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Electrochemical Behaviour of Azo Dyes in Acid/Ethanol Media

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ABSTRACT

The electrochemical reduction of four azo dyes in acid media was studied by differential-pulse polarography, cyclic voltammetry and constant-potential coulometric methods. All of the electro-reductions of the azo groups are irreversible one-step and 4-electron reduction at pH < 2*. Ortho and para electron withdrawing substituents (e.g.* —CO_2Bu-n*) cause the azo groups to be more easily reduced than meta analogues. In compounds containing both azo and nitro groups, the azo group is reduced prior to the nitro group. The dyes are very useful in silver dye bleach photographic materials.*

1 INTRODUCTION

Silver dye bleach colour photographic recording materials are widely used in colour microfilm and direct positive colour printing.[1,2] The colour

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image is formed by azo dyes which undergo a bleaching of developed silver image in a strongly acidic aqueous medium (usually pH <2):

$$\underset{\text{(silver image)}}{4\,\mathrm{Ag}} + \underset{\text{(azo dye)}}{\text{—N=N—}} + 6\mathrm{H}^+ \rightarrow \underbrace{\text{—HN}_3^+ + \text{—NH}_3^+}_{\text{(dye fragments)}} + 4\,\mathrm{Ag}^+$$

The bleaching behaviour of the image dyes is one of the most important factors for improvement of the final colour image quality. Electrochemical methods are useful in studying the redox properties of reducible compounds. Research studies have been published on the polarographic reduction of azo dyes,[3,4,5] but little data has been reported on their behaviour in strongly acidic media.

In this present paper, investigations on the polarographic reduction of some oil-soluble azo dyes in acid media, and in strongly acidic media are reported, in order to evaluate the bleaching process of azo dyes in silver dye bleach photography.

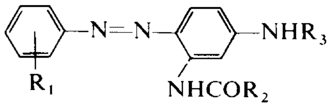
2 EXPERIMENTAL

2.1 Reagents

The azo dyes (Table 1) were prepared by conventional diazotization with sodium nitrite in dilute HCl, followed by coupling in sodium acetate/acetic acid media; they were purified by recrystallization, and characterized by elemental analysis, IR, MS and ^{1}H NMR. Stock solutions (about 10^{-5} M) were prepared by dissolving the dyes in absolute alcohol, mixing with the same volume of dilute sulphuric acid or tri-acid (H_3PO_4, CH_3COOH and H_3BO_3) standard buffer containing 0·1 M KCl, and adjusting the pH of the triacid solution with 1 N NaOH to the desired value (for pH >1·82).

TABLE 1

Structure and Properties of Dyes



Dyes	R_1	R_2	R_3	*m.p. (°C)*	λ_{max} $CHCl_3$ (*nm*)	ε_{max} $CHCl_3$
Y_1	*m*-COOBu-*n*	CH_3	CH_2CH_2CN	149–149·5	409·2	35 000
Y_2	*o*-COOBu-*n*	CH_3	CH_2CH_2CN	111–112	410·2	31 100
Y_3	*p*-COOBu-*n*	CH_3	CH_2CH_2CN	186–187	422·4	36 700
M_1	*p*-NO_2	Bu-*i*	$CH(CH_3)_2$	153–153·5	535·6	52 900

2.2 Apparatus

Differential-pulse polarography was carried out using a combination of a pulse polarographer (Fudan, Shanghai, China, F-78) and an X–Y recorder (Dahua, Shanghai, China, LZ 3-200). A three-electrode system incorporating a dropping mercury electrode, a platinum counter electrode and a saturated calomel reference electrode were used. A pulse amplitude of 50 mV, a scan rate of 5 mV s^{-1}, a forced drop time of 3 s, and a temperature of 25°C were used.

Cyclic polarography was effected by Cybernetio Potentiostate systems with a three-electrode circuit and a scan rate of 10 mV s^{-1}. A hanging mercury electrode was used as working electrode and the other two electrodes were the same as those described above.

Coulometric measurements were carried out with a 100 ml H-type vessel, with cathodic and anodic compartments. A mercury pool was the cathode, a platinum foil with a surface of 5 cm^2 was the anode and a saturated calomel electrode was used as reference electrode. During the experiments, the solutions were stirred with a magnetic stirrer.

In all the experiments, the solutions were deoxygenated for 10 min before measurements under nitrogen, and an inert atmosphere was maintained throughout with a flow of nitrogen.

3 RESULTS AND DISCUSSION

3.1 Effect of dye molecular structure

The dyes tested in our experiments are listed in Table 1. Typically, differential pulse polarograms for Y_1, Y_2 and Y_3 are given in Fig. 1. Each of

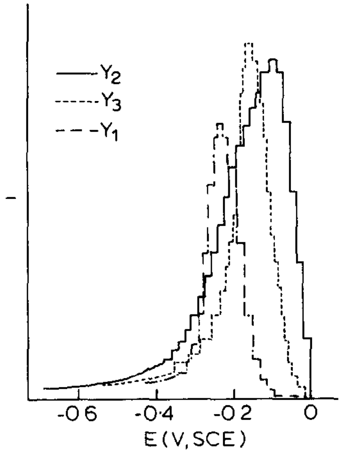


Fig. 1. Differential-pulse polarograms of Y_1, Y_2 and Y_3 (1 : 1 tri-acid/ethanol, pH = 1·82, scan rate: 5 mV s^{-1}, 25°C, $C = 2 \times 10^{-5}$ M).

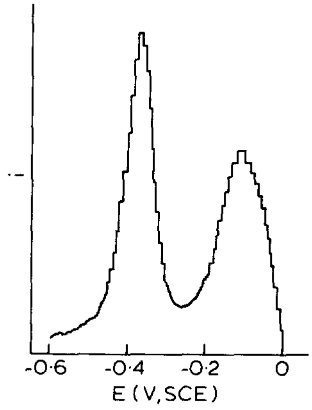


Fig. 2. Differential-pulse polarograms of M_1 (1 : 1 tri-acid/ethanol, pH = 1·82, scan rate: 5 mV s^{-1}, 25°C, $C = 2 \times 10^{-5}$ M).

the three dyes has a single reductive wave in the range of 0 to −0·700 mV (SCE), but the peak potentials (E_p) are different and decrease in the following order:

$$Y_2 > Y_3 > Y_1$$

As listed in Table 1, the dyes have the same coupling moiety and the diazo moieties differ only in the position of the substituent (—CO_2Bu-*n*). The ortho-substitution (Y_2) makes the azo group more easily reduced than in the para substituted isomer (Y_3), and meta substitution (Y_1) has the least effect. This substituent effect is related to the conjugation and electronic effects of the —CO_2Bu-*n* in relation to the azo group. The electron-withdrawing —CO_2Bu-*n* group decreases the electron density on the azo group, especially when substituted ortho and para to it. The resultant lowering of the electron density on the azo group with such substitution facilitates the reduction.

Figure 2 shows the differential pulse polarogram of M_1. There are two waves in the reductive potential range from 0 to −1·00 V(SCE). This phenomenon is rationalized by the fact that there are two reducible groups, viz. azo and nitro, which have different reduction potentials.

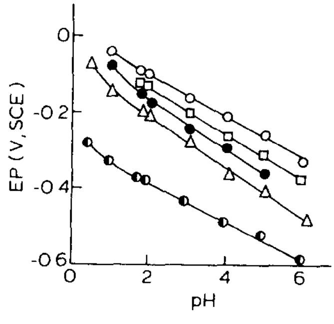


Fig. 3. Effect of pH E_p (Δ—Y_1, ○—Y_2, ●,—Y_3; □—M1, the first wave; ◐—M_1, the second wave; 25°C, $C = 2 \times 10^{-5}$ M).

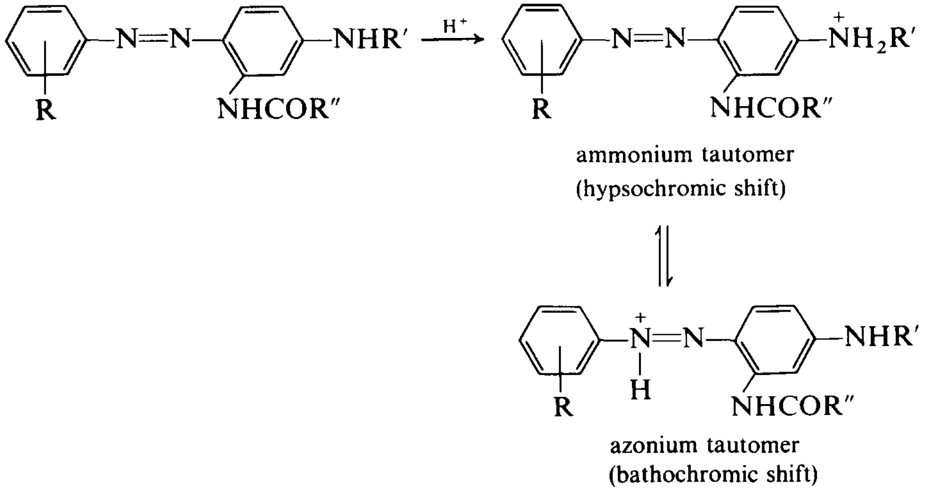
TABLE 2

E_p of Dyes in Strong Acidic Media (V(SCE))

Dyes	*Tri-acid solution pH = 1·82*	H_2SO_4 *0·033* M	H_2SO_4 *0·10* M	H_2SO_4 *0·50* M
Y_1	0·20	0·15	0·072	0·058
Y_2	0·10	0·098	0·063	0·042
Y_3	0·15	0·084	0·037	—
M_1	0·12	0·074	0·032	—
	0·37	0·34	0·28	0·21

3.2 Effect of pH

The E_p of the waves showed a shift towards negative potentials with increasing pH. The plots of E_p *versus* pH showed a linear relationship (Fig. 3), having a gradient of 60–70 mV/pH. At very low pH (pH < 2), however, the E_p deviates from linearity and has higher values, especially in H_2SO_4/ethanol media (Table 2). This implies that the dyes are more readily reduced in strongly acidic media. It is known that azo dyes can protonate in such media.[6] The colour changes of the dyes (in Y1, Y2 and Y3 from yellow to orange, and M_1 from red to orange) are evidence of the protonation, which may cause a hypsochromic or bathochromic shift, depending upon the structure of the dyes:



ammonium tautomer
(hypsochromic shift)

azonium tautomer
(bathochromic shift)

The increase in E_p is the result of protonation, since the cation reduces the electron density on the azo group.

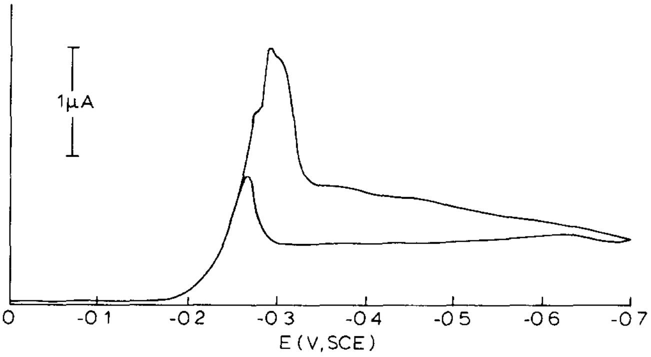


Fig. 4. Cyclic voltammetry of Y_2 (1 : 1 tri-acid/ethanol, pH = 1·82, scan rate: 10 mV s^{-1}, 25°C, $C = 2 \times 10^{-5}$ M).

3.3 Irreversibility of the reduction process

Figures 4 and 5 show the cyclic voltammetry curves of Y_2 and M_1, respectively. There are only reduction waves (one wave in Y_2 and two in M_1) and the small shoulder peaks are caused by adsorption of the dyes on the mercury drop. No oxidation wave is observed. Thus, reduction of the azo dyes is irreversible under our test conditions (pH = 1·82). This agrees with similar work on azo dyes in weakly acidic media.[3,4]

3.4 Constant-potential coulometric determination of the number of electrons exchanged

The following procedure was employed: into the cathode compartment of the coulometric vessel, 15 ml dye solution (*c*. 5×10^{-3} M containing *m* mole of the dye) of ethanol, and 15 ml triacid/ethanol solution containing 0·2 M KCl were added. After deaeration, the solution was elec-

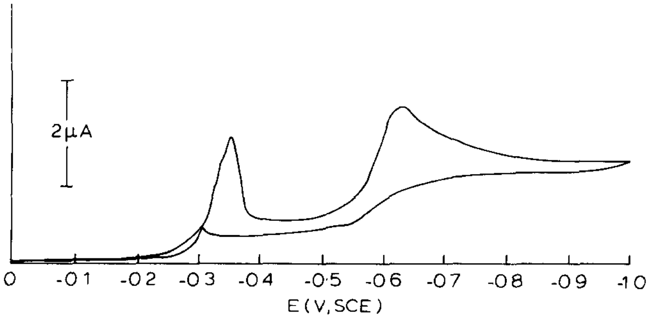


Fig. 5. Cyclic voltammetry of M_1 (1 : 1 tri-acid/ethanol, pH = 1·82, scan rate: 10 mV s^{-1}, 25°C, $C = 2 \times 10^{-5}$ M).

trolyzed at a potential 150 mV more negative than the peak potential of the appropriate wave. The electrolysis was terminated when the value of the current decreased to a constant residual current value I_0. By this time, the colour of dye solution had disappeared. The charge (Q) was measured by electronic integration. According to the conservation law, we have

$$Q = n \,.\, m \,.\, F + I_0 t$$

and thus

$$n = (Q - I_0 t)/(m \,.\, F)$$

where n is the number of electrons exchanged in the reduction, t is the electrolysis time, and F is Frank constant ($9{\cdot}648 \times 10^3$ emu mol^{-1}).

For Y_2, n values of 4·25 and 4·11 were obtained on two separate runs. For M_1, n values of 4·05 and 4·10 were assigned to the first wave, and n values of 5·57 and 5·46 to the second wave from two separate runs, respectively. From these results it can be concluded that the wave of Y_2 and the first wave of M_1 are a one-step four-electron reduction of the azo group:

$$\text{—N=N—} + 4e + 4H^+ \rightarrow \text{—}NH_2 + H_2N\text{—}$$

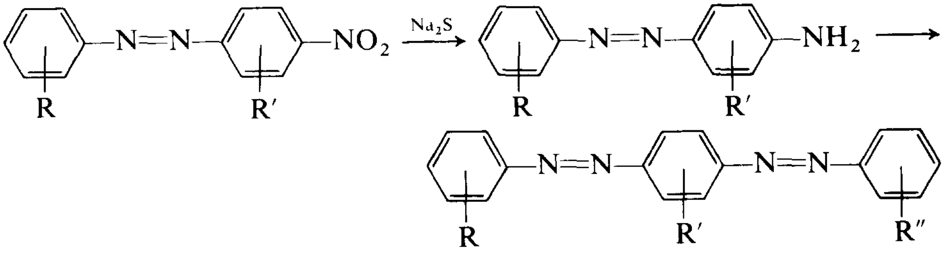
and the second wave of M_1 is a one-step six-electron reduction of the nitro group (actually, the reduction of *p*-nitroaniline):

$$\text{—}NO_2 + 6e + 6H^+ \rightarrow \text{—}NH_2 + 2H_2O$$

The nitro group reduction was confirmed by coulometric measurement of *p*-nitroaniline under similar conditions.

Thin layer chromatography of the reduction residue also supported the results. Butyl *o*-amino benzoate, *p*-nitroaniline and *p*-aminoaniline were detected in the reduction residue of Y_2, the first and the second wave of M_1, respectively.

The reduction of the azo group prior to that of the nitro group is unexpected. It is well known that in the preparation of polyazo dyes, a nitro group in the para position of a monoazo dye is reduced by Na_2S to form an aminoazo dye, which is then diazotized and coupled again to form a disazo dye:[7]



Therefore, a nitro group is usually reduced prior to an azo group in alkaline medium. However, our results show that the azo is more easily reduced than the nitro group in strongly acidic media (pH < 2). This fact is very important in silver dye bleach photography, because many oil-soluble dyes contain a nitro group and there is a tendency to use oil-soluble dyes to replace traditional water-soluble dyes used in the silver dye bleach process.[8] If the nitro group was reduced prior to the azo group, an amino azo dye with a different colour would form, which would destroy the tone reduction. The prior reduction of the azo group encouraged us to use some magenta and cyan nitroazo dyes in the photographic process and good results have been obtained.

3.5 Electro-reduction mechanisms of azo groups

In neutral or weak acid media, some 2- or 3-electron-reduction mechanisms have been suggested and hydroazo compounds were obtained as final products.[4,5] However, as mentioned above, we observed 4-electron-reduction mechanisms in acidic media. Two reduction mechanisms may be deduced, viz. firstly, the reduction takes place in the neutral form:

$$R_1—N{=}N—R_2 \overset{e}{\gtrless} [R_1—N—N—R_2]^{\cdot -} \xrightarrow{6H+,\ 3e} \cdots \rightarrow R_1NH_3^+ + R_2NH_3^+ \qquad (a)$$

Secondly, it may proceed on the protonated form:

$$[(R_1—N{=}N—R_2)H]^+ \overset{e}{\gtrless} [R_1—NH—NR_2]^{\cdot} \xrightarrow{3e,5H+} \cdots \rightarrow R_1NH_3^+ + R_2NH_3^+ \qquad (b)$$

Both mechanisms may exist in acidic media, but if the pH is very much larger than the pK_a (the acidity constant of the protonated dye), e.g. pH > 2, (a) must be the main route, since there is little protonation. In this case, the —COOBu group in the dye molecule must aid the reduction, as we observed. If $pH < pK_a$, e.g. in 0·5 M H_2SO_4, most of the dye molecules are protonated, therefore (b) must be the main process. In this case the —COOBu group also decreases the electron density, because of its electron-withdrawing properties, and thus facilitates the reduction.

In both of the cases where $pH \gg pK_a$ and $pH \leq pK_a$, the controlling step may be the first electron attack, not the protonation process. But when the pH becomes slightly larger than the pK_a, i.e. $pK_a < pH < 2$, both (a) and (b) take place, and (b) may occur prior to (a) to some extent. In this case, protonation may be the controlling step, and the —COOBu group hinders the reduction, and the pH is a more sensitive factor for E_p.

Since the process with $6H^+$ and 4e in one elementary step is not likely, the electro-reduction is carried out in a series of consecutive steps. But the differences of E_p between the steps are very small. The discrete electro-reduction step is not observable. Therefore, from an electrochemical point of view, the reduction is a one-step-4e process.

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