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Note

Kinetics of Reduction of Aza Cyanine Dyes by Bisulphite Ions in (Acetate-Acetic Acid) Buffer-Ethanol Mixtures

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The kinetics of bisulphite ions reduction of 2-[[[4-(dimethylamino)phenyl]imino]methyl]-1-ethylpyridinium iodide (I), 4-[[[4-(dimethylamino)phenyl]imino]methyl]-1-ethylpyridinium iodide (II) and 2-[[[4-(dimethylamino)phenyl]imino]methyl]-1-ethylquinolinium iodide (III) in buffer- ethanol mixtures were investigated from 18 °C to 45 °C spectrophotometrically. These reactions follow the overall second-order kinetics, first order with respect to each of the reactants. Reaction rates decrease with increasing ethanol, as well as hydrogen ion concentrations. The reduction rate (k_2) of aza cyanine dyes depends on the structure of the dye used and follows the order: dye(I) $>$ dye(II) $>$ dye(III). Activation parameters were evaluated using Arrhenius and Eyring equations.

INTRODUCTION

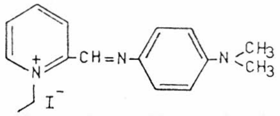
In continuation of our interest in kinetics of the reduction of organic compounds,[1,2] we aimed to investigate the reduction of aza cyanine dyes by bisulphite ions in buffer-ethanol mixtures.

Cyanine dyes have found important applications in different fields,[3] especially photographic[4] industry, electrophotography[5] and optical recording materials.[6] Their electrochemical behaviour and their application as corrosion inhibitors for copper in nitric acid medium was investigated.[7] They found medicinal[8,9] and agricultural applications in the breaking period of dormancy[10] and as potent mitodepressive and mutagenic agents.[11] The biochemical effect and charge transfer complexes of aza cyanine dyes with nucleic acid bases were recently studied.[12]

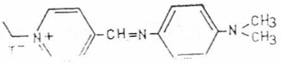
Sodium bisulphite is one of common reducing agents used in photographic developers. The effect of this reagent on photographic films containing cyanine dyes is of interest. However, kinetics of the reduction of aza cyanine dyes has not been mentioned before; therefore we were prompted to undertake the present investigation. 2-[[[4-Dimethylamino)phenyl]imino]methyl]-1-ethylpyridinium iodide (I), 4-[[[4-dimethylamino)phenyl]imino]methyl]-1-ethylpyridinium iodide(II) and 2-[[[4-(dimethylamino)phenyl]imino]methyl]-1-ethylquinolinium iodide(III) were selected to shed some light upon the structure activity relationship on the reduction rates of such dyes.

MATERIALS AND METHOD

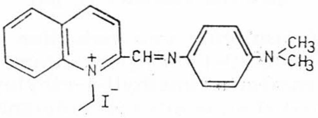
Sodium bisulphite, ethyl alcohol, acetic acid and sodium acetate were of Analar (BDH) grade. Dyes(I)—(III) were prepared as reported before[13]. The solid products obtained were recrystallized from ethanol. The results are listed in Table I. The structures of the compounds prepared are as follows:



Dye(I). CT band: $\lambda_{max} = 500$ nm (ethanol)



Dye(II). CT band: $\lambda_{max} = 502$ nm (ethanol)



Dye(III). CT band: $\lambda_{max} = 570$ nm (ethanol)

TABLE I

The Elemental Analysis Data and Melting Points of the Dyes(I—III) and Their Reduction Products(IV—VI)

Compound	Formula	m. p. (°C)	% Calc. (found)		
			C	H	N
I	$C_{16}H_{20}N_3I$	191	50.40(50.31)	5.29(5.17)	11.02(10.90)
II	$C_{16}H_{20}N_3I$	194	50.40(50.36)	5.29(5.19)	11.02(10.93)
III	$C_{20}H_{22}N_3I$	185	55.69(55.58)	5.14(5.11)	9.74 (9.65)
IV	$C_{16}H_{22}N_3I$	246	50.14(50.02)	5.79(5.65)	10.96(10.85)
V	$C_{16}H_{22}N_3I$	254	50.14(50.00)	5.79(5.67)	10.96(10.87)
VI	$C_{20}H_{24}N_3I$	235	55.44(55.32)	5.58(5.49)	9.70 (9.59)

Stock solution of the dye was prepared by dissolving an accurately weighed amount of the dye in the appropriate volume of ethanol. Stock solution of sodium bisulphite was prepared by dissolving the appropriate weighed recrystallized salt in doubly distilled conductivity water, standardized against iodine[14]. Acetic acid-sodium acetate buffer solutions with $[H^+]$ in the range $(0.59—132.30) \times 10^{-6}$ M were prepared according to Perrin[15].

Kinetic Measurements

Kinetic experiments were carried out in a temperature — controlled (±0.1 °C) water-bath. The reaction was initiated by adding the requisite quantity of pre-equilibrated sodium bisulphite solution to an equilibrated mixture of the dye, HOAc- Na OAc buffer solution, and ethanol. The course of the reaction was followed by monitoring the disappearance of the dye as a function of time at the CT band maximum absorption of the dye (490, 495 and 570 nm for dyes(I),

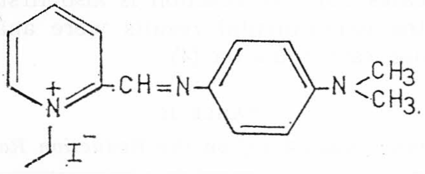
(II) and (III) respectively) against the same solvent containing the same amount of sodium bisulphite as in the kinetic solutions as blanks. Absorption measurements were followed on a Shimadzu UV-200 S double beam spectrophotometer, using a cell of 1 cm path length. It was verified that there was no interference of other reagents or reduction products at λ_{max} of the dye. The reactions were usually followed up to not less than three half-lives. The pH measurements were carried out at 20 °C on a WG PYE model 290 pH-meter accurate to ±0.005 pH units.

The kinetics of the present work were studied under pseudo-first — order conditions where [Bisulphite] $\gg$ [Dye].

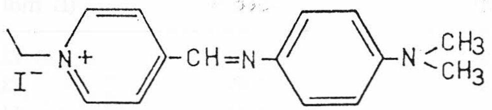
RESULTS AND DISCUSSION

1. *Stoichiometry and Product Analysis*

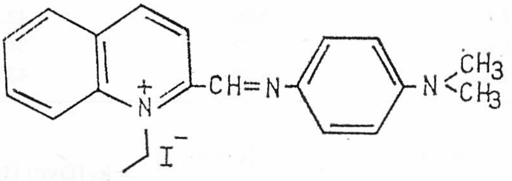
The stoichiometry of the overall reaction of bisulphite ion with excess of the dye was determined spectrophotometrically at 25 °C. The unreacted [Dye] was istimated periodically until it attained a constant value, i. e. completion of reaction. A stoichiometric ratio of 1 within experimental error ($[\text{Dye}]_{\text{consumed}}/[\text{Bisulphite}]_o$) was obtained with ten different initial [dye]. The reduction products were isolated from the reaction mixture under aerobic conditions by extraction with ether, followed by drying over anhydrous sodium sulphate. The structures of the solid products (IV)—(VI) were confirmed by elemental analysis (Table I) and spectral data (UV-Visible, IR), as follows:



2-[[[4-dimethylamino)phenyl]amino]methyl]-1-ethylpyridinium iodide (IV)



4-[[[4-dimethylamino)phenyl]amino]methyl]-1-ethylquinolinium iodide (V)



2-[[[4-dimethylamino)phenyl]amino]methyl]-1-ethylpyridinium iodide (VI)

The stoichiometry of the overall reaction can be represented by equation (1) for dye (I) as an example:

$$C_{16}H_{20}N_3I + HSO_3^- + H_2O = C_{16}H_{22}N_3I + HSO_4^- \qquad (1)$$

2. *Rate Dependence on [Dye]*

Under the reduction conditions where [Bisulphite] $\gg$ [Dye], the rate equation can be expressed as

$$-\frac{d\,[\text{Dye}]}{dt} = k'\,[\text{Dye}] \qquad (2)$$

where k' is the observed pseudo-first-order rate constant, which may be expressed by the equation:

$$k' = k_2\,[\text{Bisulphite}] \tag{3}$$

and k_2 is the second- order rate constant.

The rate-order with respect to the dye was determined by studying the reaction at different initial concentrations of the dye with constant [Bisulphite]. The [Dye(I)] was varied in the range $(0.42—4.71) \times 10^{-5}$ M, while [Bisulphite] was 2.4×10^{-3} M, the $[H^+]$ was $1.04 \times {}^{-5}$ M, ethanol content was 44.2% (w/w) at 20 °C. Under these conditions the plots of —log (absorbance) versus time were linear, indicating the first- order dependence of rate on [Dye]. The average value of k' was $(1.11 \pm 0.01) \times 10^{-3}$ sec^{-1}.

3. *Rate Dependence on [Bisulphite]*

The rate -order with respect to bisulphite ion was deduced from the measurement of the reaction rates at several bisulphite concentrations and constant [Dye]. The [Bisulphite] was varied in the range $(1.2—14.4) \times 10^{-3}$ M, while $[\text{Dye(I)}] = 3.38 \times 10^{-5}$ M, $[H^+] = 1.04 \times 10^{-5}$ M, 44.2% (w/w) ethanol at 18 °C. The plot of k' versus [Bisulphite] was linear passing through the origin, Figure 1(a). This indicates that the reaction is also first-order in [Bisulphite], Table II. Therefore, the experimental results were analyzed in the light of the overall second-order rate equation (4).

TABLE II

Effect of Varying [Bisulphite] on the Reduction Rates of Dye (I)

10^3 [Bisulphite] (M)	$k' \times 10^3$ (Sec^{-1})	$10^2\,k'$/[Bisulphite] (L mol^{-1} Sec^{-1})
1.2	0.52	43.33
2.4	1.05	43.75
3.6	1.60	44.44
6.0	2.65	44.17
2.4	3.60	42.86
10.8	4.72	34.70
14.4	6.32	43.89

$$-\frac{d\,[\text{Dye}]}{dt} = -\frac{d\,[\text{Bisulphite}]}{dt} = \frac{d\,[\text{Product}]}{dt} = k_2\,[\text{Dye}]\,[\text{Bisulphite}] \tag{4}$$

4. *Rate Dependence on [Ethanol]*

The effect of medium content of ethanol on the reduction rates was investigated at 28 °C. The solvent composition was varied in the range (8.1—54.3)% (w/w) EtOH, $[\text{Dye(I)}] = 3.38 \times 10^{-5}$ M, $[\text{Bisulphite}] = 1.0 \times 10^{-3}$ M, $[H^+] = = 1.04 \times {}^{-5}$ M. The reduction rates were found to decrease sharply with increasing the ethanol content, Figure 1(b).

Spectroscopic studies on aza cyanine dyes[16] verified that the intramolecular CT bands were largely affected by the medium content of ethanol. The intermolecular H-bond between the dye and ethanol led to the formation

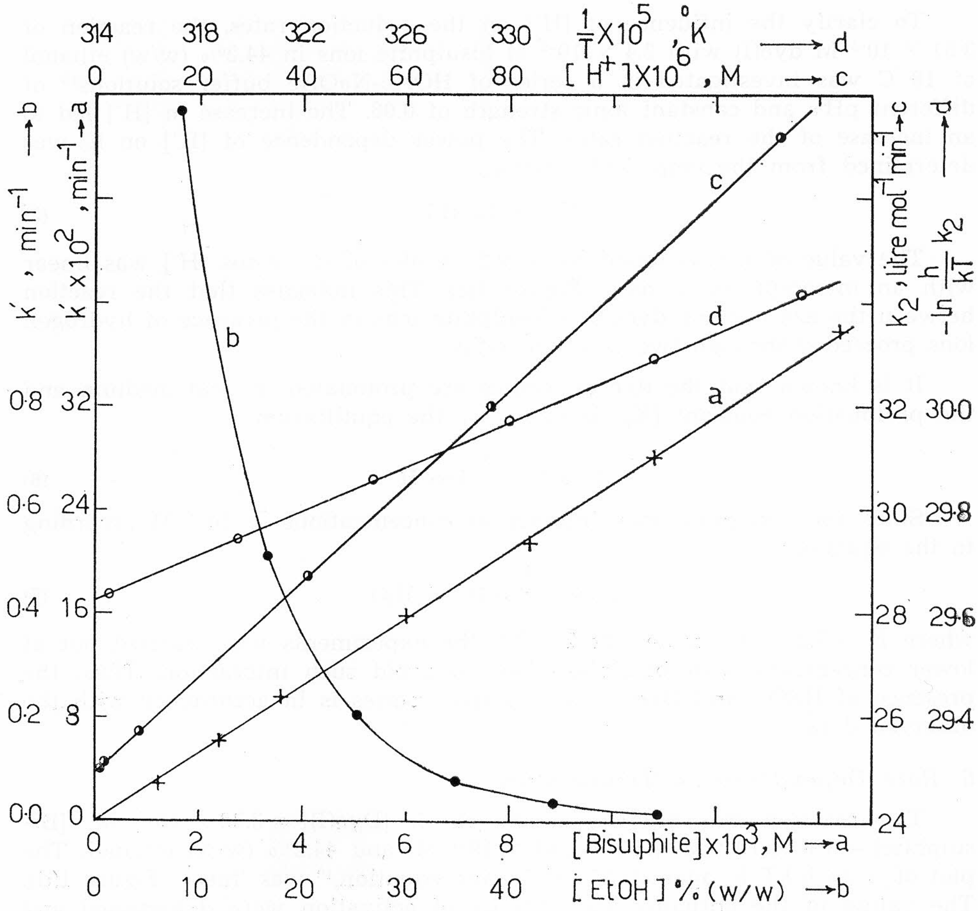


Figure 1: a) Bisulphite dependency: (Plot of k' versus [Bisulphite]: [Dye(I)] = = 3.38×10^{-5} M; [H^+] = 1.04×10^{-5} M; EtOH = 44.2% (w/w); temperature = 18 °C).

b)Effect of ethanol content on the reduction rate of dye(I) at 28 °C: [Dye(I)] = = 3.38×10^{-5} M; [Bisulphite] = 1.0×10^{-3} M; [H^+] = 1.04×10^{-5} M.

c) Effect of [H^+] on the reduction rate of dye(I) at 18 °C. Plot of k_2 versus [H^+]: [Dye(I)] = 3.51×10^{-5} M; [Bisulphite] = 2.4×10^{-3} M; EtOH = 44.2% (w/w).

d) Eyring plot of $-\ln h/kT\, k_2$ versus $1/T$ for the reduction of dye(I).

of dye-ethanol molecular complex.[16] The formation constant K_f fo the dye--ethanol complex was found to be 8.87 for dye (II) as an example. The formation of a solvent cage[2,16] between the dye and ethanol molecules via hydrogen bonding retarded the attack of HSO_3^- ions.

Schadt[17] explained the observed decrease of reactivity with the increase of EtOH content in aqueous ethanol by the differences in nucleophilicity and ionization power of the solvent.

5. *Hydrogen Ion Dependency*

To clarify the influence of $[H^+]$ on the reduction rates, the reaction of 3.51×10^{-5} M dye(I) with 2.4×10^{-3} M bisulphite ions in 44.2% (w/w) ethanol at 18 °C was investigated in a series of HOAc-NaOAc buffer solutions[15] of different pH's and constant ionic strength of 0.06. The increase in $[H^+]$ led to an increase of the reaction rates. The power dependence of $[H^+]$ on k_2 was determined from the empirical relation:

$$\ln k_2 = \ln [H^+]^n \tag{5}$$

The value of n was found to be 0.2. A plot of k_2 versus $[H^+]$ was linear with an intercept on k_2 axis, Figure 1(c). This indicates that the reaction between the aza cyanine dyes and bisulphite ions in the presence of hydrogen ions proceeded through two reaction paths.

It is known that the dye molecules are protonated in acid medium and the protonation constant (K_p) is given by the equilibrium:

$$\text{Dye} + H^+ \overset{K_p}{\rightleftharpoons} \text{Dye } H^+ \tag{6}$$

Since the bisulphite ions interact at concentrations $> 10^{-2}$ M according to the equation:

$$2\,HSO_3^- \overset{K}{\rightleftharpoons} S_2O_5^{-2} + H_2O \tag{7}$$

where $K = 7.2 \times 10^{-2}$ mole^{-1} at 25 °C[18], the experiments were carried out at lower concentrations of bisulphite ions to avoid such interaction. Thus, the presence of HSO_3^- and Dye H^+ as reactive species is in accordance with the observed data.

6. *Rate Dependence on Temperature*

The reaction was studied at 20—45 °C, [Dye(I)] = 3.38×10^{-5} M, [Bisulphite] = 1.0×10^{-3} M, $[H^+] = 1.04 \times 10^{-5}$ M, and 44.2% (w/w) ethanol. The plot of $-\ln h/kT\ k_2$ against $1/T$ of Eyring equation,[19] was linear, Figure 1(d). The values of the enthalpy and entropy of activation were determined and are summarized along with the other activation parameters in Table III.

TABLE III

Rate Constants and Activation Parameters of the Reduction Reactions

Parameter	Value		
	Dye(I)	Dye(II)	Dye(III)
$k_2 \times 10^{-2}$ (L mol^{-1} sec^{-1}) (298 °K)	53.20	38.27	19.32
E_a* (kJ. mol^{-1})	20.34	22.70	21.97
$\log A_{10}$* (kJ. mol^{-1})	15.76	17.32	16.80
$\Delta H^{\ddagger}$** (kJ. mol^{-1}) (298 K)	19.74	22.11	21.38
$\Delta G^{\ddagger}$** (kJ. mol^{-1}) (298 K)	64.39	65.20	66.90
$\Delta S^{\ddagger}$** (J. mol^{-1} deg^{-1}) (298 K)	—149.81	—144.60	—152.74

* Calculated using Arrhenius equation.

** Calculated using Eyring equation.

To shed some light upon the effect of the linkage position of the [[[4-(dimethylamino)phenyl]imino]methyl]moiety with the heterocyclic nucleus of 1-ethylpyridinium iodide on the reduction rates of aza cyanine dyes, the reduction of dye(II) was studied at 20—45 °C; [Dye(II)] = 3.39×10^{-5} M, [Bisulphite] = 1.0×10^{-3} M, [H^+] = 1.04×10^{-5} M, and the solvent was 44.2% (w/w) ethanol. The thermodynamic parameters of activation were calculated and the results are given in Table III.

The reduction of dye (III) was studied to clarify the effect of the fused benzene ring within the heterocyclic quaternary nucleus upon the reduction rate. The reaction was performed between 18 °C and 45 °C at [Dye(III)] = = 3.4×10^{-5} M, [Bisulphite] = 3.0×10^{-3} M, [H^+] = 1.04×10^{-5} M, and 44.2% (w/w) ethanol. The values of activation parameters are listed in Table III.

The experimental results indicate that the rates of reduction of aza cyanine dyes depend on their structure, i. e. on the nature of the quaternary heterocyclic nucleus as well as the linkage position. From Table III, it is quite clear that the reduction rate (k_2) of dye(I) is greater than that of its isomer (II) which, in turn, is higher than that of dye(III). This may be attributed to the effect of delocalization extension of the π-cloud over the reducible azamethine group (—CH=N—), i. e. the increase in conjugation by an ethylenic bond between the reducible centre and the quaternary nitrogen atom in case of dye(II) isomer and an extra fused benzene ring in dye(III).

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SAŽETAK

Kinetika redukcije azacijaninskih boja s pomoću bisulfita u puferskoj vodenoj otopini octene kiseline, acetata i etanola

M. M. Girgis, A. S. El-Shahawy i Z. H. Khalil

Redukcija cijaninskih boja s pomoću bisulfita istraživana je spektrofotometrijski u vodenoj puferskoj otopini octene kiseline, acetata i etanola. Reakcija je prvoga reda s obzirom na svaki reaktant, a brzina redukcije smanjuje se s porastom koncentracije vodikovih iona i etanola. Raspravlja se o mehanizmu redukcije.