is concluded that azobenzene-4,4′-disulfonamide, a suggested electrochemical oxidation product of sulfanilamide[21] is electroactive in nature and gives hydrazobenzene-4, 4′-disulfonamide under cyclic voltammetric conditions. The slow disproportionation under controlled potential electrolysis gives sulfanilamide as the final product. Hence the redox behavior involve with compound **1** appears to be most likely responsible for the bacteriostatic action of sulfanilamide.

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