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# Oxidation of Indigo Carmine by *N*-Haloarenesulfonamidates: A Kinetic Study

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Kinetics of oxidation of indigo carmine (IC) by sodium *N*-haloarenesulfonamidates (RNXNa, where $R=CH_3C_6H_4SO_2$- or $C_6H_5SO_2$- and X=Cl or Br) chloramine T (CAT), bromamine T (BAT), chloramine B (CAB), and bromamine B (BAB) in alkaline buffer (pH 9—11) has been followed spectrophotometrically at $\lambda_{max}=610$ nm. Rate law, $-d[IC]/dt=k[OX]_0[IC]_0[OH^-]^x$ where $x<1$, is obeyed. The reaction products, benzenesulfonamide and toluenesulfonamide retard the rate. Sulfonated anthranilic acid formed was quantitatively determined. Variation of ionic strength or dielectric constant of medium and addition of halide ions have no effect on the reaction. A two pathway mechanism is proposed in which the hypohalous acid (HOX) and the anion of *N*-haloamine $RNX^-$ interact with the substrate in rate limiting steps. The rate increases in the order: BAT>BAB>CAT>CAB, which is attributed to the difference in electrophilicities of halogen cations $Br^+$ and $Cl^+$ involved in the oxidation process and the ease with which these species are formed in reactions.

Considerable attention has centered around the chemistry of *N*-haloarenesulfonamidates because of their diverse properties to act as halonium cations, hypohalites and *N*-anions which behave both as bases and nucleophiles. The subject has been reviewed by Campbell and Johnson[1)] and more recently by Banerji et al.[2)] The prominent members of this class of compounds are chloramine T ($p$-$CH_3C_6H_4SO_2NClNa\cdot 3H_2O$ or CAT) and chloramine B ($C_6H_5SO_2NClNa\cdot 1.5H_2O$ or CAB) and analytical and kinetic aspects of their reactions have been extensively studied.

Indigo carmine (IC) is employed as a redox indicator in analytical chemistry. The *N*-haloarenesulfonamides have been used for estimating this compound[3)] in solution but very few kinetic studies of this indole derivative are reported in literature.[4,5)] The present paper is the first report discussing the spectrophotometric kinetics of oxidation of indigo carmine by chloramine T, chloramine B, bromamine T, and bromamine B in alkaline buffer (pH 9—11) with a view to elucidate the mechanism of oxidation of the dye in solution and also to assess the relative rates of oxidation of the substrate by the *N*-haloarenesulfonamidates.

## Results

The reaction was first order in $[IC]_0$ as shown by the linear plots of log (absorbance) vs. time under conditions, $[IC]_0 \ll [OX]_0$ ($r>0.9980$; $s\leq 0.03$; Fig. 1). The pseudo-first-order rate constants $k'$ given in Table 1, were found to be independent of $[IC]_0$ confirming the first-order dependence on substrate. The rate increased with increase in $[OX]_0$ and plot of $\log k'$ vs. $\log [OX]_0$ gave a straight line with unit slope ($r>0.9982$; $s\leq 0.01$).

The rate of reaction increased with pH of medium (Table 2). Plots of $\log k'$ vs. pH were linear ($r<0.9859$; $s\leq 0.03$) with fractional slopes. Further, plots of $k'$ vs. $[OH^-]$ were linear with a Y- intercept corresponding to a rate law of the type: rate$=a+b[OH^-]$.

Addition of reaction product, *p*-toluenesulfonamide (TSA) or benzenesulfonamide (BSA) to reaction mixture retarded the rate (Table 3), in oxidations involving the respective oxidants.

Ionic strength variation (0.2—0.8 mol dm$^{-3}$) or addition of bromide or chloride ions in the form of NaBr or NaCl ($2\times10^{-4}$—$2\times10^{-3}$ mol dm$^{-3}$) had no effect on reaction. The rate was not significantly altered on varying the dielectric constant of medium by the addition of methanol (5—20% v/v).

The reaction was studied at different temperatures (298—313 K) and from the Arrhenius plots ($r>0.9961$; $s\leq 0.04$) activation parameters were calculated (Table 4).

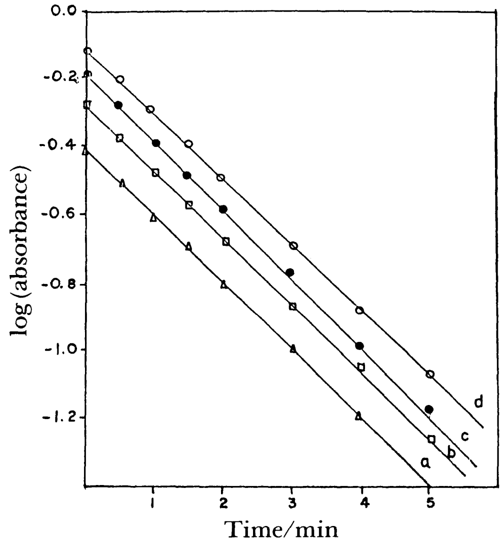


Fig. 1. Typical kinetic plots for the oxidation of indigo carmine by bromamine T at 30 °C.
pH=9.94, $[BAT]_0=5\times10^{-4}$ mol dm$^{-3}$; $\mu=0.5$ mol dm$^{-3}$.
a,b,c,d represent different concentrations of indigo carmine (in mol dm$^{-3}$).
$a=4\times10^{-5}$; $b=5\times10^{-5}$; $c=6\times10^{-5}$; $d=7\times10^{-5}$.

Table 1. Effect of Variation of Reactant Concentrations on the Rate of Reaction at 30 °C
pH=9.94; $\mu$=0.5 mol dm$^{-3}$

| $10^4[OX]_0$ /mol dm$^{-3}$ | $10^5[IC]_0$ /mol dm$^{-3}$ | $10^3k'/s^{-1}$ | | | | $k'_{BAT}/k'_{CAT}$ | $k'_{BAB}/k'_{CAB}$ |
|---|---|---|---|---|---|---|---|
| | | BAT | BAB | CAT | CAB | | |
| 2.0 | 5.0 | 2.86 | 2.14 | 0.61 | 0.38 | 4.7 | 5.6 |
| 3.0 | 5.0 | 4.44 | 3.26 | 0.90 | 0.63 | 4.9 | 5.2 |
| 4.0 | 5.0 | 5.80 | 4.42 | 1.21 | 0.77 | 4.8 | 5.7 |
| 5.0 | 5.0 | 7.54 | 5.45 | 1.51 | 1.04 | 5.0 | 5.2 |
| 6.0 | 5.0 | 8.59 | 6.50 | 1.78 | 1.23 | 4.8 | 5.3 |
| 7.0 | 5.0 | 10.34 | 7.90 | 2.10 | 1.43 | 4.9 | 5.5 |
| 8.0 | 5.0 | 11.69 | 8.96 | 2.44 | 1.57 | 4.8 | 5.7 |
| 9.0 | 5.0 | 13.19 | 9.85 | 2.85 | 1.72 | 4.6 | 5.7 |
| 5.0 | 3.0 | 7.42 | 5.49 | 1.53 | 1.03 | | |
| 5.0 | 3.5 | 7.53 | 5.41 | 1.55 | 1.01 | | |
| 5.0 | 4.0 | 7.67 | 5.37 | 1.50 | 1.07 | | |
| 5.0 | 4.5 | 7.48 | 5.40 | 1.54 | 1.10 | | |
| 5.0 | 5.5 | 7.77 | 5.50 | 1.54 | 1.02 | | |
| 5.0 | 6.0 | 7.58 | 5.52 | 1.53 | 1.05 | | |
| 5.0 | 6.5 | 7.45 | 5.54 | 1.48 | 1.00 | | |
| 5.0 | 7.0 | 7.63 | 5.47 | 1.56 | 1.08 | | |
| 5.0 | 7.5 | 7.62 | 5.59 | 1.50 | 1.04 | | |
| 5.0 | 8.0 | 7.66 | 5.63 | 1.44 | 1.06 | | |
| 5.0[a] | 5.0[a] | 7.68[a] | 5.64[a] | 1.59[a] | 1.10[a] | | |

a) Values refer to reaction in $D_2O$ medium.

Table 2. Effect of Variation of pH on the Rate of Reaction at 30 °C
$[OX]_0=5\times10^{-4}$ mol dm$^{-3}$; $[IC]_0=5\times10^{-5}$ mol dm$^{-3}$; $\mu$=0.5 mol dm$^{-3}$

| pH | $10^3k'/s^{-1}$ | | | |
|---|---|---|---|---|
| | BAT | BAB | CAT | CAB |
| 9.24 | 4.55 | 3.10 | 0.57 | 0.45 |
| 9.60 | 5.62 | 3.95 | 0.95 | 0.70 |
| 9.94 | 7.54 | 5.45 | 1.51 | 1.04 |
| 10.20 | 9.56 | 7.90 | 2.20 | 1.48 |
| 10.49 | 13.25 | 12.25 | 3.40 | 2.35 |

Table 3. Effect of Reaction Product Sulfonamide on the Rate of Reaction at 30 °C
$[OX]_0=5\times10^{-4}$ mol dm$^{-3}$; $[IC]_0=5\times10^{-5}$ mol dm$^{-3}$
pH=9.94; $\mu$=0.5mol dm$^{-3}$

| $10^4$[TSA] or $10^4$[BSA] /mol dm$^{-3}$ | $10^3k'/s^{-1}$ | | | |
|---|---|---|---|---|
| | BAT | BAB | CAT | CAB |
| 5.0 | 5.47 (5.52) | 4.03 (4.79) | 1.10 (1.29) | 0.77 (0.84) |
| 10.0 | 4.42 (4.12) | 3.26 (2.98) | 0.90 (0.84) | 0.65 (0.59) |
| 15.0 | 4.11 (3.65) | 2.97 (2.38) | 0.80 (0.69) | 0.59 (0.50) |
| 18.0 | 3.95 (3.53) | 2.86 (2.21) | 0.75 (0.64) | 0.56 (0.48) |
| 20.0 | 3.82 (3.42) | 2.78 (2.08) | 0.72 (0.61) | 0.54 (0.46) |

Values in parentheses are obtained from Eq. 7.

Solvent isotope studies in $D_2O$ medium showed that the solvent isotope effect, $k'_{H_2O}/k'_{D_2O}$ is about unity (Table 1).

Addition of reaction mixture to acrylamide in nitrogen atmosphere failed to initiate polymerization of the latter, showing the absence of free radical species.

Table 4. Kinetic and Thermodynamic Parameters for the Oxidation of Indigo Carmine by CAT, CAB, BAT, and BAB

| | $E_a$ | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | $\Delta G^{\neq}$ | log $A$ |
|---|---|---|---|---|---|
| | kJ mol$^{-1}$ | kJ mol$^{-1}$ | J K$^{-1}$ mol$^{-1}$ | kJ mol$^{-1}$ | |
| BAT | 36.3 | 33.8 | −174.0 | 87.0 | 5.5 |
| BAB | 40.9 | 38.4 | −161.8 | 87.8 | 6.7 |
| CAT | 43.5 | 40.9 | −164.1 | 91.1 | 6.4 |
| CAB | 53.3 | 50.7 | −134.8 | 91.9 | 7.8 |

## Discussion

Investigations of Pryde and Soper,[6] Morris et al.,[7] Bishop and Jennings,[8] and Hardy and Johnston[9] on sodium *N*-haloarenesulfonamidates have shown that similar equilibria exist in acid and alkaline solutions. The following equilibria are noted in acid medium:

$$\mathrm{RNX\,Na} \rightleftarrows \mathrm{RNX^- + Na^+} \qquad (1)$$

$$\mathrm{RNX^- + H^+} \rightleftarrows \mathrm{RNXH} \qquad (2)$$

$$\mathrm{2\,RNXH} \rightleftarrows \mathrm{RNX_2 + RNH_2} \qquad (3)$$

$$\mathrm{RNXH + H_2O} \rightleftarrows \mathrm{RNH_2 + HOX} \qquad (4)$$

$$\mathrm{HOX} \rightleftarrows \mathrm{H^+ + OX^-} \qquad (5)$$

Here X=Cl or Br and R=$p$-$CH_3C_6H_4SO_2$- or $C_6H_5SO_2$-.

The free acid RNXH and dihaloamine $RNX_2$ are present in fairly high concentrations in acid medium. The oxidation potential of haloamine-sulfonamide system is pH dependent[10] and decreases with increase in pH of medium. In alkaline solutions, $RNX_2$ does not exist, and the predominant species are $RNX^-$, RNXH, HOX, and $OX^-$ ion. Hardy and Johnston[9] have calculated the concentrations of species present in alkaline BAB solutions. At pH<11, concentration of $OX^-$ ion is small and it does not make a significant contribution to the oxidation of indigo carmine. Hence $RNX^-$, RNXH, and HOX are the likely oxidizing agents in alkaline solutions of *N*-haloamines.

In the present investigations, there is a first-order dependence of rate each on $[IC]_0$ and $[OX]_0$. A fractional order dependence on $[OH^-]$ is observed. The rate is retarded by the reaction product, sulfonamide ($RNH_2$), indicating that it is involved in a preequilibrium. Further a plot of $k_{obs}$ vs. $[OH^-]$ is linear ($r$>0.9924; Fig. 2) with an intercept. Hence, a two pathway mechanism shown in Schemes 1 and 2 can be proposed to account for the experimental observations:

$$RNXH + OH^- \underset{}{\overset{K_1}{\rightleftarrows}} RNX^- + HOX \qquad \text{(i) fast}$$

$$HOX + IC \xrightarrow{k_2} Y \qquad \text{(ii) slow}$$

$$Y + 3HOX \xrightarrow{k_3} \text{Products} \qquad \text{(iii) fast}$$

Scheme 1.

$$RNX^- + IC \xrightarrow{k_4} Y' \qquad \text{(i) slow}$$

$$Y' + 3\,RNX^- \xrightarrow{k_5} \text{Products} \qquad \text{(ii) fast}$$

Scheme 2.

The combined rate law from Schemes 1 and 2 can be obtained as in Eq. 6:

$$\text{Rate} = \frac{k_2K_1[OX]_0\,[OH^-]\,[IC]}{[RNH^-]} + k_4[IC]\,[OX]_0 \qquad (6)$$

From Eq. 6

$$k_{obs} = k' = \left[\frac{k_2K_1[OH^-]}{[RNH^-]} + k_4\right][OX]_0. \qquad (7)$$

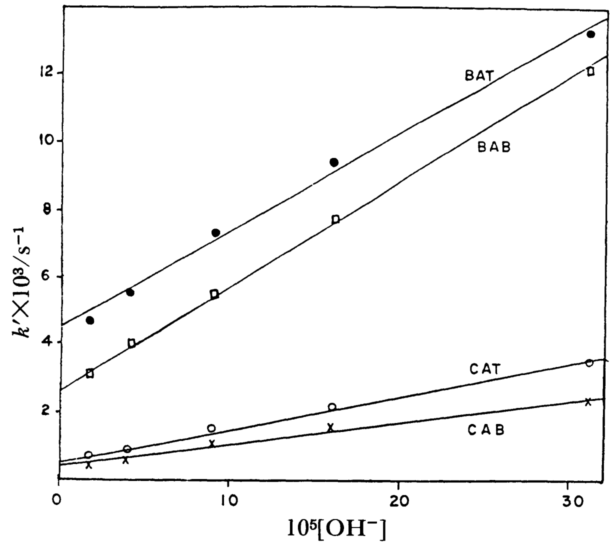


Fig. 2. Plot of $k'$ vs. $[OH^-]$ for the oxidation of IC by *N*-haloamines.
$[OX]_0=5\times10^{-4}$ mol dm$^{-3}$; $[IC]_0=5\times10^{-5}$ mol dm$^{-3}$; $\mu=0.5$ mol dm$^{-3}$; temp: 30 °C.

Table 5. Variation of pH on the Rate of Reaction in Presence of Added Sulfonamide.

$[OX]_0=5\times10^{-4}$ mol dm$^{-3}$; $[IC]_0$—$5\times10^{-5}$ mol dm$^{-3}$; $\mu=0.5$ mol dm$^{-3}$; $[TSA]_a=[BSA]_a=0.001$ mol dm$^{-3}$. Temp: 30 °C

| pH | $10^3k'/s^{-1}$ | | | |
|---|---|---|---|---|
| | BAT | BAB | CAT | CAB |
| 9.24 | 2.78 (3.55) | 1.25 (1.85) | 0.41 (0.68) | 0.35 (0.52) |
| 9.60 | 3.33 (3.83) | 2.02 (2.23) | 0.60 (0.74) | 0.45 (0.56) |
| 9.94 | 4.42 (4.41) | 3.26 (3.03) | 0.90 (0.87) | 0.65 (0.64) |
| 10.20 | 5.28 (5.27) | 4.56 (4.23) | 1.25 (1.07) | 0.82 (0.75) |
| 10.49 | 7.60 (7.13) | 7.50 (6.77) | 1.98 (1.49) | 1.21 (1.01) |

Values in parentheses were calculated from Eq. 7.

To test the validity of Eq. 7 the reaction was studied at different $[OH^-]$ with a constant concentration of added sulfonamide $[RNH_2]_a$ (Table 5). The concentration of $RNH^-$ ion was obtained from the relation,

$$[RNH^-] = \frac{K_s}{K_s + [H^+]}[RNH_2]_a \qquad (8)$$

where $K_s$ is the dissociation constant of sulfonamide in aqueous solution ($2.88\times10^{-11}$ and $1.55\times10^{-11}$ for TSA and BSA respectively at 30 °C). Plots of $k'$ vs. $[OH^-]$ under these conditions were found to be linear ($r$>0.9934; Fig. 3) and from the slope and intercept, values of $k_2K_1$ and $k_4$ are determined:

| | BAT | BAB | CAT | CAB |
|---|---|---|---|---|
| $k_4$ | 5.44 (6.68) | 2.34 (3.12) | 0.76 (1.26) | 0.68 (0.98) |
| $k_2K_1$ | 6.42 (4.91) | 5.00 (4.05) | 2.10 (1.20) | 0.69 (0.40) |

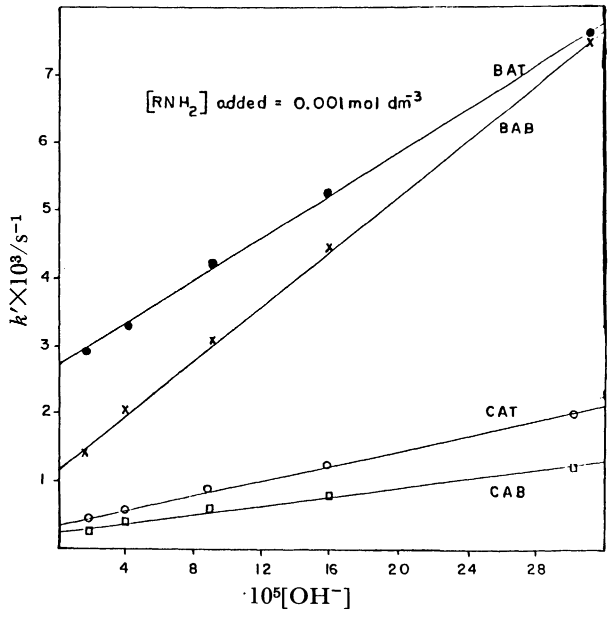


Fig. 3. Plot of $k'$ vs. $[OH^-]$ for the oxidation of IC by *N*-haloamines in presence of added sulfonamide $(RNH_2)_a$.
$[OX]_0=5\times10^{-4}$ mol dm$^{-3}$; $[IC]_0=5\times10^{-5}$ mol dm$^{-3}$; $[RNH_2]_a=0.001$ mol dm$^{-3}$; $\mu=0.5$ mol dm$^{-3}$; temp: 30 °C.

Values of $k_4$ and $k_2K_1$ thus obtained were used to predict the rate constants $k'$ when $[RNH_2]$ was varied in the reaction mixture. The values of $k'$ thus obtained are shown in parenthesis in Table 3. It is seen that there is fair agreement with the experimental values. Further, a plot of $k_{obs}$ vs. $1/[RNH^-]$ (Table 3) at constant $[OH^-]$ and $[OX]_0$ is found to be linear ($r > 0.9912$; Fig. 4) and a second set of $k_4$ and $k_2K_1$ values could be extracted from these plots, which are shown in parenthesis above. These values of $k_4$ and $k_2K_1$ can be employed for predicting the rate constants $k'$ obtained with varying $[OH^-]$ at constant $[RNH_2]=0.001$ mol dm$^{-3}$ (Table 5). The value of $k'$ so obtained are shown in parentheses in Table 5. Thus a fair agreement with the experimental values supports the proposed mechanism for oxidation of IC by the *N*-haloamines.

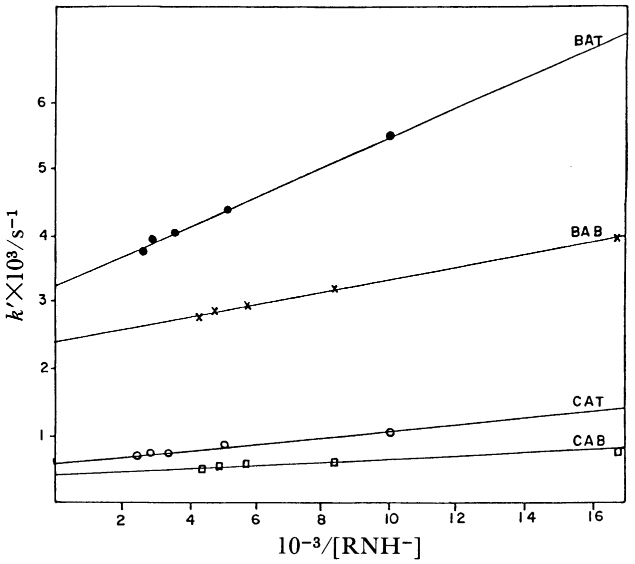


Fig. 4. Plot of $k'$ vs. $1/[RNH^-]$ for the oxidation of IC by *N*-haloamines.
$[OX]_0=5\times10^{-4}$ mol dm$^{-3}$; $[IC]_0=5\times10^{-5}$ mol dm$^{-3}$; pH=9.94; $\mu=0.5$ mol dm$^{-3}$; temp: 30 °C.

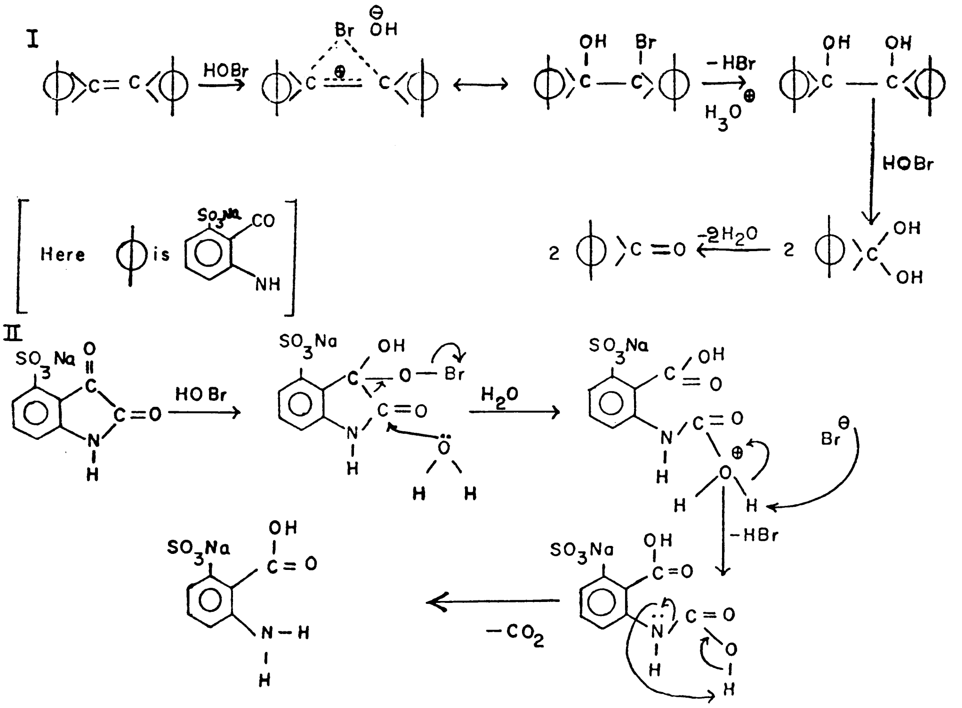
A detailed mechanism showing the electron transfer during the oxidation of indigo carmine by the *N*-haloamines is given in Scheme 3. An electrophilic attack by $X^+$ species of oxidant forms a halohydrin across the C-C double bond in the substrate which subsequently leads to bond rupture. Isatinsulfonate formed undergoes further oxidation to sulfonated anthranilic acid by HOX. A similar scheme can be written for the oxidation of substrate by the anion $RNX^-$.

The solvent isotope effect[11] shows that the rate is not very much affected in $D_2O$ medium as $OH^-$ ion is involved in an equilibrium (Scheme 1) and only a part of the reaction proceeds through a pH dependent path.

Variation of dielectric constant ($D$) of medium does not affect the rate. An explanation can be offered in terms of the Born treatment applied by Laidler[12] for a dipole-dipole reaction.

$$\ln k' = \ln k_0 + \frac{3}{8kT}(2/D - 1)\left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3}\right] \quad (9)$$

Here $k_0$ is the rate constant in a medium of infinite dielectric constant and $\mu$ and $r$ refer to the dipole moment and radii of reactants A and B and the activated complex. It is seen from Eq. 9 that rates should be higher in a medium of lower dielectric constant



Scheme 3.

when $r^3_{\ddagger} > r^3_A + r^3_B$ indicating that the extent of charge dispersal in the transition state is different. On the other hand, $r^3_{\ddagger} \approx r^3_A + r^3_B$ implies the absence of dielectric effect of solvent on rate, as was observed in the present investigations.

The rates are found to be higher with BAB and BAT than the chlorine analogues by a factor of 5 (Table 1), and follow the sequence: BAT>BAB>CAT>CAB. This could be attributed, to the difference in electrophilicities of the halogen cations $Br^+$ and $Cl^+$ involved in the oxidation process and is related to the ease with which these species can be formed in reactions. A similar behavior has been noted in the oxidation of dialkylsulfides[13] and conjugated alcohols,[14] by the *N*-haloamines.

## Experimental

Chloramine T (Merck) was purified by the method of Morris et al.[7]

Chloramine B was prepared[15] by passing chlorine through benzenesulfonamide dissolved in 4 mol dm$^{-3}$ NaOH over a period of 1 h at 70 °C. The mass obtained was filtered, dried, and recrystallized from water.

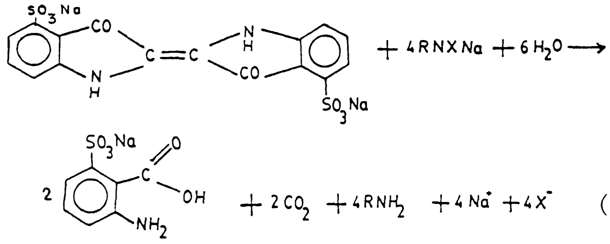
Bromamine T was obtained[16] by the partial debromination of dibromamine T (DBT). To a solution containing ca. 20 g of CAT in 400 ml of water, about 4 ml of liquid bromine were added dropwise from a microburette, with constant stirring at room temperature. The dibromamine separated out was filtered under suction, washed thoroughly with water until all the absorbed bromine was completely eliminated and then vacuum dried for 24 h. About 20 g of DBT was dissolved with stirring in ca. 30 ml of 4 mol dm$^{-3}$ NaOH at room temperature and the resultant aqueous solution was cooled in ice. Pale yellow crystals of BAT formed were filtered under suction, washed quickly with the minimum amount of ice cold water, and dried over $P_2O_5$.

Bromamine B was prepared[17] by the partial debromination of dibromamine B (DBB) which was obtained as follows: Pure chlorine was bubbled through an aqueous solution of CAB (30 g in 560 ml of water) and liquid bromine (6 ml) was added dropwise from a burette with constant stirring. The yellow precipitate of DBB formed was thoroughly washed with water, filtered under suction and dried in a vacuum desiccator. Dibromamine B (31.5 g) was digested in small lots with constant stirring in 50 ml of 4 mol dm$^{-3}$ NaOH. The mass was cooled in ice, filtered under suction and the product dried over anhydrous calcium chloride.

The purity of all oxidants was checked by iodometric assay of the active halogen and by recording their Fourier transform $^1$H and $^{13}$C NMR spectra. Aqueous solutions of compounds were standardized by the iodometric method and preserved in brown bottles to prevent photochemical deterioration.

Aqueous solutions of indigo carmine (Merck) were prepared. Koch-Light (England) benzenesulfonamide and *p*-toluenesulfonamide were used. All other reagents were of Analar grade. Heavy water (99.2%) employed for solvent isotope studies was supplied by the Bhabha Atomic Research Centre, Trombay, India. The ionic strength of system was kept at a high value with a concentrated solution of sodium perchlorate. Standard buffer systems (borax+NaOH)[18] were used. The p$K_s$ values of sulfonamides were determined by emf methods. Regression analysis of experimental data to get the regression coefficient *r* and *s*, the standard deviation of points from the regression line were performed on a TDC-316 computer and EC-72 statistical calculator.

**Stoichiometry.** Varying ratios of oxidant to indigo carmine in presence of buffer (pH 9.94) were equilibrated at 30 °C for 24 h. The unchanged oxidant in the reaction mixture was determined by iodometric titrations. The analysis showed that one mole of IC reacted with four moles of oxidant. The observed stoichiometry is shown by Eq. 10:



(10)

Here R=*p*-$CH_3C_6H_4SO_2$– for CAT and BAT and $C_6H_5SO_2$– for CAB and BAB; X=Cl or Br.

**Product Analysis.** *p*-Toluenesulfonamide was detected by paper chromatography. Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ethanol as spray reagent ($R_F$ 0.905). Benzenesulfonamide was identified by TLC using pet. ether-$CHCl_3$-1-butanol (2:2:1 v/v) as the solvent system and iodine as spray reagent ($R_f$ 0.88). The anthranilate was precipitated as its zinc salt.[19] To the reaction mixture calculated volumes of 1 mol dm$^{-3}$ NaOH were added followed by 10 ml of pH 5 buffer and 10 ml of 1% zinc sulfate. The ppt formed was filtered, dried at 105—110 °C and weighed; recovery of $(C_7H_6O_2N)_2$ Zn was 85—90%.

**Kinetic Procedure.** The kinetic runs were carried out under pseudo-first-order conditions. The course of reaction was followed spectrophotometrically by measuring the absorbance of unreacted indigo carmine at 610 nm using an Elico Model CL 24 spectrophotometer, for three half-lives. Plots of log(absorbance) versus time were linear. The pseudo-first-order rate constants ($k'$) calculated from these plots were reproducible within ±3%.

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