

Electrochemical Behaviour of Bisazo Dye, Acid Red-150

R N GOYAL* & ANOOP KUMAR

Department of Chemistry, University of Roorkee, Roorkee 247 667

Received 30 July 1987; revised 21 September 1987; accepted 16 October 1987

The electrochemical behaviour of Acid Red-150 has been studied in the pH range of 2.2-11.2. Unlike the reduction of bisazobenzene to bishydrazo-benzene, the reduction of azo group attached to naphthol moiety in this dye takes place in a ($4e, 4H^+$) reduction step to give amino compound as product of electrode reaction. The products of electrolysis have been separated and identified.

An excellent review is available on the polarographic reduction of azo dyes in aqueous and non-aqueous media¹. However, most of the studies are confined to the reduction of monoazo compounds and very little is known about the azo compounds containing two azo groups and hence the title investigation was undertaken.

Materials and Methods

Acid Red-150 (I) (Sigma Chemical Co) was used as received. Its stock solution (2 mM) was prepared in doubly distilled water. Universal Britton-Robinson² buffers (pH 2.2-11.2) were used. The pH was measured using an ECIL expanded scale pH meter (model pH 821) after due standardisation with potassium hydrogen phthalate and borax buffers.

Polarograms were recorded on a Cambridge pen recording polarograph. The capillary used had the following characteristics: $m = 1.25 \text{ mgs}^{-1}$, and $t = 3.90 \text{ at } h = 60 \text{ cm}$.

For recording polarograms and voltammograms 1 ml of the stock solution of the dye was mixed with 9.0 ml of buffer of appropriate pH under total nitrogen blanket. Voltammetric studies were carried out using Micronic cyclic voltammeter and a digigraphic X, Y-t recorder. The details of instruments used for spectral studies have been described elsewhere³. Pyrolytic graphite electrode was prepared by the method reported earlier⁴. It had an area $\sim 1.8 \text{ mm}^2$. All potentials refer to SCE at 25°C.

Controlled potential electrolysis and product identification

Controlled potential electrolysis of 1 mM solution of the dye was carried out in a three-compartment cell at potential more negative to peak Ic or IIc or at the plateau potential of the first or second polarographic wave. The working electrode was pyrolytic graphite

plate (area 6 cm^2) or mercury pool, counter electrode was the cylindrical platinum gauze and the reference electrode was a saturated calomel electrode. Nitrogen was bubbled throughout electrolysis and progress of electrolysis was monitored by recording cyclic voltammograms at different intervals of time until the reduction wave completely disappeared.

For the separation and identification of products, the dye (8-10 mg) was electrolysed in a H-type cell. At Hg pool, plateau potential corresponding to first or second wave was applied and at pyrolytic graphite electrode potential more negative to peak Ic or IIc was applied. When electrolysis was complete ($\sim 99\%$) the electrolysed solution was made sufficiently acidic and lyophilised. The freeze-dried material was dissolved in water (1-2 ml) and passed through a glass column ($70 \times 1.6 \text{ cm}$) packed with sephadex G-10 (Sigma Chemical Co) using doubly distilled water as the eluent. Different fractions (10 ml each) were collected. The absorbance of each tube was monitored at 215 nm and was plotted against volume. The first peak (volume 50-200 ml) contained phosphate, borate and acetate, hence was discarded. Other three peaks in the volume ranges 200-270, 280-350, 360-450 ml, respectively were collected separately, freeze-dried and analysed. TLC of electrolysed solution was carried out on silica gel-G plates using methanol-acetic acid-benzene (80:10:10) as developer.

Results and Discussion

Polarographic behaviour

Polarographic reduction of Acid Red-150 occurred in one well-defined diffusion-controlled wave below pH 5.5. In the pH range of 5.6-8.0, the wave splitted into two waves and the limiting current of the first wave was almost $1/3$ of the second wave. At pH > 8.0 , two waves of equal height were observed. The nature of the waves was found to be diffusion-con-

Table 1—Polarographic Characteristics of Acid Red-150 in B.R. buffers of different pH

pH	$(-E_{1/2})$ (V)	i_d (μA)	αn	
			log plot method	Oldham's method
2.2	0.22	2.62	1.10	1.12
3.4	0.26	2.62	1.00	1.16
4.4	0.34	2.69	0.90	1.00
5.5	0.45	2.54	1.12	0.98
6.4	0.32	0.825	0.96	0.98
	0.48	1.500	0.98	1.06
7.2	0.37	0.750	1.13	0.98
	0.54	1.650	1.08	1.08
8.6	0.44	1.275	1.12	1.06
	0.65	1.350	0.96	0.96
10.0	0.52	1.350	1.00	1.10
	0.70	1.275	1.10	1.14
11.2	0.58	1.275	1.14	1.12
	0.73	1.275	1.12	1.12

trolled as evidenced by i_d versus $\sqrt{h}$ and low temperature coefficient value ($1.2\% \text{ deg}^{-1}$). The $E_{1/2}$ was dependent on pH and shifted towards more negative value with increase in pH. The plots of $E_{1/2}$ versus pH were linear for both the waves and can be represented by Eqs (1) and (2),

$$(-E_{1/2})_1 = [0.054 \text{ pH} + 0.02] \quad \dots (1)$$

$$(-E_{1/2})_2 = [0.066 \text{ pH} + 0.09] \quad \dots (2)$$

The limiting current of the wave < 5.5 was practically equal to the sum of the limiting current of the two waves at $\text{pH} > 5.5$. This indicates that overall electrode reaction is the same in the entire pH range. The effect of dye concentration on $E_{1/2}$ and limiting current was studied in the dye concentration range of 0.05–1.0 mM. The i_d versus concentration plot was linear passing through the origin indicating that this dye can be safely estimated in this concentration range by polarographic method. However, $E_{1/2}$ shifted towards more negative value with increase in dye concentration showing irreversible nature (also confirmed by log plot analysis⁵) of the electrode process and possible role of adsorption⁵. The values of αn were determined by log plot analysis as well as the method of Oldham and Perry⁶. The values of αn determined by the two methods at different pH values are practically same (Table 1).

Linear and cyclic sweep voltammetry

Linear sweep voltammetry at a sweep rate of 5 mVs^{-1} exhibited one well-defined reduction peak in the pH range of 2.2–11.2. The peak potential was de-

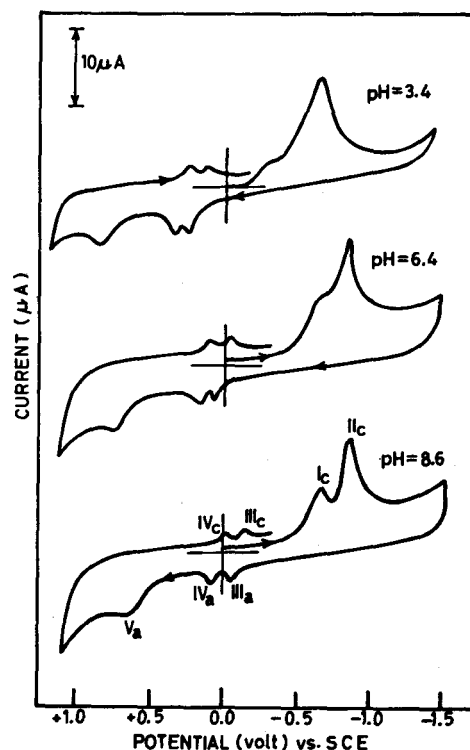


Fig. 1—Cyclic voltammograms observed for 0.2 mM Acid Red-150 at PGE. Sweep rate 150 mVs^{-1}

pendent on pH and shifted towards more negative potential with increase in pH. Cyclic sweep voltammetry at a sweep rate of 100 mVs^{-1} exhibited two reduction peaks Ic and IIc, when sweep was initiated in the negative direction. In the reverse sweep, three oxidation peaks were observed. On the second sweep towards positive potential two new cathodic peaks (IIIc and IVc) were noted (Fig. 1). To confirm whether oxidation peaks are due to the oxidation of products formed in Ic/IIc reaction or are due to an independent oxidation of Acid Red-150, cyclic voltammograms were also recorded by initiating the sweep in the positive direction. The absence of oxidation peaks clearly indicated that peaks IIIa–Va are due to oxidation of the product formed in Ic/IIc reaction.

At pH 8.6 where two reduction peaks were well-defined, cyclic voltammograms were recorded by changing the direction of the sweep after peak Ic. The peaks IIIa–Va and reduction peaks IVc and Vc were not visible, indicating that these peaks are observed only after complete reduction of the dye. Peaks IIIa/IIIc and IVa/IVc formed an irreversible couple and were observed clearly only at a scan rate $> 100 \text{ mVs}^{-1}$. The peak potential of the reduction peaks Ic to IVc was dependent on pH and shifted towards more negative potential with increase in pH. On the

other hand peak potentials of oxidation peaks IIIa to Va also shifted towards less positive value with increase in pH.

Controlled potential coulometry of Acid Red-150 was carried out at mercury pool cathode and at plateau potential of first or second wave. Below pH 5.5, where only one wave was observed the value of n determined by graphical integration of current-time curve was found to be 8.0 ± 0.2 . In the pH range 5.6-8.0 the first wave involved 2.0 ± 0.1 electrons whereas second wave involved 6.0 ± 0.2 electrons. This observation was in accordance with the observed limiting currents for the first and second wave. At pH > 8.0, the two waves involved 4.0 ± 0.15 electrons as confirmed by practically same equal limiting currents. The values of n were also determined using pyrolytic graphite plate. At pH < 8.0, the first peak was not very well-defined; hence the value of n determined at potentials more negative to peak IIc was found to be 8.0 ± 0.15 . At pH > 8.0, the value of n for the peaks Ic and IIc, was 4.0 ± 0.3 electrons each. The large deviation in n -value from the average value at pH > 8.0 may be due to the fact that the potential applied for peak Ic also contributed partially to peak IIc, as the potentials of peaks Ic and IIc are very close.

The progress of electrolysis was monitored by recording cyclic voltammograms at different time intervals. On applying potential corresponding to peak IIc, a systematic decrease in peaks Ic and IIc was observed. Whereas the peaks IIIa to Va and IIIc, IVc were clearly visible in exhaustively electrolysed solution. A cyclic voltammogram of exhaustively electrolysed solution at pH 3.4 is presented in Fig. 2D. This voltammogram did not change even when the electrolysed solution was left at room temperature for several hours. Thus it is concluded that product or products of electroreduction are electroactive in nature. Similar behaviour was observed at pH 7.0 and 10.6.

The progress of electrolysis was also monitored by UV/vis spectra at different interval of times. The UV/VIS spectra of Acid Red-150 in the entire pH range, exhibit $\lambda_{\max}$ at 235, 356 and 513 nm, indicating that the dye exists as a neutral species in the entire pH range studied. At pH 6, upon application of potential more negative to peak IIc, absorbances at 356 and 513 nm systematically decrease whereas the absorbance at 235 nm increases. After about 3 hr of electrolysis the absorbance at 235 nm reaches a maximum while those at 356 and 513 nm reach minimum values. These observations show that no intermediate with sufficient half-life is generated during electrooxidation of the dye.

Product identification

The products of electroreduction at pH 3.0, 6.0 and

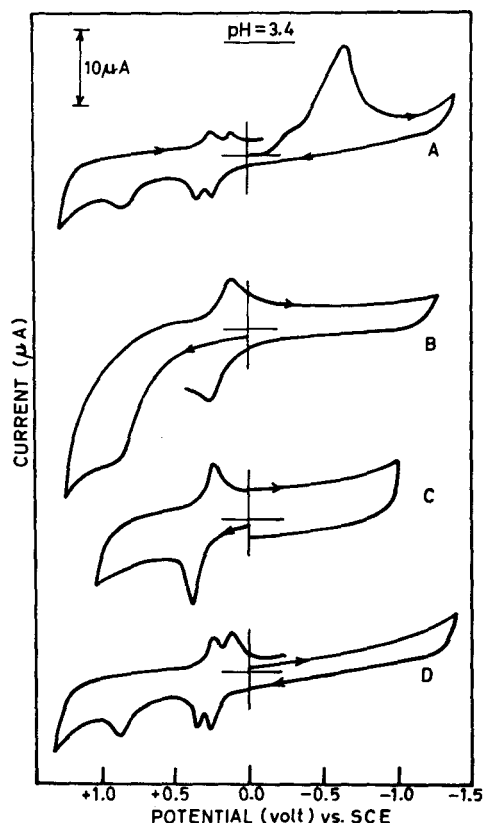


Fig. 2—Cyclic voltammograms observed at pH 3.4 for (A) Acid Red-150, (B) aniline, (C) *p*-phenylenediamine, (D) exhaustively electrolysed solution of Acid Red-150 at pH 3.4.

10.2 at mercury pool or at pyrolytic graphite electrode were characterised as follows: The volumes obtained corresponding to three peaks in liquid chromatography over sephadex G-10 were lyophilised and analysed by TLC, m.p.s and IR spectra. The volumes 200-270 (peak 2), 280-350 (peak 3) and 360-450 (peak 4) ml were lyophilised and exhibited R_f values 0.65, 0.47, and 0.19 respectively. Thus it is clear that three products are formed during complete electroreduction of the dye.

The product with R_f 0.65 (peak 2) was identified as aniline by comparison (R_f and IR) with an authentic sample. The product with R_f 0.47 (peak 3) had the m.p. 290° . The IR spectrum of this product exhibited peaks corresponding to SO_3H ($1030, 1100 \text{ cm}^{-1}$) and phenolic OH ($1250, 1360 \text{ cm}^{-1}$). Based on this the product should have structure similar to 1-amino-2-hydroxynaphthalene-3, 6-disulphonic acid. This product could not be completely identified at this stage due to non-availability of its authentic sample.

The product with R_f 0.19 (peak 4), melted at 140° and exhibited in its IR spectrum bands at 820, 1120, 1260, 1300, 1500 and 1600 cm^{-1} . This product was

identified as *p*-phenylenediamine by direct comparison with an authentic sample.

Hence it is clear that the products of complete electroreduction of Acid Red-150 are aniline, *p*-phenylenediamine and 1-amino-2-hydroxynaphthalene-3, 6-disulphonic acid.

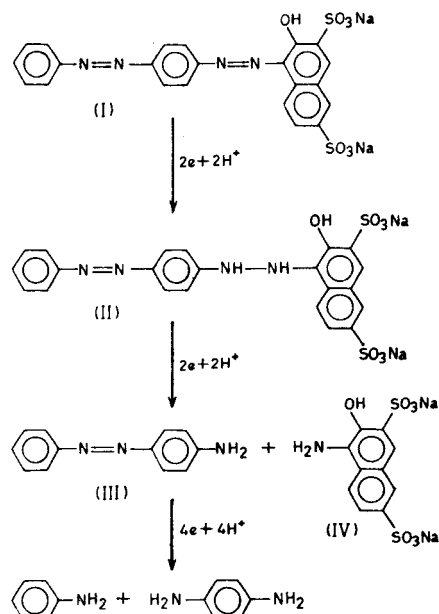
The formation of aniline and *p*-phenylenediamine was further confirmed by recording cyclic voltammograms of authentic samples of aniline and *p*-phenylenediamine, which have been reported electroactive in nature^{7,8}. It was interesting to observe that aniline exhibits peaks IIIa, Va and IIIc as reported in literature^{9,10} and *p*-phenylenediamine gives peaks IVa and IVc at the same potentials as observed for the dye. Cyclic voltammograms of Acid Red-150, *p*-phenylenediamine and aniline at pH 3.4 are presented in Fig. 2, for comparison.

The products corresponding to (4e, 4H⁺) reduction of the dye (I) were also characterised at neutral and alkaline pH, where two waves in polarography and two peaks in cyclic voltammetry with equal limiting currents were observed. For this purpose the dye was reduced at peak Ic potential or plateau potential of the first wave. The TLC of this solution gave two spots with R_f = 0.47 and 0.56 thus indicating that (4e, 4H⁺) reduction of the dye gives two products. The spot with R_f 0.47 indicates the formation of 1-amino-2-hydroxynaphthalene-3, 6-disulphonic acid as observed earlier. Cyclic voltammogram of this solution was recorded by initiating the sweep in the positive direction. The absence of oxidation peak IIIa-Va and reduction peaks IIIc-IVc clearly indicate that 4e, 4H⁺ reduction of the dye does not give aniline or *p*-phenylenediamine as the product. Thus (4e, 4H⁺) reduction causes cleavage of bulky naphthol moiety to give 1-amino-2-naphthol-3, 6-disulphonic acid (sodium salt) and 4-aminoazobenzene.

Redox mechanism

On the basis of the results obtained, it is clear that the dye undergoes reduction by 8e, 8H⁺ process at d.m.e and pyrolytic graphite electrode in the pH range of 2.2-11.2. The (4e, 4H⁺) reduction in neutral and alkaline pH ranges does not indicate the formation of aniline and *p*-phenylenediamine. It can be safely concluded that reduction of -N=N- attached to bulkier naphthol moiety takes place easily in comparison to azo group attached to phenyl moiety.

As the final products of electroreduction are aniline, *p*-phenylenediamine and 1-amino-2-naphthol-3, 6-disulphonic acid it is clear that electroreduction of the two azo groups does not stop at hydrazo stage but further reduction of hydrazo group in II takes place to give amino compounds as the ultimate products (Scheme 1). The first (4e, 4H⁺) reduction of the



Scheme 1- Tentative mechanism proposed for the electroreduction of Acid Red-150.

dye causes cleavage of -N=N- to give *p*-aminoazobenzene (III) and aminonaphthol moiety (IV). Further (4e, 4H⁺) reduction causes the cleavage of second -N=N- to give aniline and *p*-phenylenediamine as the products.

Previous results¹² reported in literature indicate that electroreduction of bisazodyes occurs by first taking (4e, 4H⁺) to give bishydrazo derivatives. Bisazobenzene and similar dyes have been reported^{13,14} to form bishydrazobenzene at d.m.e. Further (4e, 4H⁺) reduction of bishydrazo derivatives is reported to give amino compounds as the products of reduction. However, in our case bishydrazo derivative is not formed, rather cleavage at -N=N- attached to bulkier naphthol moiety takes place. This difference in behaviour can be due to steric hindrance to coplanarity^{15,16} in the molecule, due to the bulkier naphthol group, thereby facilitating cleavage via -N=N-. It has also been observed that reduction potentials at pyrolytic graphite are 250 to 500 mV more negative in comparison to that at d.m.e. This behaviour can be explained on the basis of adsorption on the solid electrodes¹⁷. The solid electrodes also do not permit the free orientation of the species undergoing reduction and hence the potentials observed are always more negative in comparison to those at d.m.e.

Acknowledgement

Thanks are due to M/s Pfizer, USA for the gift of pyrolytic graphite. One of the authors (AK) is thankful to the UGC, New Delhi for the award of a junior research fellowship.

References

- 1 Eisner U & Eisner E K, in *Encyclopedia of electrochemistry of the elements*, edited by A J Bard (Marcel Dekker, New York) 1979.
- 2 Britton H T S, *Hydrogen ions* (D Van Nostrand, New York) 1956 P 360.
- 3 Goyal R N, Bhushan R & Agarwal A, *J electroanal Chem*, **171** (1984) 281.
- 4 Goyal R N, Srivastava S K & Agarwal R, *Bull Soc Chim Fr*, **4** (1985) 656.
- 5 Meites L, *Polarographic techniques* (Interscience, New York) 1967 pp 228.
- 6 Oldham K B & Perry E P, *Analyt Chem*, **40** (1968) 65.
- 7 Lee H Y & Adams R N, *Analyt Chem*, **34** (1962) 1587.
- 8 Bacon J & Adams R N, *J Am chem Soc*, **65** (1945) 1938.
- 9 Wawzonek S & McIntyre T W, *J electrochem Soc*, **114** (1967) 1025.
- 10 Melchior & Maki A H, *J chem Phys*, **34** (1961) 471.
- 11 Zewig A, Lancaster J E, Negalia M T & Jura W H, *J Am chem Soc*, **86** (1964) 4130.
- 12 Saber T M H, Ali M I & Abed N M, *J electroanal Chem*, **28** (1970) 177.
- 13 Florence T M, Johnson D A & Batley G E, *J electroanal Chem*, **50** (1974) 411.
- 14 Florence T M, *J electroanal Chem*, **52** (1974) 115.
- 15 Zuman P, *Colln Czech chem Commun*, **27** (1962) 648.
- 16 Charton M, *J org Chem*, **34** (1969) 278.
- 17 Adams R N, *Electrochemistry at solid electrodes* (Marcel Dekker, New York) 1969, pp 120.