Chloraminometric and Bromaminometric Oxidation of Sulfanilic Acid in Alkaline Medium: A Comparative Kinetic and Mechanistic Study

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ABSTRACT: The kinetics of oxidation of sulfanilic acid (SAA) by chloramine-B (CAB) and bromamine-B (BAB) has been investigated in alkaline medium at 35 ± 0.1°C. The oxidation reaction follows identical kinetics in the case of both the oxidants with first-order dependence on each $[\text{oxidant}]_o$ and $[\text{SAA}]_o$ and an inverse first-order dependence on $[\text{OH}^-]$. The variation of ionic strength, dielectric constant of the medium, addition of the reaction product (benzenesulfonamide), and halide ions showed no significant influence on the reaction rate. Proton inventory studies made in H_2O–D_2O mixtures for CAB and BAB have been utilized to calculate the isotopic fractionation factor. The reaction has been studied at different temperatures, and activation parameters for the composite reaction have been computed from the Arrhenius plots. *N*-Hydroxylaminobenzene-4-sulfonic acid was identified as the oxidation product of SAA from IR and GC-MS analysis. A mechanism consistent with the kinetic results is proposed in which $PhSO_2NHX$ ($X = Cl$ or Br) interact with the substrate in the rate-limiting step. A suitable rate law is derived. The rate of oxidation of sulfanilic acid is about fourfold faster in BAB compared to CAB. The oxidation of SAA brought about by CAT and BAT was also investigated under identical experimental conditions, and the overall rate of oxidation of SAA increases in the order: BAB > BAT > CAB > CAT. This may be attributed to the difference in electrophilicities of Cl^+ and Br^+ ions and also the van der Waal's radii of chlorine and bromine. © 2005 Wiley Periodicals, Inc. Int J Chem Kinet 38: 48–56, 2006

INTRODUCTION

The *N*-metallo-*N*-haloarylsulfonamides generally known as *N*-haloamines are a class of compounds capable of producing halonium cations, hypohalites, and N-anions, behave both as bases and as nucleophiles, depending on the reaction conditions. The subject has been extensively reviewed by Campbell and Johnson [1], Bremner [2], and Banerji et al. [3]. The prominent member of this group is chloramine-T (CAT,

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p-$CH_3C_6H_4SO_2NClNa{\cdot}3H_2O$), and the mechanistic aspects of its reaction have been very well documented [1–3]. The benzene analogue of CAT, chloramine-B (CAB, $C_6H_5SO_2NClNa{\cdot}1.5H_2O$), and the bromine analogues of CAT and CAB are (bromamine-T (BAT, *p*-$CH_3C_6H_5SO_2NBrNa{\cdot}3H_2O$) and bromamine-B (BAB, $C_6H_5SO_2NBrNa{\cdot}1.5H_2O$)) are becoming important as mild oxidants. There is very little information available in the literature on CAB and BAB [4–6].

Sulfanilic acid (SAA, *p*-aminobenzenesulfonic acid) finds widespread use in the syntheses of various organic dyes [7]. The sulfanilamide and certain related substituted amides have significant medicinal importance as sulfa drugs. Although their use has been superseded to a large extent by the antibiotics such as penicillin, terramycin, chloromycetin, and aureomycin, the sulfa drugs still have their medicinal use and make up a large proportion of the output from pharmaceutical industry [8]. Although SAA has been oxidized by various oxidants [9,10], there seems to be no report in the literature on the kinetics of oxidation of SAA by positive halogen compounds. These facts obviate the need for us to undertake the title investigation.

In continuation of our work on oxidation kinetic studies using organic *N*-haloamines, the present paper reports a systematic investigation on oxidation kinetics of sulfanilic acid by CAB and BAB in alkaline medium. The main objectives of the present investigations are (i) to elucidate the plausible mechanism, (ii) to put forward the appropriate rate law, (iii) to ascertain the reactive species of the oxidants, (iv) to find the stoichiometry and to identify the oxidation products, and (v) to assess the relative reactivity of CAT, CAB, BAT, and BAB toward SAA.

EXPERIMENTAL

Materials

Chloramine-T (E. Merck) was purified by the method of Morris and co-workers [11]. Preparation of chloramine-B, bromamine-B, and bromamine-T has been described earlier [12–14]. Further, the purity of all the four oxidants was assayed iodometrically to determine the active halogen content. Aqueous solution of the oxidants was standardized by the iodometric procedure and preserved in brown bottles to prevent photochemical deterioration [11]. An aqueous solution of AnalaR grade sulfanilic acid (BDH, England) of desired strength was freshly prepared whenever required. All the other reagents used were of analytical grade. Solvent isotope studies were made with D_2O (99.4%) supplied by the Bhabha Atomic Research Centre, Mumbai, India. Double distilled water was used throughout the studies.

Kinetic Measurements

The reaction was carried out in glass-stoppered Pyrex boiling tubes whose outer surface was coated black to eliminate photochemical effects. Solution containing appropriate amounts of substrate, NaOH and water (to keep the total volume constant for all runs) were placed in the reaction tube and thermostatted at 35 ± 0.1°C. A known amount of oxidant was also thermostatted at the same temperature and was rapidly added to the mixture, and the progress of the reaction was monitored by iodometric determination of unreacted oxidant in a known aliquot (5 mL each) of the reaction mixture at regular intervals of time. The course of the reaction was studied up to two half-lives. Pseudo-first-order rate constants (k') calculated from log [oxidant] vs. time plots were reproducible to within ±4%. Regression analysis of the experimental data to obtain regression coefficient (r) was carried out on an f_x-100W scientific calculator.

Reaction Stoichiometry

The reaction mixture containing SAA, alkali, and an excess of oxidant (CAB or BAB) was kept for 48 h at 35°C. Determination of the unreacted oxidant iodometrically in the reaction mixture showed that 1 mole of SAA consumed 1 mole of oxidant, which can be stoichiometrically represented as

$$\begin{aligned} &C_6H_4(NH_2)SO_3H + PhSO_2NXNa + H_2O \\ &\quad \rightarrow C_6H_4(NHOH)SO_3H + PhSO_2NH_2 + Na^+ + X^- \end{aligned} \tag{1}$$

where X = Cl for CAB and Br for BAB.

Product Analysis

The reactions were allowed to progress under stirred conditions and were allowed to progress for 48 h at 35°C. After completion of the reaction, the products were neutralized with HCl and extracted with ether. The organic products were subjected to spot tests and chromatographic analysis (TLC technique), which revealed the formation of *N*-hydroxylaminobenzene-4-sulfonic acid as the oxidation product of SAA; the separation of which from benzenesulfonamide is achieved using column chromatography.

The reaction product of oxidant, benzenesulfonamide ($PhSO_2NH_2$), was detected by thin-layer

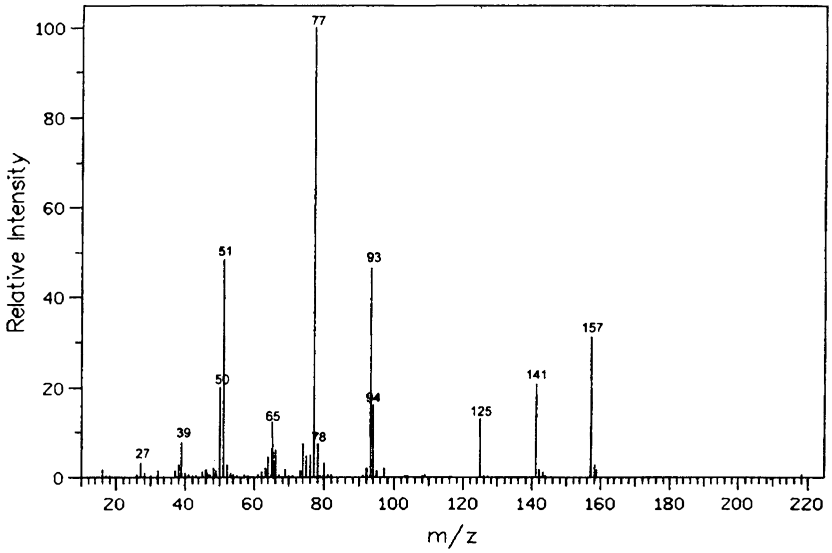


Figure 1 GC-Mass spectrum of benzenesulfonamide with its molecular ion peak at 157 amu.

chromatography [15] using petroleum ether : chloroform : 1-butanol (2 : 2 : 1, v/v/v) as the solvent system and iodine as the spray reagent ($R_f = 0.88$). The determined R_f value agrees with the value reported in the literature [15]. It was further confirmed by its melting point of 150°C (lit. mp 150–152°C). Further, benzenesulfonamide was subjected to GC-mass spectrum analysis. GC-MS data were obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer using the EI ionization technique. The mass spectrum showed a molecular ion peak at 157 amu confirming benzenesulfonamide (Fig. 1).

The presence of *N*-hydroxylaminobenzene-4-sulfonic acid was confirmed by spot test [16] and by IR spectrum: IR (KBr) showed band at (γ) 3431 cm^{-1} for —OH stretching and 3064 cm^{-1} for —NH stretching. It was further confirmed by GC-MS analysis. The mass spectrum showed a parent ion peak at 189 amu confirming *N*-hydroxylaminobenzene-4-sulfonic acid (Fig. 2). All other peaks observed in GC-MS can be interpreted in accordance with the observed structure. Further, quantitative determination of the product, *N*-hydroxylaminobenzene-4-sulfonic acid, was made by mixing known quantities of oxidant

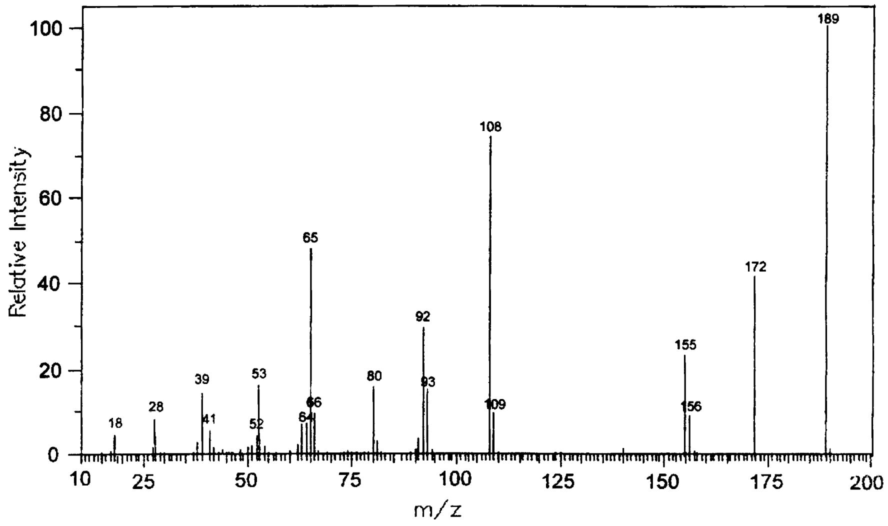


Figure 2 GC-Mass spectrum of *N*- hydroxylaminobenzene-4-sulfonic acid with its molecular ion peak at 189 amu.

and substrate in the presence of 2.0×10^{-2} mol dm^{-3} NaOH. The product recovered was found to be 84%. It was further observed that *N*-hydroxylaminobenzene-4-sulfonic acid does not undergo oxidation any further under the present set of experimental conditions.

RESULTS

The kinetics of oxidation of sulfanilic acid by CAB and BAB was investigated at several initial concentrations of reactants in NaOH medium. A similar oxidation kinetic behavior was observed for both the oxidants (OX).

Reaction Kinetics

Effect of Reactants on the Rate of Reaction. Under pseudo-first-order conditions of $[\mathrm{SAA}]_o \gg [\mathrm{OX}]_o$ at constant $[\mathrm{OH}^-]$ and temperature, plots of log [OX] vs. time were linear ($r > 0.9910$), showing a first-order dependence of the reaction rate on $[\mathrm{OX}]_o$. The values of pseudo-first-order rate constants (k') are listed in Table I. Further, the rate constant did not alter with the change in $[\mathrm{OX}]_o$, confirming the first-order dependence on $[\mathrm{OX}]_o$. The rate was found to increase with increase in $[\mathrm{SAA}]_o$ (Table I), and plots of log k' vs. log [SAA] were linear ($r > 0.9984$) with unit slopes. Further, plots of k' vs. [SAA] gave straight lines ($r > 0.9961$) passing through the origin, confirming the first-order dependence on $[\mathrm{SAA}]_o$.

Effect of [NaOH] on the Rate of Reaction. At constant $[\mathrm{OX}]_o$, $[\mathrm{SAA}]_o$, and temperature, the reaction rate was decreased with an increase in [NaOH] (Table I). Plots of log k' vs. log [NaOH] were linear ($r > 0.9994$) with negative slopes of unity for each of the two oxidants, thus indicating an inverse first-order dependence on [NaOH].

Effect of [BSA] on the Rate of Reaction. Addition of the reaction product, benzenesulfonamide (BSA or $\mathrm{PhSO_2NH_2}$; 2.0×10^{-3} mol dm^{-3}) to the reaction mixture did not affect the rate significantly, indicating its noninvolvement in pre-equilibrium to the rate-limiting step (RLS).

Effect of Ionic Strength on the Rate of Reaction. The effect of ionic strength on the reaction rate was carried out in a range of concentration 0.10–0.40 mol dm^{-3} with $\mathrm{NaClO_4}$, keeping all other experimental conditions constant. It was noticed that the ionic strength had negligible effect on the reaction rate, indicating the involvement of nonionic species in the rate-limiting step. Hence, no attempt was made to keep ionic strength constant during kinetic runs.

Effect of Dielectric Constant of the Medium on the Rate of Reaction. The dielectric constant (D) of the medium was varied by adding methanol (0–20% v/v) to the reaction mixture. The rates were not significantly affected in the case of both the oxidants.

Table I Effect of Varying Concentrations of Oxidant, Substrate, and NaOH on the Rate of Reaction[a]

$[\mathrm{Oxidant}]_o \times 10^4$ (mol dm^{-3})	$[\mathrm{SAA}]_o \times 10^2$ (mol dm^{-3})	$[\mathrm{OH}^-] \times 10^2$ (mol dm^{-3})	$k' \times 10^4$ (s^{-1}) CAB	$k' \times 10^4$ (s^{-1}) BAB
2.50	1.0	2.0	2.10	7.60
5.00	1.0	2.0	2.08	7.68
10.0	1.0	2.0	2.03	7.67
15.0	1.0	2.0	2.00	7.70
20.0	1.0	2.0	2.15	7.84
10.0	0.5	2.0	1.11	3.83
10.0	1.0	2.0	2.03	7.67
10.0	1.5	2.0	2.90	10.6
10.0	2.0	2.0	4.00	14.7
10.0	3.5	2.0	6.65	22.5
10.0	1.0	0.5	8.44	34.5
10.0	1.0	1.0	4.21	15.7
10.0	1.0	2.0	2.03	7.65
10.0	1.0	4.0	1.09	3.45
10.0	1.0	6.0	0.70	2.46

[a] Temperature = 308 K.

Table II Temperature Dependence on the Rate of Reaction and Activation Parameters for the Oxidation of SAA by CAB, BAB, CAT, and BAT in Alkaline Medium[a]

	$k' \times 10^4$ (s^{-1})			
Temperature (K)	CAB	BAB	CAT	BAT
298	0.72	3.75	0.45	2.35
303	1.14	5.56	0.70	3.71
308	2.03	7.67	1.21	5.40
313	2.85	10.1	2.14	8.00
318	5.00	15.4	3.49	12.0
E_a (kJ mol^{-1})	71.8	50.7	83.7	61.9
$\Delta H^{\neq}$ (kJ mol^{-1})	69.3 ± 0.10	48.1 ± 0.15	81.2 ± 0.05	59.4 ± 0.01
$\Delta G^{\neq}$ (kJ mol^{-1})	97.4 ± 0.20	93.8 ± 0.41	98.3 ± 0.46	95.0 ± 0.90
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-91.6 ± 0.90	-149 ± 0.20	56.9 ± 0.20	115 ± 0.40
log A	8.45 ± 0.09	5.46 ± 0.02	10.2 ± 1.0	6.40 ± 0.09

[a] $[\text{Oxidant}]_o = 1.0 \times 10^{-3}$ mol dm^{-3}; $[\text{SAA}]_o = 1.0 \times 10^{-2}$ mol dm^{-3}; $[\text{NaOH}] = 2.0 \times 10^{-2}$ mol dm^{-3}.

Effect of Halide Ions on the Rate of Reaction. Addition of halide ions, Cl^- or Br^-, in the form of their sodium salts (1.0×10^{-2}–4.0×10^{-2} mol dm^{-3}) showed no effect on the rate of reaction. This suggests that no interhalogen or chlorine (or bromine) is formed and that there is a direct interaction of oxidizing species with the substrate.

Effect of Temperature on the Rate of Reaction. The effect of temperature on the rate was studied by performing the kinetic experiments at various temperatures (25–45°C), while keeping other experimental conditions constant. From the linear Arrhenius plots of log k'vs. $1/T$ ($r > 0.9908$), values of activation parameters for the overall reaction were computed for CAB, BAB, CAT, and BAT. These results are summarized in Table II.

Solvent Isotope Studies. The rate studies in D_2O medium for CAB and BAB revealed that while k' $(H_2O) = 2.03 \times 10^{-4}$ s^{-1} and 7.67×10^{-4} s^{-1}, and k' (D_2O) is 1.04×10^{-4} s^{-1} and 4.20×10^{-4} s^{-1}, respectively. The formal solvent isotope effect k' $(H_2O)/k'$ $D_2O) = 1.95$ and 1.83 for these two oxidants. Proton inventory studies were made by carrying out the reaction in H_2O–D_2O mixtures with CAB and BAB, and these results are given in Table III.

Table III Proton Inventory Studies for the Oxidation of SAA by CAB and BAB in H_2O-D_2O Mixtures[a]

	$k'_n \times 10^4$ (s^{-1})	
Atom Fraction of Deuterium (n)	CAB	BAB
0.00	2.03	7.67
0.24	1.74	6.32
0.49	1.42	5.25
0.74	1.21	4.62
0.92	1.04	4.20

[a] $[\text{Oxidant}]_o = 1.0 \times 10^{-3}$ mol dm^{-3}; $[\text{SAA}]_o = 1.0 \times 10^{-2}$ mol dm^{-3}; $[\text{NaOH}] = 2.0 \times 10^{-2}$ mol dm^{-3}; temperature = 308 K.

Test for Free Radicals. Addition of the reaction mixture to the acrylamide monomer did not initiate polymerization indicating the absence of any free radicals produced during the course of reaction.

DISCUSSION

Reaction Mechanism

In general, organic haloamines undergo two electron changes in their reactions. The oxidation potential of haloamine/sulfonamide couple is pH dependent, and the value decreases with increase in the pH of the medium. Since the organic haloamines have the same chemical properties, it is expected that similar equilibria to exist in solution of these compounds [17,18]. Depending on the pH of the medium, CAB or BAB furnishes different equilibria in acid and alkaline solutions [11,17,19,20]. The possible oxidizing species in acid medium are $PhSO_2NHX$, $PhSO_2NX_2$, HOX, and H_2OX^+. In alkaline solutions of haloamine, dihaloamine does not exist, and the possible oxidizing species are $PhSO_2NX^-$ and OX^- anions, which would be transformed into more reactive oxidizing species $PhSO_2NHX$ and HOX, during the course of the reaction in alkali retarding steps. Several workers have observed the retarding effect of OH^- ions on the rate of haloamine reactions with a number of substrates

$$PhSO_2NX^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhSO_2NHX + OH^- \qquad \text{(i) fast}$$

$$PhSO_2NHX + SAA \xrightarrow{k_2} Y \qquad \text{(ii) slow and RLS}$$

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

Scheme 1

[5,17,21–27] and have suggested that the reactivity of weakly alkaline solutions of haloamines is due to the formation of the conjugate acid $PhSO_2NHX$ from $PhSO_2NX^-$ in a OH^- retarding step. Based on the preceding discussion and the observed kinetic results, a mechanism (Scheme 1) is proposed for the oxidation of sulfanilic acid by CAB and BAB in alkaline medium.

In Scheme 1, Y represents the complex intermediate species whose structure is shown in Scheme 2, in which a detailed mechanistic interpretation of SAA oxidation by CAB and BAB in alkaline medium is proposed.

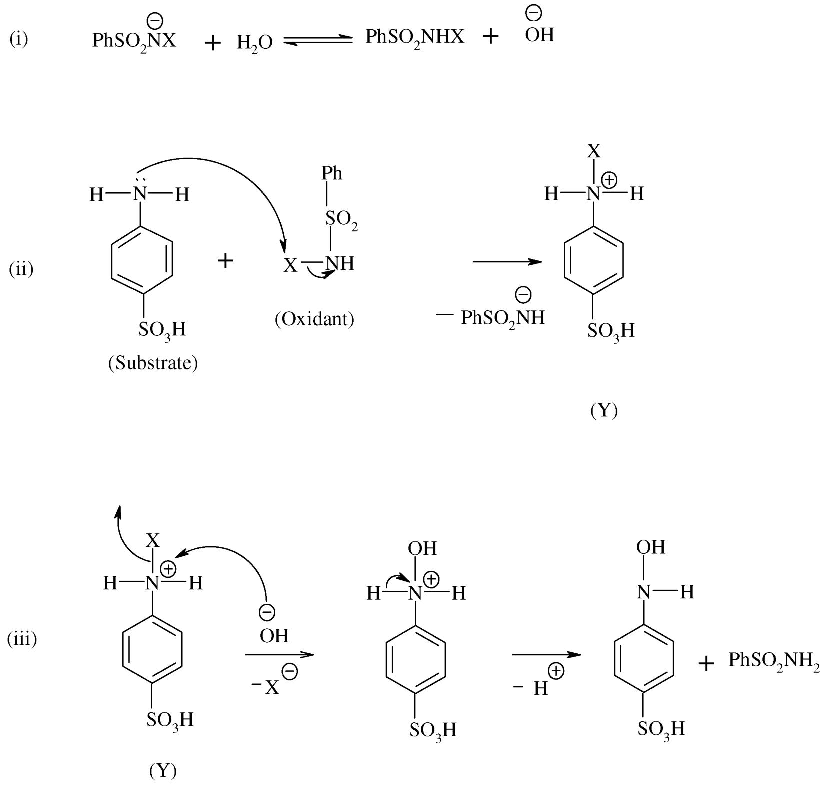
Step (ii) of Scheme 1 determines the overall rate

$$\text{Rate} = k_2[PhSO_2NHX][SAA] \qquad (2)$$

If $[OX]_t$ represents the total concentration of the oxidant, then

$$[OX]_t = [PhSO_2NX^-] + [PhSO_2NHX] \qquad (3)$$

from which, solving for $[PhSO_2NHX]$ and substituting its value in Eq. (2), rate law (4) can be derived.



Scheme 2

$$\text{Rate} = \frac{-\mathrm{d}[\mathrm{OX}]_\mathrm{t}}{\mathrm{d}t} = \frac{k_1 k_2 [\mathrm{OX}]_\mathrm{t}\,[\mathrm{SAA}][\mathrm{H_2O}]}{k_1[\mathrm{H_2O}] + k_{-1}[\mathrm{OH^-}]} \qquad (4)$$

If it is assumed that $k_{-1}[\mathrm{OH^-}] \gg k_1[\mathrm{H_2O}]$, rate law (4) is reduced to Eqs. (5) and (6)

$$\text{Rate} = \frac{k_1 k_2 [\mathrm{OX}]_\mathrm{t}\,[\mathrm{SAA}][\mathrm{H_2O}]}{k_{-1}[\mathrm{OH^-}]} \qquad (5)$$

$$\text{Rate} = \frac{k'[\mathrm{OX}]_\mathrm{t}\,[\mathrm{SAA}]}{k_{-1}[\mathrm{OH^-}]} \qquad (6)$$

Scheme 1 and rate law (6) account for the observed first-order dependence of rate each on $[\mathrm{OX}]_\mathrm{o}$ and $[\mathrm{SAA}]_\mathrm{o}$ and the inverse first-order dependence on $[\mathrm{OH^-}]$. The following results support the above conclusions.

For the dipole–dipole interaction, Laidler [28] has proposed Eq. (7):

$$\ln k' = \ln k_\mathrm{o} + 3/8\ \mathrm{kT}\ (2/D - 1) \times \left[\mu_\mathrm{A}^2/r_\mathrm{A}^3 + \mu_\mathrm{B}^2/r_\mathrm{B}^3 - \mu_\neq^2/r_\neq^3\right] \qquad (7)$$

Here k_o is the rate constant in a medium of infinite dielectric constant, while μ represents the dipole moment, r refers to the radii of the reactants and activated complex, k is the Boltzmann constant, and T is the absolute temperature. It is seen that the rate should be greater in a medium of lower dielectric constant, when $r_\neq^3 > r_\mathrm{A}^3 + r_\mathrm{B}^3$. On the other hand, $r_\neq^3 \approx r_\mathrm{A}^3 + r_\mathrm{B}^3$ implies the absence of dielectric effect of solvent on the rate, which was found to be true in the present case.

The mechanism proposed was also supported by the observed solvent isotope effect since the rate is retarded in $\mathrm{D_2O}$ medium leading to a solvent isotope effect, $k'(\mathrm{H_2O})/k'(\mathrm{D_2O}) = 1.95$ and 1.83 for CAB and BAB, respectively. For a reaction involving a fast equilibrium $\mathrm{H^+}$ or $\mathrm{OH^-}$ ion transfer, the rate was found to increase in $\mathrm{D_2O}$ medium since $\mathrm{D_3O^+}$ and $\mathrm{OD^-}$ are stronger acid and base, respectively, than $\mathrm{H^+}$ and $\mathrm{OH^-}$ ions [29,30]. In the present case, the observed solvent isotope effect is greater than unity which is due to the greater basicity of $\mathrm{OD^-}$ compared to $\mathrm{OH^-}$. Further, for chemical reactions carried out in $\mathrm{H_2O}$ and $\mathrm{D_2O}$ mixtures, the dependence of rate on atom fraction of deuterium (n) can be shown [31,32] by Eq. (8):

$$k'_n/k'_\mathrm{o} = \underset{i}{\overset{\mathrm{TS}}{\pi}}(1 - n + n\Phi_i)/\ \underset{j}{\overset{\mathrm{RS}}{\pi}}(1 - n + n\Phi_j) \qquad (8)$$

Here Φ_i and Φ_j are isotopic fraction factors for isotopically exchangeable hydrogenic sites in the transition state (TS) and reactant state (RS), respectively. If the reaction proceeds through a single transition state, Eq. (8) takes the form shown by Eqs. (9) and (10):

$$k'_n = k'_\mathrm{o}(1 - n + n\Phi_j)^{-2} \qquad (9)$$

$$(k'_\mathrm{o}/k'_n)^{1/2} = [1 + n(\Phi_j - 1)] \qquad (10)$$

Equation (10) shows that a plot of $(k'_\mathrm{o}/k'_n)^{1/2}$ vs. n should be linear. In the present investigations, plots of $(k'_\mathrm{o}/k'_n)^{1/2}$ vs. n were indeed found to be linear ($r > 0.9926$) with slopes of $(\Phi_j - 1) = -0.29$ and $= -0.27$ for CAB and BAB, from which fractionation factor Φ_j of $\mathrm{OH^-}$ is 0.71 and 0.73, respectively, for these two oxidants. Kresge and Allred [33] have obtained a value of 0.80 from NMR studies for the isotopic fractionation factor of $\mathrm{OH^-}$ ion, which was confirmed by the works of Gold and Crist [34]. There is a fair agreement between the present value and the values reported [33–36] for the fractionation factor of $\mathrm{OH^-}$ ion.

From Tables I and II, it is evident that the k' (BAB) > k' (CAB) is obtained under identical set of experimental conditions. This may be attributed to the difference in electrophilicities of bromine and chlorine. In these reactions electronegativity of halogens play an important role. Electronegativity of chlorine is 2.8 and that of bromine is 2.7. As the electronegativity increases there is a decrease in electropositive nature. Since the positive halogen atoms forms the reactive species in these oxidation reactions, the electropositive nature is in the order Br > Cl. Therefore, reactivity of CAB and BAB toward SAA is in the order: BAB > CAB. In addition, it is also partially due to the moderate difference in van der Waal's radii of bromine and chlorine.

It was felt desirable to compare the rate of oxidation of SAA by CAT and BAT with that of CAB and BAB. Similarly in the case of benzene analogues of haloamines, the reactivity is in the order: BAT > CAT, and the overall reactivity follows: BAB > BAT > CAB > CAT. Further, it is also observed that the reactivity is higher in benzene analogues of haloamines compared with toluene analogues. It is due to the fact that there is a slight difference in the electrophilicities of toluene derivatives due to inductive effect of methyl group and hence the observation made in the present case indicates the +I effect due to $\mathrm{CH_3}$ group of toluene derivatives. From the above facts, it can be generalized that bromamines are strong oxidants compared to chloramines and also benzene derivatives of haloamines are more reactive than toluene derivatives for the oxidation of SAA. In the present study, it is substantiated by the overall reactivity is BAB > BAT > CAB > CAT.

Furthermore, these results are also compared with the results of oxidation kinetics of several

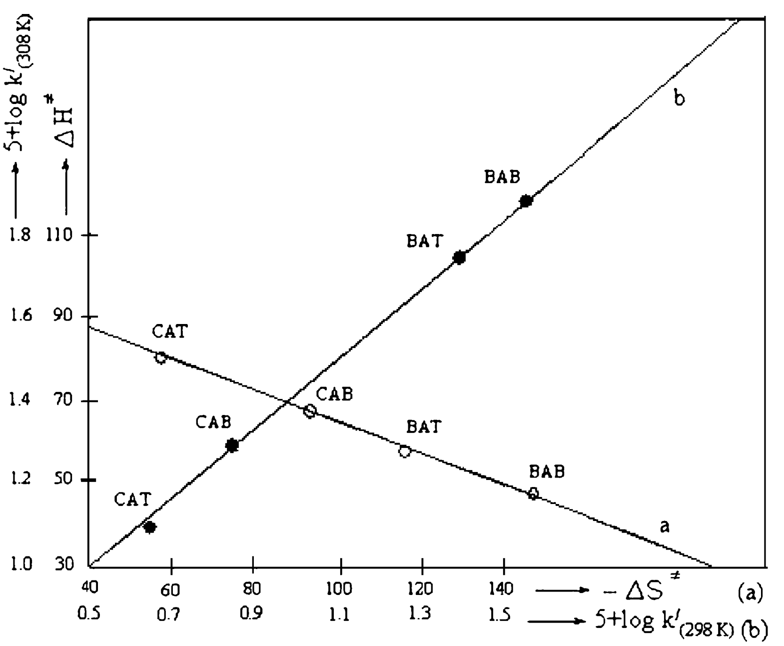


Figure 3 Isokinetic plots of (a) $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ (b) log $k'_{(308\,\mathrm{K})}$ vs. log $k'_{(298\,\mathrm{K})}$. Experimental conditions are as in Table II.

substrates studied using N-haloamines. The ratio of k' (bromamines)/k' (chloramines) in the case of indigo carmine [37], isoniazid [5], indoles [38], dialkylsulfides [39], conjugate alcohols [40], phenethyl alcohols [41], and monosaccharides [42] lies between 2 and 10. In the present case this ratio is about 4. This indicates that the relative rates of oxidation by these oxidants are dependent on the type of substrates chosen.

The proposed mechanism is also substantiated by the moderate values of energy of activation observed and other activation parameters. The data in Table II show that the energy of activation is highest for the slowest reaction and vice versa as expected, indicating that the reaction is enthalpy controlled. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the oxidation of SAA by all the four oxidants are linearly related ($r = 0.9992$; Fig. 3) and the isokinetic temperature $\beta = 358$ K. The genuine nature of the isokinetic relationship was verified by the Exner criterion [43] by plotting log $k'_{(308\mathrm{K})}$ vs. log $k'_{(298\mathrm{K})}$; this plot is linear ($r = 0.9980$; Fig. 3). The values of β calculated from the equation $\beta = T_1\,(1\text{–}q)/(T_1/T_2) - q$, where q is the slope of the Exner plot and $T_1 > T_2$. The value of β was found to be 368 K. The values of β evaluated from both the plots are much higher than the range of temperature employed in the present work (298–318 K). This indicates a common enthalpy controlled pathway for all the reactions. The fairly high positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ suggest that the transition state is highly solvated, while the high negative entropy of activation indicates the formation of a rigid transition state. Further, the values of $\Delta G^{\neq}$ are almost the same in the cases of all the oxidants used, suggesting that the oxidation of SAA by CAT, CAB, BAT, and BAB proceeds by a similar mechanism. The constancy of rate constant on addition of neutral salts, benzenesulfonamide, and halide ions also supports the proposed mechanism and the derived rate law.

CONCLUSION

The oxidation of sulfanilic acid to N-hydroxylaminobenzene-4-sulfonic acid by CAB and BAB in alkaline medium followed the identical kinetics with the first-order dependence of the reaction rate each on [oxidant]$_o$ and [substrate]$_o$, and the inverse first-order dependence on [OH$^-$]. Activation parameters for overall reaction were deduced. Proton inventory studies have been made. The proposed mechanism and the derived rate law are consistent with the observed kinetics. The relative reactivity of CAT, CAB, BAT, and BAB toward SAA was compared and discussed.

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