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Kinetics and Mechanism of Oxidation of Indigocarmine by N-Sodio-N-bromobenzenesulphonamide (Bromamine-B) in Acid Buffer Medium

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Kinetics of oxidation of indigocarmine [IC] by bromamine-B in pH 5 buffer medium has been studied at 30°C spectrophotometrically at λ_{max} 610 nm. The reaction is first order with respect to [IC] and second order with respect to [BAB]. The reaction rate shows an inverse first order on [benzenesulphonamide]. Addition of halide ions and variation of ionic strength of the medium have no influence on the reaction rate. There is a negative effect of dielectric constant of the solvent. Activation parameters have been calculated. Mechanism proposed and the derived rate laws are consistent with observed kinetics.

INTRODUCTION

Indigocarmine (IC) (5,5′-indigodisulfonic acid, disodium salt) finds applications as a redox indicator in analytical chemistry and as a microscopic stain in biology.[1] The chemistry of indigocarmine and its derivatives has been reviewed by Rodd.[2] Although there are several analytical methods available for indigocarmine[3, 4], only a few studies of the kinetics of indigocarmine oxidation have been reported in the literature. Several studies on the mechanistic aspects of oxidation of diverse organic substrates including indigocarmine by aromatic haloamines have been reported by us and others.[5–11] Bromamine-B or BAB ($PhSO_2NNaBr\cdot 1.5H_2O$) is a haloamine containing a positive bromine which is implicated in the reaction of functional groups of the substrates. To our knowledge, however, no study on the kinetics of IC-BAB reaction has been reported. In the present paper, we report the spectrophotometrically monitored kinetics of oxidation of indigocarmine by BAB in pH 5 buffer medium with a view to elucidate the reaction mechanism.

EXPERIMENTAL

Preparation of bromamine-B (BAB) and its purification has been reported already.[12] Aqueous solution of BAB was standardized iodometrically and preserved in brown bottles to prevent photochemical deterioration. Aqueous solution of indigocarmine (Merck) was prepared using triply distilled water, standard buffer systems[13] (potassium hydrogen phthalate + NaOH) were prepared and used. All other chemicals were of analytical grade. Triply distilled water was used for preparing aqueous solution. Ionic strength of reaction mixture was kept at a high value with a concentrated solution of $NaClO_4$.

Kinetic Measurements

Kinetic runs were performed under pseudo-first-order conditions of a large excess of the oxidant over indigocarmine at 30°C. For each run, requisite amounts of IC, $NaClO_4$ (to maintain a constant ionic strength) and a buffer of known pH were mixed in a stoppered pyrex glass tube whose outer surfaces was coated black. Required amount of water was added to maintain a constant total volume. The tube was thermostated in a water bath at a given temperature. To this solution, was added a measured amount of preequilibrated BAB solution to give a known overall concentration. The reaction mixture was shaken for uniform concentration. The course of the reaction was monitored spectrophotometrically by measuring the absorbance at the λ_{max} of 610 nm for IC at regular time intervals for three half lives. The pseudo first order rate constants K' calculated were reproducible within ±3%. Since the total ionic strength maintained was 0.2 M, molar concentrations were used in the expression of rate constants instead of activities, in first approximation, neglecting the activity coefficients. Regression analysis of experimental data to get the regression coefficient r, is carried out on a TDC-316 computer and on an EC-72 statistical calculator.

Reaction Stoichiometry

Varying ratios of the oxidant (BAB) to IC in pH 5 buffer medium were equilibrated at 30°C for 12 h. Aliquots of the reaction mixture were iodometically titrated with a standard thiosulphate solution, using starch indicator, to determine the concentrations of unchanged BAB. The mole ratio (number of moles of BAB consumed per mole of IC) was calculated.

The stoichiometric reaction can be represented as below,

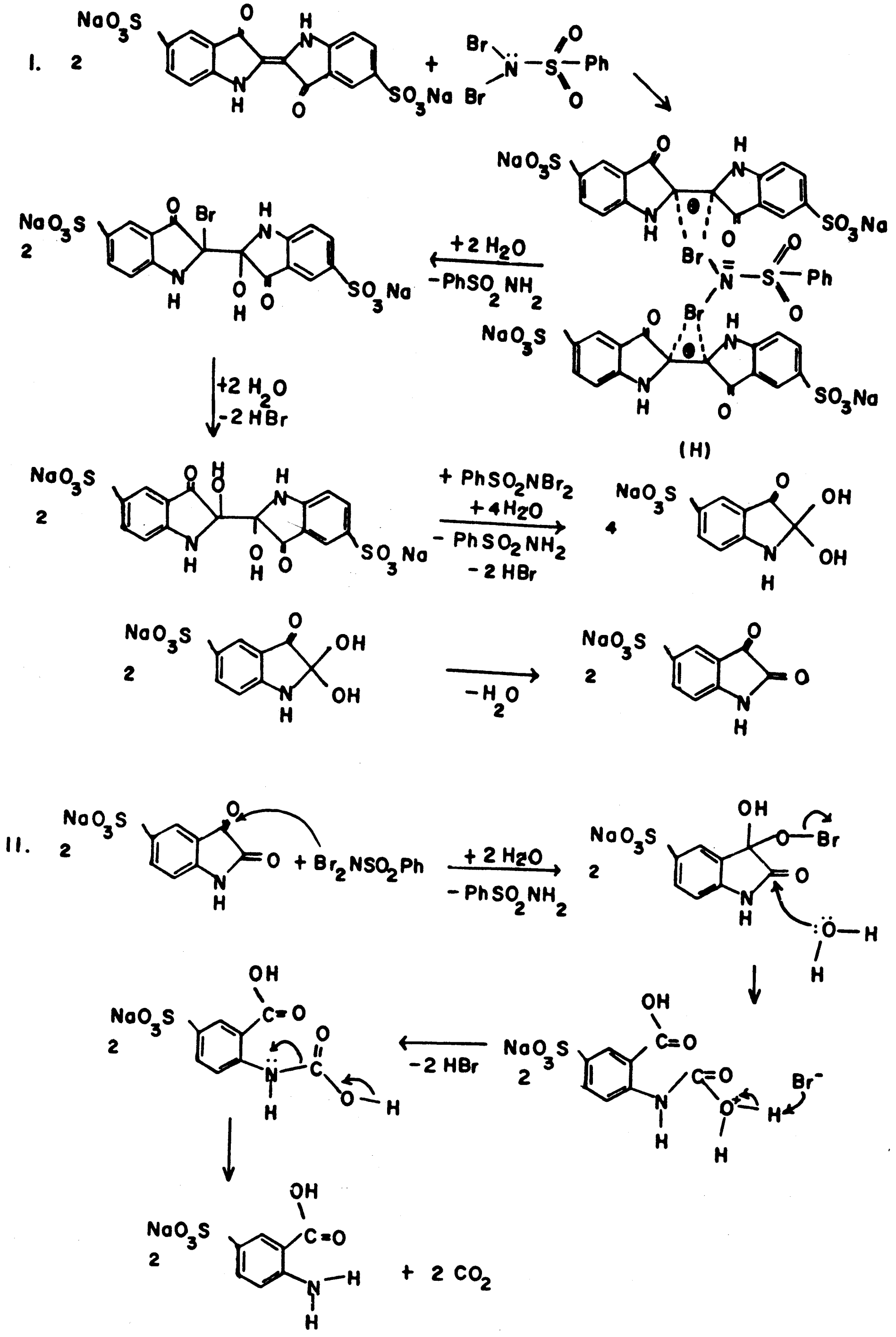
$$\underset{\text{(IC)}}{C_{16}H_8O_8S_2N_2Na_2} + \underset{\text{(anion of BAB)}}{4PhSO_2NBr^-} + 6H_2O$$

$$\rightarrow \underset{\text{(SAA)}}{2C_7H_6O_5NSNa} + 2CO_2 + \underset{\text{(BSA)}}{4PhSO_2NH_2} + 4Br^- \quad (1)$$

where Ph = C_6H_5 and the structures of IC are as shown in Scheme II.

Product Analysis

The presence of benzenesulphonamide or (BSA) which is the reduction product of BAB, was detected by thin layer chromatography.[11] The oxidation product of IC, sodium salt of sulphonated anthranilic acid (SAA), was analysed.[4] The SAA present in the reaction mixture was quantitatively determined using a standard method involving its precipitation as zinc(II) salt, $Zn(C_7H_5O_5NSNa)_2$.[14] The recovery of SAA from different reaction mixtures in pH 5 buffer was in the range 85–95%. Another product, CO_2, was detected by the conventional lime water test. Attempts to quantitate the amount of CO_2 evolved were unsuccessful.



Scheme II

Here (Ph = C_6H_6) for dibromamine-B (DBB) and benzenesulphonamide (BSA)

RESULT AND DISCUSSION

The reaction was first order in [IC] as shown by the linear plots of log (absorbance) versus time under conditions [IC] << [BAB] ($r > 0.9988$). The pseudo first order rate constant K′ given in Table-1, were found to be independent of [IC] confirming the first order dependence on substrate. The rate increased with [BAB] and plot of log K′ *vs*. log [BAB] gave a straight line with slope 2.0 ($r = 0.9981$) showing a second order dependence of the rate on [BAB].

TABLE-1
EFFECT OF VARYING REACTANT CONCENTRATIONS ON THE RATE

Buffer pH = 5; $\lambda_{max} = 610$ nm; $\mu = 0.2$ mol dm^{-3}; temp. = 30 ± 0.1°C.

[BAB] × 10^5 (mol dm^{-3})	[IC] × 10^5 (mol dm^{-3})	K′ × 10^3 sec^{-1}
6.0	5.0	0.82
8.0	5.0	1.45
10.0	5.0	2.44
12.0	5.0	3.22
14.0	5.0	4.37
16.0	5.0	5.61
18.0	5.0	7.94
12.0	3.0	3.18
12.0	4.0	3.25
12.0	6.0	3.14
12.0	7.0	3.27
12.0	8.0	3.22

The rate of reaction decreased with increase in pH of medium (Table-2). Plot of log K′ versus pH is linear ($r = 0.9859$) with negative fractional slope (*ca.* –0.57). Further log K′ versus log [H$^+$] were linear with positive fractional slope (*ca.* 0.6) ($r = 0.9851$).

TABLE-2
EFFECT OF pH ON THE RATE OF REACTION

[BAB] = 12.0 × 10^{-5} mol dm^{-3}; [IC] = 5.0 × 10^{-5} mol dm^{-3};
$\mu = 0.2$ mol dm^{-3}; $\lambda_{max} = 610$ nm; temp = 30 ± 0.1°C

pH	K′ × 10^3 Sec^{-1}
4.2	19.33
4.6	6.53
5.0	3.22
5.4	2.77
5.8	1.48

Addition of reaction product benzenesulphonamide ($2.0 \times 10^{-4} - 10.0 \times 10^{-4}$ mol dm^{-3}) to the reaction mixture retarded the reaction rate. Further plots of log K′ *versus* log [BSA] was linear (Table-3; $r \geq 0.9992$) with a negative unit slope. Variation of ionic strength by adding $NaClO_4$ (0.05–0.20 mol dm^{-3} overall) had no effect on reaction. Addition of bromide or chloride ions in the form of NaBr or NaCl ($8.0 \times 10^{-5} - 20.0 \times 10^{-5}$ mol dm^{-3}) had no effect on the reaction.

TABLE-3

EFFECT ON THE REACTION RATE OF VARYING BENZENESULPHONAMIDE CONCENTRATION

[BAB] = 12.0×10^{-5} mol dm^{-3}; [IC] = 5.0×10^{-5} mol dm^{-3};
$\mu = 0.2$ mol dm^{-3}; $\lambda_{max} = 610$ nm; temp = 30 ± 0.1°C; pH = 5.

$[BSA] \times 10^4$ mol dm^{-3}	$K' \times 10^4$ sec^{-1}
2.0	28.00
5.0	11.08
7.5	7.25
10.0	5.30

The effect of dielectric constant (D) of the solvent of the reaction mixture of IC and BAB was studied by varying the CH_3OH content (0–10% v/v) at pH 5 (Table-4). The rate decreased with an increase in MeOH content of the medium. This effect is in conformity with the Amis concept for dipole-dipole or dipole-ion interactions.[15] Further more plots of log K′ *versus* 1/D were linear with a negative slope ($r = 0.9992$). The reaction rates were determined at diferent temperatures (298–313 K) keeping the other experimental conditions the same (Table-5). A plot of log K′ *versus* reciprocal of absolute temperature obtained was linear ($r = 0.9952$). Activation energy and other parameters were computed for overall reaction.

TABLE-4

EFFECT OF DIELECTRIC CONSTANT OF THE MEDIUM ON THE RATE OF REACTION AT pH = 5

[BAB] = 12.0×10^{-5} mol dm^{-3}; [IC] = 5.0×10^{-5} mol dm^{-3};
$\mu = 0.2$ mol dm^{-3}; $\lambda_{max} = 610$ nm; temp. = 30 ± 0.1°C

Methanol % (v/v)	D	$10^2/D$	$K' \times 10^3$ (sec^{-1})
0.0	76.73	1.30	3.22
2.5	75.6	1.32	2.78
5.0	74.50	1.34	2.34
7.5	73.4	1.36	1.86
10.0	72.37	1.38	1.48

Bromamine-B ($PhSO_2NBrNa \cdot 1.5H_2O$), like chloramine-B (CAB) which behaves as an electrolyte[16], dissociates in aqueous solutions to furnish an anion (eq. (2)). This anion undergoes protonation in acid medium to form the free acid, $PhSO_2NHBr$, as in eq. (3). Although the free acid has not been isolated, the conductometric studies of CAB have provided ample evidence of its formation.[16, 17] In acid medium, the free acid undergoes disproportionation to form dibromamine-B ($PhSO_2NBr_2$) and benzenesulphonamide ($PhSO_2NH_2$) (eq. (4)). Dibromamine-B and the free acid hydrolyze to give HOBr as one of the products.

$$PhSO_2NBrNa \rightleftharpoons PhSO_2NBr^- + Na^+ \tag{2}$$

$$PhSO_2NBr^- + H^+ \rightleftharpoons PhSO_2NHBr \tag{3}$$

$$2PhSO_2NHBr \rightleftharpoons PhSO_2NBr_2 + PhSO_2NH_2 \tag{4}$$

$$PhSO_2NBr_2 + H_2O \rightleftharpoons PhSO_2NHBr + HOBr \tag{5}$$

$$PhSO_2NHBr + H_2O \rightleftharpoons PhSO_2NH_2 + HOBr \tag{6}$$

The possible reactive oxidising species in acidified BAB solutions are therefore $PhSO_2NHBr$, $PhSO_2NBr_2$ and HOBr. In the present study of IC oxidation, the reaction shows a second order in $[BAB]_0$ and a retardation by the added BSA [$PhSO_2NH_2$], *i.e.*, an inverse first order on $[BSA]_0$ indicating the involvement of $PhSO_2NBr_2$ as the kinetically active species in a fast preequilibrium. Additionally, the reaction rate shows dependencies of a first order on $[IC]_0$ and a fractional-order on $[H^+]$. Based on the preceding discussion, a mechanism (Scheme 1) is proposed to account for the experimental observations.

$$PhSO_2NBr^- + H^+ \overset{K_1}{\rightleftharpoons} PhSO_2NHBr \qquad \text{(fast)} \qquad \text{(i)}$$

$$2PhSO_2NHBr \overset{K_2}{\rightleftharpoons} \underset{\text{(DBB)}}{PhSO_2NBr_2} + \underset{\text{(BSA)}}{PhSO_2NH_2} \qquad \text{(fast)} \qquad \text{(i)}$$

$$\underset{\text{(DBB)}}{PhSO_2NBr} + IC \xrightarrow{k_3} \underset{\text{(complex)}}{X} \qquad \text{(slow)} \qquad \text{(ii)}$$

$$PhSO_2NBr_2 + X \rightarrow \text{Products} \qquad \text{(fast)} \qquad \text{(iii)}$$

Scheme-1

In Scheme-1, X represents the indigocarmine-dibromamine-B (DBB) complex intermediate whose possible structure is shown in Scheme-2. A detailed mechanism showing the electron transfer reaction between IC and DBB or $PhSO_2NBr_2$ (an active oxidising species of BAB) is presented in Scheme-2. An electrophilic attack of Br^+ of $PhSO_2NBr_2$ across the carbon-carbon double bond of IC leads to the formation of the complex X which on hydrolysis yields a bromohydrin. The bromohydrin intermediate undergoes further interactions with water to form a diol intermediate which on interaction with the oxidant and water undergoes a carbon-carbon bond rupture and dehydration to form 5-isatin sulphonate. The isatin sulphonate intermediate undergoes further oxidation with

$PhSO_2NBr_2$ followed by nucleophilic attacks by water and intermolecular rearrangements to form the end product, sulfonated anthranilic acid (SAA).

Scheme-1 leads to the rate law as follows:

$$\text{rate} = \frac{-d[IC]}{dt} = K_3[DBB][IC] \tag{7}$$

The total effective concentration of BAB is given by

$$[BAB]_t = [PhSO_2NBr^-] + [PhSO_2NHBr] + [DBB] \tag{8}$$

From equilibria (i) and (ii) in Scheme-1,

$$[PhSO_2NBr^-] = \frac{[PhSO_2NHBr]}{K_1[H^+]} \tag{9}$$

$$[PhSO_2NHBr] = \frac{\{[DBB][BSA]\}^{1/2}}{K_2^{1/2}} \tag{10}$$

Substitution for $[PhSO_2NHBr]$ from eq. (10) in eq. (9) gives

$$[PhSO_2NBr^-] = \frac{\{[DBB][BSA]\}^{1/2}}{K_2^{1/2}K_1[H^+]} \tag{11}$$

By solving for $[BAB]_t$ of eq. (8) using eqs. (10) and (11) one gets

$$[BAB]_t = \frac{[DBB]\{[BSA]^{1/2} + K_1[H^+] + K_1K_2^{1/2}[H^+][DBB]^{1/2}\}}{K_1K_2^{1/2}[H^+][DBB]^{1/2}}$$

or

$$[DBB] = \frac{K_1K_2^{1/2}[H^+][BAB]_t[DBB]^{1/2}}{[BSA]^{1/2} + K_1[H^+]\ K_1K_2^{1/2}[H^+][DBB]^{1/2}} \cdot \tag{12}$$

from eq. (10), $[DBB]^{1/2} = \dfrac{K_2^{1/2}[BAB]}{[BSA]^{1/2}}$ as $BAB = PhSO_2NHBr$

By substituting for $[DBB]^{1/2}$ in eq. (12), one gets

$$[DBB] = \frac{K_1K_2[BAB]^2[H^+]}{[BSA]\{1 + K_1[H^+]\} + K_1K_2[H^+][BAB]} \tag{13}$$

Substitution for [DBB] from eq. (12) in eq. (7) leads to eq. (14).

$$\text{rate} = \frac{K_1K_2K_3[IC][BAB]^2[H^+]}{[BSA]\{1 + K_1[H^+]\} + K_1K_2[H^+][BAB]} \tag{14}$$

Assuming that the magnitude of the third term is smaller than that of the first or the second term, in the denominator of eq. (14), the third term can be neglected. Therefore, the above rate law reduces to eq. (15) below.

$$\text{rate} = \frac{K_1K_2K_3[IC][BAB]^2[H^+]}{[BSA] + K_1[BSA][H^+]} \tag{15}$$

This rate law supports the following observed orders in participants: 1.0 for IC, 2.0 for BAB, fractional for H^+ and –1.0 for BSA.

If one assumes that the values of protonation constant K_1 and disproportionation constant K_2 of chloramine-B are nearly equal and close to those of BAB, then of $K_1[BAB] = K_2[BAB] = 0.380$ at pH 5.0 and 303 K.[9] Using this approximate equilibrium constant value of BAB, it can be shown that the third term tends to be the smallest of the three terms in eq. (14) justifying its omission.

Amis[15] has shown that, for a limiting case of zero angle of approach between two dipoles or between an ion and a dipole, a plot of log K′*vs.* 1/D (where D = delectric constant of the solvent medium) has a negative slope for dipole-dipole or anion-dipole interactions and a positive slope for cation-dipole interactions in the rds. In the present study, the observed negative effect of D supports the proposed dipole-dipole interactions in the rds in Scheme-1 of the mechanism.

The moderate value of enthalpy of activation ($\Delta H^{\neq}$) is supportive of the proposed mechanism in Schemes 1 and 2. The highly negative entropy of activation ($\Delta S^{\neq}$) indicates the formation of a rigid transition state by an associative process.

TABLE-5

TEMPERATURE DEPENDENCE OF THE REACTION RATE AND ACTIVATION PARAMETERS FOR THE INDIGOCARMINE OXIDATION BY BROMAMINE-B

Temperature	$K' \times 10^3$ Sec^{-1}	Activation parameters
298 K	2.65	$E_a = 38.76$ kJ mol^{-1}
303 K	3.22	$\Delta H^{\neq} = 36.22$ kJ mol^{-1}
308 K	4.41	$\Delta S^{\neq} = -173.08$ J K^{-1} mol^{-1}
313 K	5.49	$\Delta G^{\neq} = 89.08$ kJ mol^{-1}

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