Oxidation of Ethanolamines by Sodium *N*-Bromobenzenesulfonamide in Alkaline Buffer Medium: A Kinetic and Mechanistic Study

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ABSTRACT: The kinetics of oxidation of ethanolamines, monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA), by sodium *N*-bromobenzenesulfonamide or bromamine-B (BAB) in alkaline buffer medium (pH 8.7–12.2) has been studied at 40°C. The three reactions follow identical kinetics with first-order in [oxidant] and fractional-order each in [substrate] and [OH⁻]. Under comparable experimental conditions, the rate of oxidation increases in the order: DEA > TEA > MEA. The added reaction product, benzenesulfonamide, retards the reaction rate. The addition of halide ions and the variation of ionic strength of the medium have no significant effect on the rate. The dielectric effect is negative. The solvent isotope effect $k'(H_2O)/k'(D_2O) \approx 0.92$. Activation parameters for the composite reaction and for the rate-limiting step were computed from the Eyring plots. Michaelis-Menten type of kinetics is observed. The formation and decomposition constants of ethanolamine-BAB complexes are evaluated. An isokinetic relationship is observed with $\beta = 430$ K indicating that enthalpy factors control the rate. For each substrate, a mechanism consistent with the kinetic data has been proposed. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 480–490, 2001

INTRODUCTION

Ethanolamines (EAs) are organic bases containing amino and alcoholic functional groups. The compounds find extensive applications in the synthesis of surfactants, pharmaceuticals, and as addition agents in the metal finishing industry [1]. The kinetic studies

have been reported in the literature on the oxidation of ethanolamines with various oxidizing agents [2–6]. However, there is meager information in the literature on the kinetics of oxidation of these substrates by *N*-haloamines.

Considerable attention has been centered on the chemistry of *N*-halomines, because of their versatility in behaving as mild oxidants, halogenating agents, and *N*-anions, which act as both bases and nucleophiles. The important chlorine compound of this group is

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chloramine-T (CAT), which is a byproduct in saccharin manufacture, and is a well-known analytical reagent for the determination of diverse substrates. The benzene analogue of chloramine-T is chloramine-B (CAB). Mechanistic aspects of many of these reactions have been documented [7,8]. The bromine analogue bromamine-B (sodium-*N*-bromobenzenesulfonamide; $C_6H_5SO_2NBrNa \cdot 1.5H_2O$ or BAB) is becoming important and is found to be a better oxidizing agent than the chloro compound. The compound can be easily prepared by the bromination of CAB. A survey of literature indicates limited information [9–11] on the mechanisms of oxidation reactions of BAB. Hence, it was thought interesting to investigate the oxidative behavior of BAB toward ethanolamines. As a part of our broad program on the mechanistic studies of ethanolamines with organic haloamines, we report the kinetics of oxidation of monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) by BAB in alkaline buffer medium (pH 8.7–12.2) at 40°C in the present communication. Attempt has been made to identify the most probable reactive species of the oxidant in alkaline medium. Activation parameters have been calculated and an isokinetic relationship has also been deduced.

EXPERIMENTAL

Materials

Bromamine-B (BAB) was prepared by partial debromination of dibromamine-B (DBB) in NaOH medium [12]. Pure chlorine was bubbled through an aqueous solution of chloramine-B (30 g in 560 ml of water) and liquid bromine (6 ml) was added dropwise 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 batches with constant stirring in 50 ml of 4.0 mol dm^{-3} NaOH. The solution was cooled in ice, filtered under suction, and the product was dried over anhydrous calcium chloride. The purity of BAB was checked iodometrically through its active bromine content and the compound was further characterized by its ^{13}C FT-NMR spectrum (obtained on a Bruker WH 270-MHz nuclear magnetic resonance spectrometer) with D_2O as solvent and TMS as the internal standard (ppm relative to TMS) 143.38 (C-1, carbon attached to S atom), 134.30 (C-4, para to the hetero atom), 131.26 (C-2, 6), and 129.31 (C-3, 5). An aqueous solution of BAB was standardized iodometrically and preserved in brown bottles to prevent its photochemical deterioration.

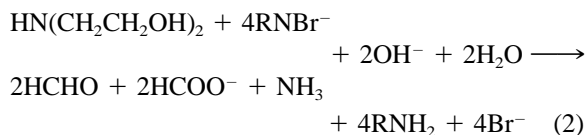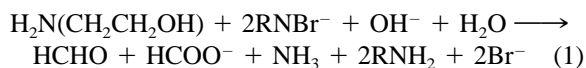Because ethanolamines were of the accepted grades of purity, they were used without further purification. An aqueous solution of desired strength was prepared freshly each time. All other chemicals used were of analytical grade. Heavy water (D_2O 99.2%) was supplied by the Bhaba Atomic Research Centre, Mumbai, India. The ionic strength (I) of the system was maintained at a constant high value (0.5 mol dm^{-3}) using a concentrated solution of sodium perchlorate "to swamp" the reaction. The dielectric constant or permittivity (D) of the reaction medium was altered by the addition of methanol in varying proportions (% v/v) and values of D of methanol–water mixtures reported in literature [13] were employed. Standard buffer systems (NH_2CH_2COOH–NaOH) were employed [14]. Triply distilled water was used in preparing all aqueous solutions.

Kinetic Measurements

Reactions were carried out under pseudo-first-order conditions ([substrate]$_o \gg$ [oxidant]$_o$) at constant temperature (e.g., 40°C) in glass stoppered Pyrex boiling tubes coated black on the outside to eliminate photochemical effects. The oxidant and requisite amounts of substrate, NaClO$_4$, and buffer solutions taken in separate boiling tubes were thermostated for 30 min at 40°C. The reaction was initiated by the rapid addition of a measured amount of BAB to the mixture and was shaken intermittently for uniform concentration. The progress of the reaction was monitored by iodometric titration of unconsumed BAB in known aliquots (5 ml each) of the reaction mixture withdrawn at regular time intervals. The reactions were followed up to 70% completion. The psuedo-first-order rate constants (k') calculated from the linear plots of log[BAB] vs time were reproducible within ± 3–5%.
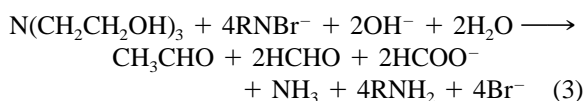
Stiochiometry

Different sets of reaction mixtures containing different amounts of oxidant and substrate ([BAB] $\gg$ [EA]) in an alkaline buffer medium (pH = 9.69) were kept for 24 h at 40°C. Determination of the unreacted oxidant showed the following stoichiometric reactions (eqs. (1–3)):

$$H_2N(CH_2CH_2OH) + 2RNBr^- + OH^- + H_2O \longrightarrow$$
$$HCHO + HCOO^- + NH_3 + 2RNH_2 + 2Br^- \quad (1)$$

$$HN(CH_2CH_2OH)_2 + 4RNBr^-$$
$$+ 2OH^- + 2H_2O \longrightarrow$$
$$2HCHO + 2HCOO^- + NH_3$$
$$+ 4RNH_2 + 4Br^- \quad (2)$$

Table I Effects of Varying Reactant Concentrations on the Rate of Reaction[a]

10^3 [BAB]$_o$ (mol dm^{-3})	10^2 [EA]$_o$ (mol dm^{-3})	$k' \times 10^4$ (s^{-1})		
		MEA	DEA	TEA
0.60	1.00	0.28	12.7	1.64
0.80	1.00	0.24	12.5	1.78
1.00	1.00	0.25	12.6	1.75
1.20	1.00	0.26	12.6	1.88
1.60	1.00	0.23	12.7	1.70
2.00	1.00	0.24	12.8	1.76
1.00	0.50	0.15 (0.09)	8.14 (4.24)	1.18 (0.68)
1.00	1.00	0.25 (0.14)	12.6 (6.65)	1.75 (1.05)
1.00	2.00	0.36 (0.21)	17.9 (9.10)	2.58 (1.50)
1.00	4.00	0.53 (0.30)	24.9 (12.3)	3.25 (2.07)
1.00	6.00	0.65 (0.35)	31.3 (15.0)	3.90 (2.68)
1.00	8.00	0.78 (0.41)	35.5 (17.2)	4.53 (2.95)

[a] pH = 9.94; I = 0.50 mol dm^{-3}; T = 313 K; Values in parentheses are the rate constants for the variation of [EA] at fixed [RNH$_2$] = 3.0×10^{-3} mol dm^{-3}. Remaining conditions are as in "a".

$$N(CH_2CH_2OH)_3 + 4RNBr^- + 2OH^- + 2H_2O \longrightarrow$$
$$CH_3CHO + 2HCHO + 2HCOO^-$$
$$+ NH_3 + 4RNH_2 + 4Br^- \quad (3)$$

where R = $C_6H_5SO_2$.

Product Analysis

The reduction product of BAB, benzenesulfonamide (RNH$_2$), in the reaction mixtures was identified by TLC [15] using petroleum ether : chloroform : 1-butanol (2:2:1, v/v) as the solvent system and iodine as spray reagent (R_f = 0.88). The experimental R_f value is consistent with the literature value [10]. Sodium salt of formic acid was treated with a known excess of standard HCl solution and HCOOH formed was extracted into ether and identified by TLC [16] and by the chromotropic acid procedure [16]. HCOOH was also quantitatively determined by acid-base titrations. Formaldehyde was detected by Schiff's reagent test, whereas acetaldehyde was identified by iodoform and nitroprusside tests [17]. Also, formaldehyde and acetaldehyde were quantitated through their 2,4-DNP derivatives [16]. Ammonia was detected by Nessler's reagent test according to the method of Vogel [18] and quantitatively determined by the microKjeldahl procedure.

RESULTS

The kinetics of oxidation of ethanolamines (EAs) by BAB was investigated at several initial concentrations of the reactants in alkaline buffer medium. The same oxidation behavior was observed for all three EAs.

Effect of Reactants on the Rate

With the substrate in excess, at constant [EA]$_o$ and pH, plots of log [BAB] vs time are linear, indicating a first-order dependence of the rate on [BAB]. The rate constant k' was not affected by a change in [BAB]$_o$, confirming the first-order dependence of the rate on [BAB] (Table I). Values of k' increase with increase in [EA]$_o$ (Table I). Plots of log k' vs log[EA]$_o$ are linear with fractional slopes (0.4–0.6), indicating a fractional-order dependence on [EA]. Furthermore, plots of k' vs [EA]$_o$ are linear with y-intercept, further confirming the factional-order dependence on [EA].

Effect of pH on the Rate

The rate increases with increase in pH of the medium (Table II). Plots of log k' vs pH are linear with fractional slopes (0.3–0.4), indicating a fractional-order dependence of the rate on [OH$^-$] of the medium.

Effect of Benzenesulfonamide on the Rate

Addition of the reaction product, benzenesulfonamide (RNH$_2$), to the reaction mixture retards the rate (Table II). Furthermore, plots of log k' vs log[RNH$_2$] are linear with negative fractional slopes ($-$0.2 to $-$0.3), indicating a negative fractional-order dependence of the rate on [RNH$_2$]. It also indicates that RNH$_2$ is involved in a fast pre-equilibrium to the rate-determining step.

Table II   Effect of Varying pH and Benzenesulfonamide (RNH_2) Concentration on the Rate of Reaction

pH* or 10^4 [RNH_2]** (mol dm^{-3})	$k' \times 10^4$ (s^{-1})		
	MEA	DEA	TEA
8.72 (0.0)	0.11 (0.25)	4.52 (12.6)	0.68 (1.75)
9.10 (5.0)	0.15 (0.22)	6.10 (11.3)	0.91 (1.60)
9.65 (10.0)	0.20 (0.19)	9.35 (9.10)	1.40 (1.38)
9.94 (20.0)	0.25 (0.16)	12.6 (7.45)	1.75 (1.18)
10.20 (30.0)	0.31 (0.14)	15.1 (6.65)	2.16 (1.05)
10.49	0.38	19.8	2.63
10.85	0.50	27.6	3.32
11.58	0.77	48.0	5.52
12.20	1.20	89.2	9.70

* [BAB]$_o$ = 1.00×10^{-3} mol dm^{-3}; [EA]$_o$ = 1.00×10^{-2} mol dm^{-3}; I = 0.5 mol dm^{-3}; T = 313 K.

** For values in parentheses, pH = 9.94 while other conditions are the same as above *.

Effects of Ionic Strength and Halide Ions on the Rate

Variation of the ionic strength (I) of the medium by adding $NaClO_4$ (0.10–0.80 mol dm^{-3}) has no effect on the rate. Also, addition of Cl^- or Br^- ions in the form of NaCl or NaBr (5.0×10^{-4}–5.0×10^{-3} mol dm^{-3}) has negligible effect on the rate.

Effect of Varying Dielectric Constant on the Rate

The dielectric constant (D) of the medium was varied by adding MeOH (0–40% v/v) to the reaction mixture. A decrease in the rate was noticed with decreasing D (Table III). Plots of log k' vs $1/D$ were linear (Fig. 1) with negative slopes supporting a rate-determining step with a charge dispersal. Control experiments with MeOH indicated that its oxidation by BAB was negligible (<2%) under the experimental conditions. However, the rate constants were corrected to represent only the oxidation of ethanolamines.

Table III   Effect of Varying Dielectric Constant (D) of Medium on the Rate of Reaction[a]

% MeOH (v/v)	D	$k' \times 10^4$ (s^{-1})		
		MEA	DEA	TEA
0	76.73	0.250	12.6	1.75
10	72.37	0.210	10.3	1.40
20	67.48	0.170	8.10	1.21
30	62.71	0.140	6.25	0.920
40	58.06	0.110	4.80	0.740

[a] [BAB]$_o$ = 1.00×10^{-3} mol dm^{-3}; [EA]$_o$ = 1.00×10^{-2} mol dm^{-3}; pH = 9.94, I = 0.50 mol dm^{-3}; T = 313 K; Values of D are from the literature [13].

Effect of Temperature on the Rate

The reaction was studied at different temperatures (308–323 K). From the Eyring plots of ln(k'/T) vs $1/T$, the activation parameters, namely enthalpy of activation ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$), for the composite reaction were computed. These data are presented in Table IV. Additionally, the activation parameters calculated from k_3 values from the rate-determining step are presented in Table VI.

Solvent Isotope Studies

Studies of the reaction rate in D_2O medium for MEA, DEA, and TEA revealed that while $k'(H_2O)$ =
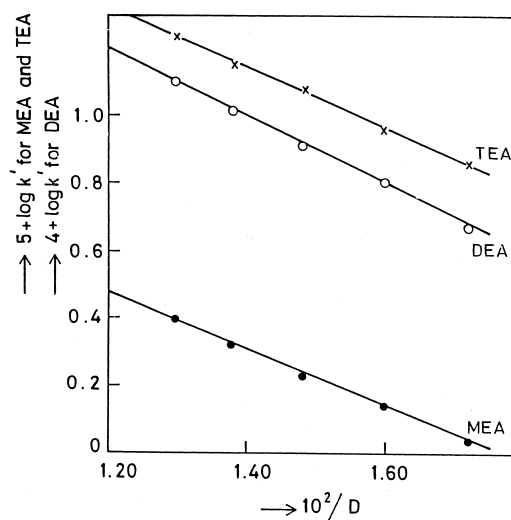
Figure 1   Plots of log k' vs $1/D$: [BAB]$_o$ = 1.00×10^{-3} mol dm^{-3}; [EA]$_o$ = 1.00×10^{-2} mol dm^{-3}; pH = 9.94; I = 0.50 mol dm^{-3}; T = 313 K.

Table IV Effect of Varying Temperature on the Reaction Rate and Activation Parameters for the Composite Reaction[a]

Ethanolamine	$k' \times 10^4$ (s^{-1})				$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
	308K	313K	318K	323K		
MEA	0.12	0.25	0.43	0.85	97.0	−23.6
DEA	8.00	12.6	16.4	24.8	64.4	−95.4
TEA	1.10	1.75	2.46	3.36	74.0	−80.9

[a] [BAB]$_o$ = 1.00 × 10^{-3} mol dm^{-3}; [EA]$_o$ = 1.00 × 10^{-2} mol dm^{-3}; pH = 9.94, I = 0.50 mol dm^{-3}.

0.25 × 10^{-4} s^{-1}, 1.26 × 10^{-3} s^{-1}, 1.75 × 10^{-4} s^{-1}, and k'(D$_2$O) = 0.27 × 10^{-4} s^{-1}, 1.37 × 10^{-3} s^{-1}, and 1.92 × 10^{-4} s^{-1}, respectively. The solvent isotope effect k'(H$_2$O)/k'(D$_2$O) ≈ 0.92.

Test for Free Radicals

Olefinic monomers such as acrylonitrile and freshly prepared 10% acrylamide solution in water under nitrogen atmosphere were added to the reaction mixture to enable free radicals, if present, to initiate polymerization. The lack of polymerization indicated the absence of free radicals in the reaction mixture. Proper control experiments were also conducted.

DISCUSSION

Because organic haloamines have similar chemical properties, it is expected that similar equilibria exist in solutions of these compounds. Bromamine-B, which is analogous to chloramine-T, behaves like a strong electrolyte in both acidic and alkaline media [19,20]. In general, BAB undergoes a two-electron change in its reactions. The oxidation potential of BAB/RNH$_2$ is pH-dependent and decreases with increase in the pH of the medium (1.14 V at pH 0.65 and 0.50 V at pH 12.0).

Hardy and Johnston [21] and Higuchi et al. [22,23] have explained the several types of equilibria present in acid and alkaline solutions of *N*-haloamines. BAB ionizes in aqueous solution (eq. (4)) and the anion picks up a proton in acid solution to give the free acid [19], monobromamine-B, RNBrH (eq. (5)):

$$\text{RNBrNa} \rightleftharpoons \text{RNBr}^- + \text{Na}^+ \quad (4)$$

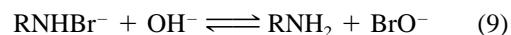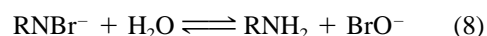$$\text{RNBr} + \text{H}^+ \rightleftharpoons \text{RNBrH} \quad (5)$$

Although the free acid has not been isolated, there is sufficient experimental evidence for its formation in solution [20,24]. It can further undergo disproportion (eq. (6)) and hydrolysis (eq. (7)) giving RNH$_2$, dibromamine-B (RNBr$_2$), and HOBr.

$$2\text{RNBrH} \rightleftharpoons \text{RNH}_2 + \text{RNBr}_2 \quad (6)$$

$$\text{RNBrH} + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_2 + \text{HOBr} \quad (7)$$

Several workers have observed the retarding influence of OH$^-$ ions on the rate of BAB reactions with a number of substrates [22–24] and suggested that the reactivity of weakly alkaline solutions is due to RNBrH formed from RNBr$^-$ in a OH$^-$ retarding step, as shown in the following.

In alkaline solutions of BAB, the following equilibria are reported:

$$\text{RNBr}^- + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_2 + \text{BrO}^- \quad (8)$$

$$\text{RNHBr}^- + \text{OH}^- \rightleftharpoons \text{RNH}_2 + \text{BrO}^- \quad (9)$$

The possible oxidizing species in alkaline BAB solutions are therefore RNBr$^-$, RNBrH, and BrO$^-$. The observed retardation of rate by the reaction product (RNH$_2$) can best be explained by Schemes Ia–c for MEA, DEA, and TEA oxidations.

For DEA, the first two fast equilibria are similar to steps (i) and (ii) in Scheme Ia.

For TEA, the first two fast equilibria are similar to steps (i) and (ii) in Scheme Ia.

A detailed mechanism of oxidation by BAB for each of the three ethanolamines is shown in Scheme I. In the reactions, as shown in stoichiometric equations (1)–(3), each mole of the ethanolamine substrate reacts with two moles of BAB in the case of MEA and four moles of BAB in the Case of DEA or TEA in alkaline medium. The reactive oxidizing species (BrO$^-$) formed in a fast equilibrium [step (i)] interacts
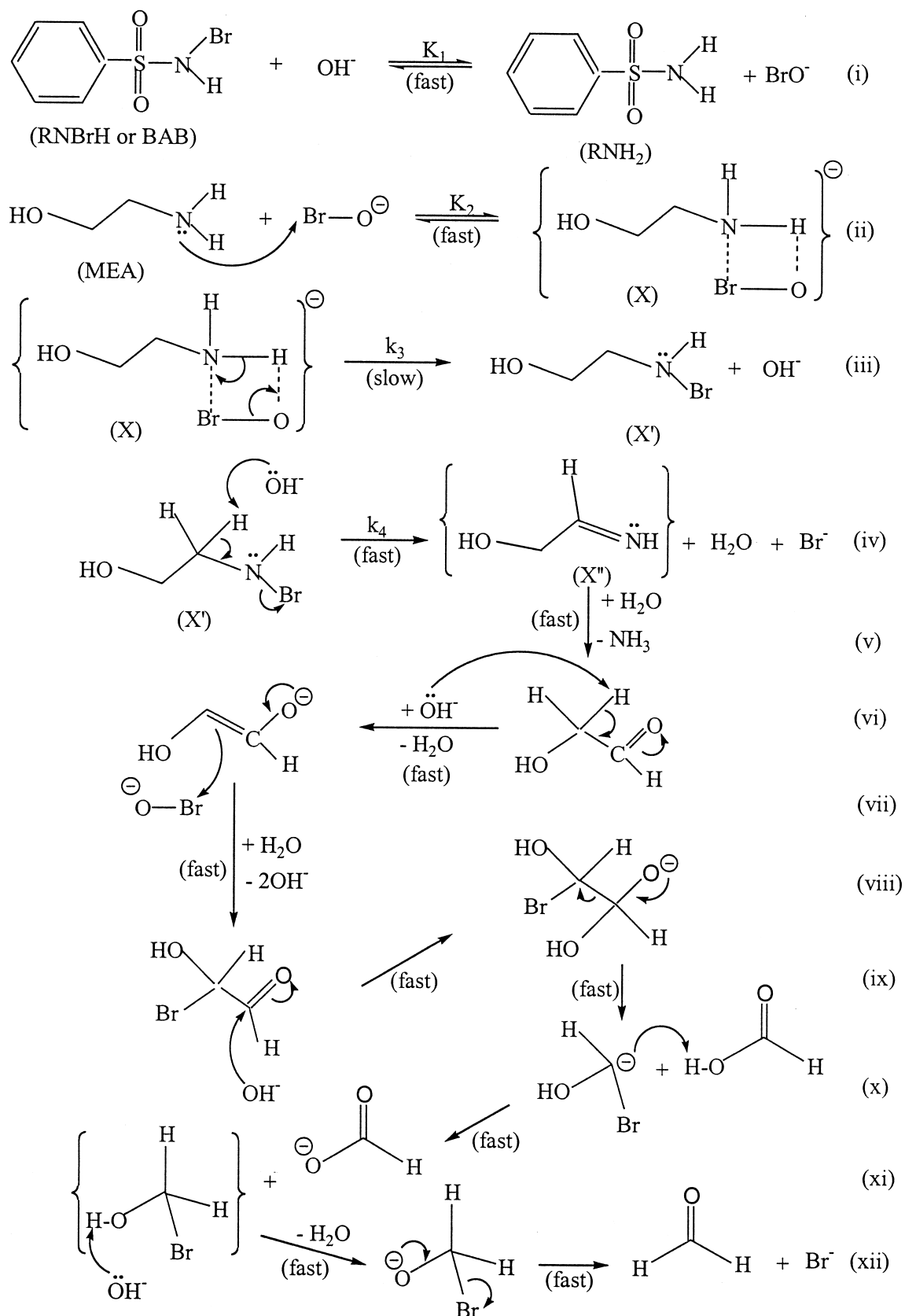
**Scheme Ia** MEA oxidation.
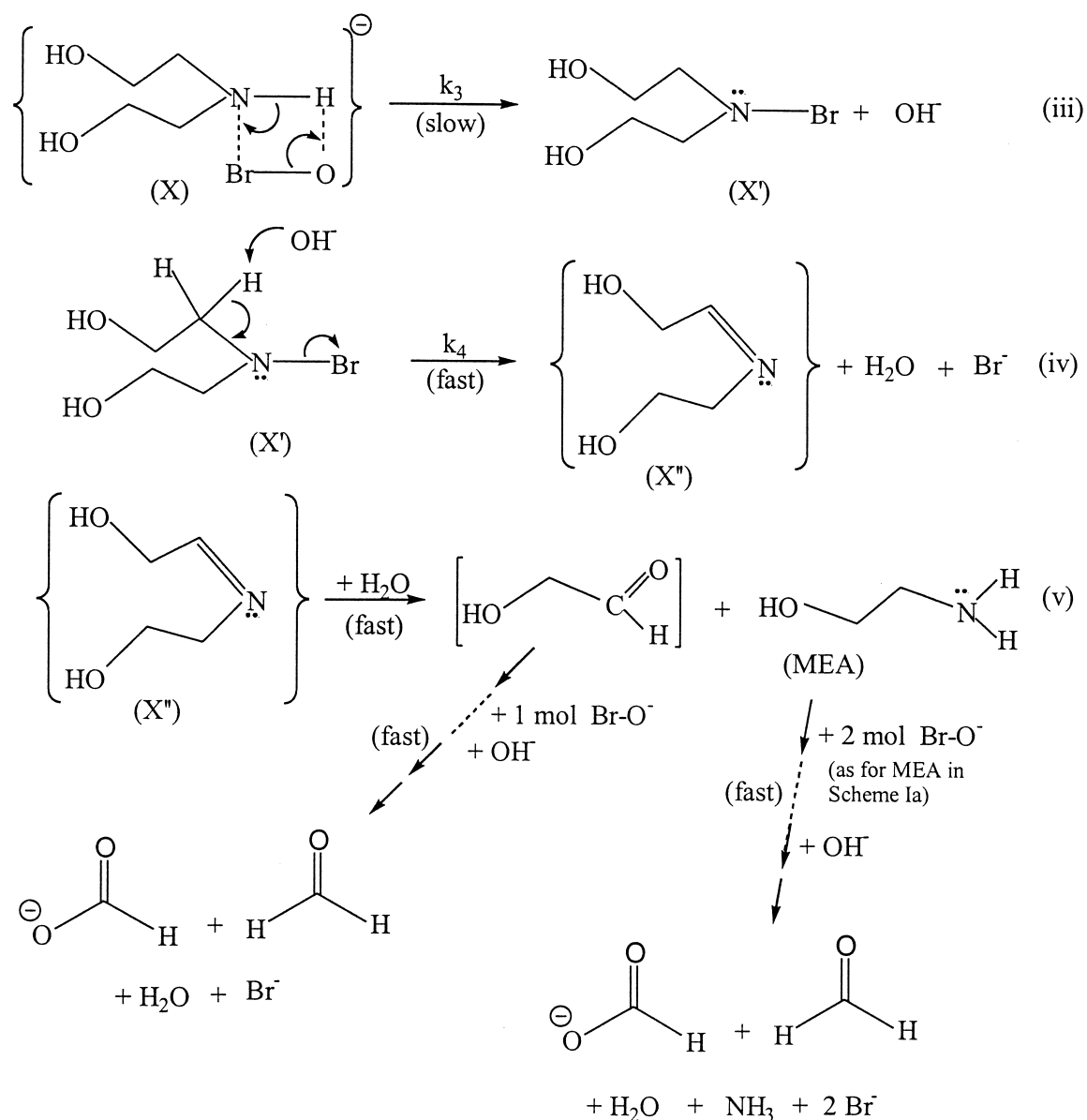
Scheme Ib DEA oxidation.

with the substrate in a fast equilibrium [step (ii)] forming a transition state X, which contains a four- or seven-membered ring. This transient species X in a slow/rate-determining step (iii) disproportionates into an N-bromo intermediate X' and OH$^-$ ion (plus an acetaldehyde molecule in the case of TEA). The slow/rate-determining step (iii) is followed by several fast steps leading to the formation of main products, formaldehyde, formate ion, and ammonia. The lone electron pair on the nitrogen atom is important in the chemistry of amines, since it is responsible for the typical basic and nucleophilic properties of these compounds. In the series MEA, DEA, and TEA, because the ethanoyl ($-$CH$_2$CH$_2$OH) substituent in an aliphatic system is an electron-withdrawing group, the larger the number of these substituents at the reaction center (i.e.., nitrogen atom) the lesser will be the electron density on the heteroatom. The decreasing negative charge on the central nitrogen atom favors the attack by the oxidizing BrO$^-$ species at this center to form X.

In the present study, the increasing order of the reaction rate, MEA < TEA < DEA, is attributed to a combination of inductive and steric effects arising

Scheme Ic   TEA oxidation.
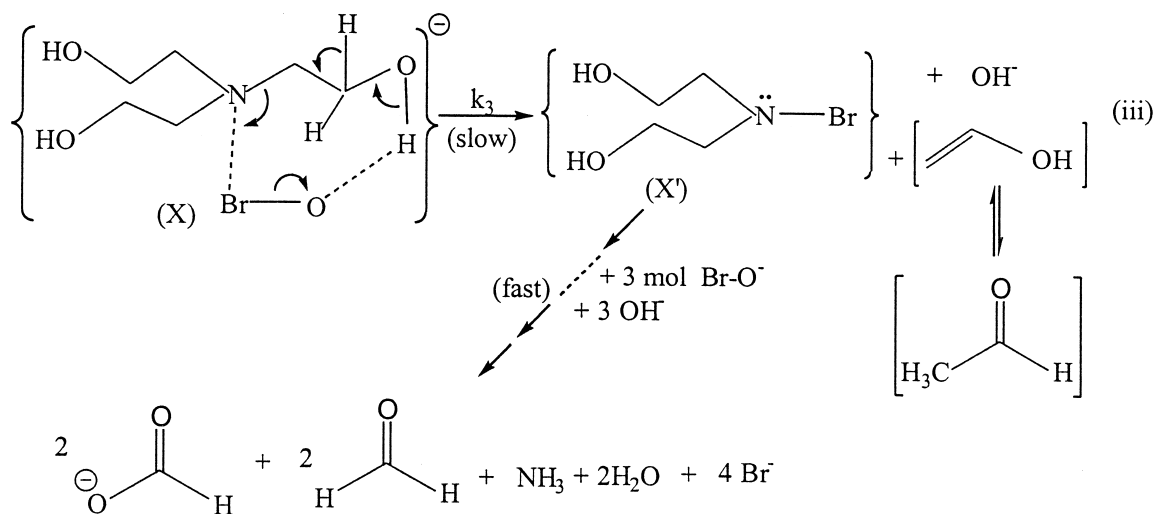
from an increase in the number of ethanoyl substituents on the nitrogen atom. The Taft inductive substituent constant (σ^*), which is largely a measure of the inductive effect in aliphatic compounds, has a value of 0.555 for —CH$_2$OH group and −0.10 for —CH$_3$ or —CH$_2$CH$_3$ group [25]. Therefore, —CH$_2$CH$_2$OH in ethanolamines is an electron-withdrawing substituent [25]. An introduction of another —CH$_2$ unit to

CH$_2$OH is not likely to change it to an electron-donating group. Purely based on the electronic effect, the transition state of TEA formed is expected to be more stabilized than that of DEA as the N–H bond (Schemes Ia and Ib) or α-C–H bond (Scheme Ic) of the cyclic ring of X becomes more labile, making the OH$^-$ elimination easier in the slow step. In the case of DEA, the decreased electronic effects stabilizing the
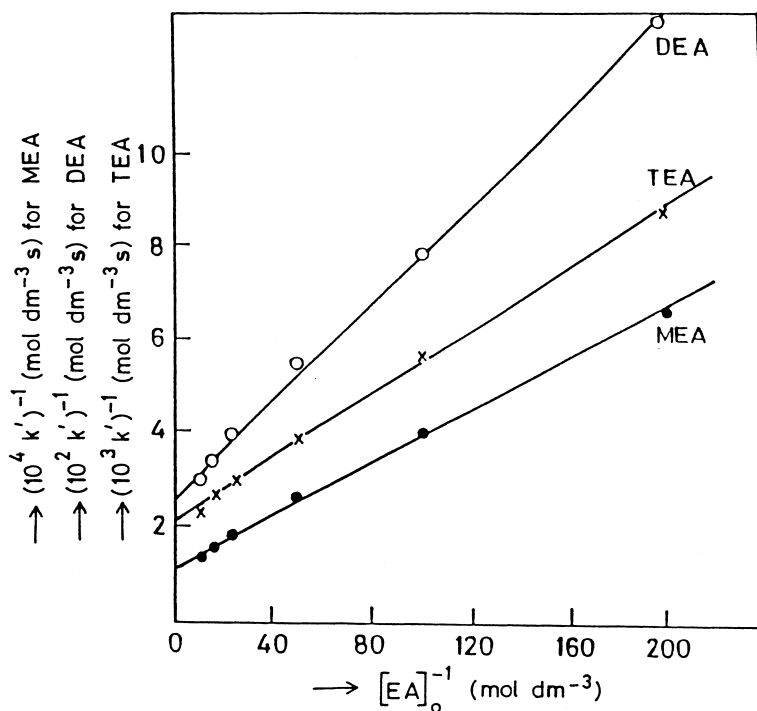
Figure 2   Plots of $1/k'$ vs $1/[EA]_o$: $[BAB]_o = 1.00 \times 10^{-3}$ mol dm^{-3}; pH $= 9.94$; $I = 0.50$ mol dm^{-3}; $T = 313$ K.
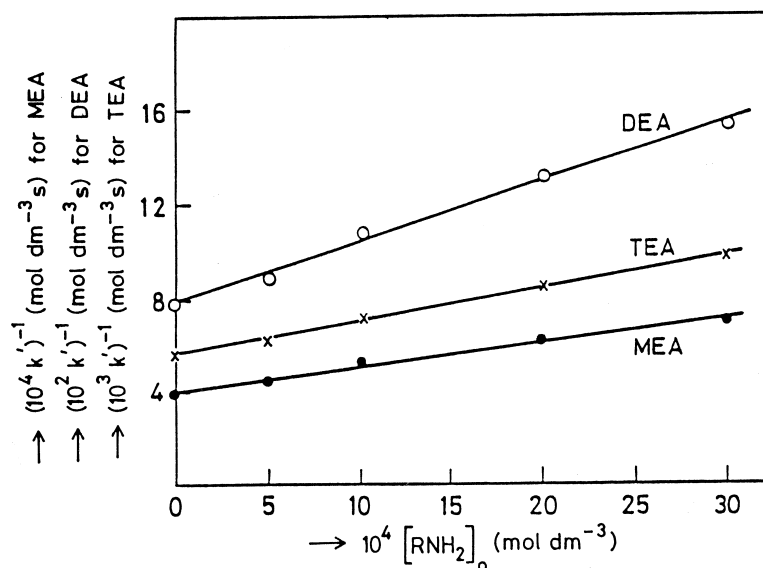
Figure 3 Plots of $1/k'$ vs $[RNH_2]_o$: $[BAB]_o = 1.00 \times 10^{-3}$ mol dm^{-3}; $[EA]_o = 1.00 \times 10^{-2}$ mol dm^{-3}; pH $= 9.94$; $I = 0.50$ mol dm^{-3}; $T = 313$ K.

transition state seem to be predominant over the steric factor favoring the overall reaction. In the case of TEA, the increased steric interactions of three relatively bulky ethanoyl substituents predominate over the electronic effects, thereby decreasing the overall reactivity of this substrate as compared to that of DEA. Here the steric interactions destabilize the transition state by inhibiting the oxidant species from approaching the reaction site (nitrogen atom) to form a new N–Br bond as in the transient species X'.

If $[BAB]_t$ represents the total concentration of the oxidant, from important steps (i), (ii), and (iii) of Scheme I,

$$[BAB]_t = [RNBrH] + [BrO^-] + [X]$$

for which the rate law (eq. (10)) can be derived:

$$\text{Rate} = \frac{-d[BAB]}{dt}$$

$$= \frac{K_1 K_2 k_3 [BAB]_t [EA][OH^-]}{[RNH_2] + K_1 [OH^-] \{1 + K_2 [EA]\}} \quad (10)$$

where EA represents MEA, DEA, or TEA. The rate law (eq. (10)) is in accordance with the observed kinetic data.

Since rate $= k' [BAB]_t$, eq. (10) can be transformed into eqs. (11) and (12):

$$\frac{1}{k'} = \frac{[RNH_2]}{K_1 K_2 k_3 [EA][OH^-]} + \frac{1}{K_2 k_3 [EA]} + \frac{1}{k_3} \quad (11)$$

$$\frac{1}{k'} = \frac{1}{K_2 k_3 [EA]} \left\{ \frac{[RNH2]}{K_1 [OH^-]} + 1 \right\} + \frac{1}{k_3} \quad (12)$$

From double reciprocal plots of $1/k'$ vs $1/[EA]_o$ (Fig. 2) and plots of $1/k'$ vs $[RNH_2]_o$ (Fig. 3), values of K_1, formation constant K_2, and decomposition constant k_3 were calculated using eq. (12) (Table V). Furthermore, ethanolamines concentrations were varied at fixed $[RNH_2]$ and $[OH^-]$ and the values of K_1, K_2, and k_3 were calculated using eq. (12). The corresponding rate constants and K_1, K_2, and k_3 values are given in parentheses in Tables I and V, respectively. The near constant values of K_1, K_2, and k_3 support the proposed mechanism. Because the rate was fractional in $[EA]$,

Table V Equilibrium and Decomposition Constants[a]

Ethanolamine	K_1	K_2 (dm^3 mol^{-1})	k_3 (s^{-1})
MEA	30.6 (24.0)	46.5 (86.5)	7.69×10^{-5} (5.26×10^{-5})
DEA	24.9 (16.8)	53.9 (131)	3.57×10^{-3} (2.22×10^{-3})
TEA	29.5 (23.8)	58.4 (96.6)	4.76×10^{-4} (3.57×10^{-4})

[a] Calculated from plots of $1/k'$ vs $1/[EA]$ and $1/k'$ vs $[RNH_2]$ using eq. (12). Conditions are as given in Tables I and II. Values in parentheses were calculated using eq. (12) at fixed $[RNH_2] = 3.0 \times 10^{-3}$ mol dm^{-3}. Other conditions are as given in Tables I and II.
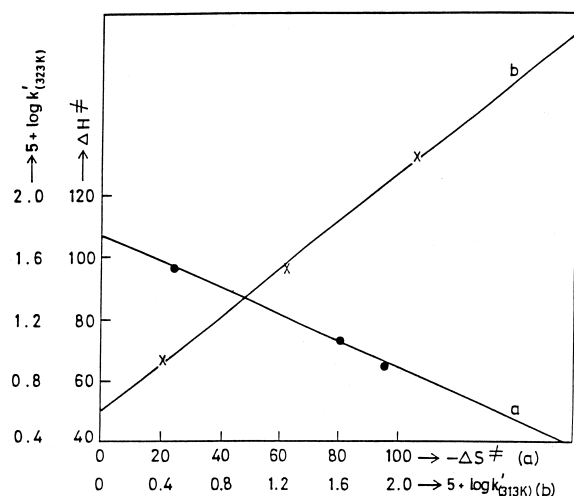
Table VI Decomposition Constant (k_3) of EA–BAB Complex at Different Temperatures and Activation Parameters for Rate Limiting Step[a]

Ethanolamine	$k_3 \times 10^4$ (s^{-1})				$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
	308 K	313 K	318 K	323 K		
MEA	0.45	0.70	1.33	2.70	70.8	−69.0
DEA	26.3	35.7	50.0	89.2	60.6	−98.7
TEA	2.49	4.76	7.14	11.7	68.3	−67.1

[a] All conditions except temperature are as in Table III.

Michaelis-Menten kinetics [26] were adopted to study the effect of [EA]$_o$ on the rate at different temperatures (308–323 K). The decomposition constant k_3 for the rate-limiting step was calculated using eq. (12) for each ethanolamine. Activation parameters for the decomposition step of the EA–BAB complex (step (iii) in Scheme I), were evaluated using the Arrhenius and Eyring plots of ln k_3 vs $1/T$ and ln(k_3/T) vs $1/T$, respectively. These data are presented in Table VI.

The negative values of $\Delta S^{\neq}$ suggest the formation of more ordered and rigid transition states (Table IV). The isokinetic temperature (β) was determined from the slope of the linear plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ (Fig. 4). The value of β is found to be 430 K, which is much higher than the experimental temperature of 313 K. The isokinetic relationship was further proven through the Exner criterion [27] by plotting log $k'_{(323K)}$ vs log $k'_{(313K)}$ (data are taken from Table IV). The value of β (426 K) was calculated using the equation $\beta = T_1 (1 - q)/(T_1/T_2) - q$, where q is the slope of the Exner plot (Fig. 4). The higher β value indicates common enthalpy-controlled pathways for the oxidation of EAs by BAB.

For a limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis [28] has shown that a plot of log k' vs $1/D$ is linear with a negative slope for a reaction between anion and a dipole or between two dipoles and positive slope for a cation–dipole interaction. The negative dielectric effect observed in the present studies (Table III, Fig. 1) clearly supports the anion–dipole interaction as shown in the proposed scheme. Solvent isotope studies show that $k'(H_2O)/k'(D_2O) < 1$. This is generally correlated with the fact that OD$^-$ is a stronger base than OH$^-$ and in the present base catalyzed reactions, increase in the rate in D$_2$O medium is expected [29]. The magnitude, however, is small compared to the expected value of 2 to 3 times greater, which can be attributed to the fractional-order dependence on [OH$^-$].

The zero effect of halide ions on the rate indicates that no interhalogen or free bromine is formed. The variation of the ionic strength of the medium does not alter the rate, indicating that one of the interacting species involved in the rate-limiting step is nonionic in nature while the other is ionic. These observations are also in conformity with the proposed mechanism, which shows the decomposition of a complex species, X, in the slow step.

Figure 4 Isokinetic Plots of: (a) $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ and (b) log $k'_{(323K)}$ vs. log $k'_{(313K)}$.

BIBLIOGRAPHY

1. Mayanna, S. M.; Maruthi, B. N. Metal Finish 1996, 94, 42.
2. Smith, A.; Willford, J. J. Am Chem Soc 1954 76, 2502.
3. Shukla, K. S.; Bansal, O. P. Monatsh Chem 1974, 105, 1266.
4. Reddy, P. G.; Ramesh, V.; Kandalikar, S. Oxid Commun 1984, 7, 89.

5. Aswathi, A. K.; Upadhaya, S. K. Indian J Chem 1986, 25A, 292.

6. Reddy, M. S.; Rajanna, K. C.; Naseeruddin, A. Proc Nat Acad Sci India 1995, 65(A), 29.

7. Campbell, M. M.; Johnson, G. Chem Rev 1978, 78, 65.

8. Banerji, K. K.; Jayaram, B.; Mahadevappa, D. S. J Sci Ind Res 1987, 46, 65.

9. Kothari, S.; Sharma, V.; Banerji, K. K. J Chem Research (s) 1985, 234.

10. Puttaswamy; Mahadevappa, D. S.; Rangappa, K. S. Bull Chem Soc Jpn 1989, 63, 3343.

11. Puttaswamy. Indian J Chem 1997, 36A, 970.

12. Ahmed, M. S.; Mahadevappa, D. S. Talanta 1980, 27, 669.

13. Akerloff, G. J Am Soc 1932, 54, 4125.

14. Findley, A. Practical Physical Chemistry; Longmans: London, 1952; Gomori, G. Methods Enzymol 1955 1, 138.

15. Mahadevappa, D. S.; Made Gowda, N. M. Talanta 1975, 22, 771.

16. Feigl, F. Spot Tests in Organic Analysis; Elsevier: Amsterdam, 1956, p. 340; Vogel, A. I. A Text Book of Practical Organic Chemistry; 3rd ed.; ELBS and Longman: London, 1973, p. 344.

17. Mann, F. G.; Saunders, B. C. Physical Organic Chemistry, ELBS: London, 1970, pp. 339–342.

18. Vogel, A. I. A Text Book of Quantitative Inorganic Analysis, 4th ed., Longman: London, 1978, p. 393.

19. Bishop, E.; Jennings, V. J. Talanta 1958, 1, 197.

20. Morris, J. C.; Salazar, J. A.; Wineman, M. A. J Am Chem Soc 1948, 70, 2036.

21. Hardy, F. F.; Johnston, J. P. J Chem Soc Perkin Trans II 1973, 742.

22. Higuchi, T.; Hussain, A. J Chem Soc B 1967, 549.

23. Higuchi, T.; Ikeda, K.; Hussain, A. J Chem Soc B 1967, 546; 1968, 1031.

24. Mahadevappa, D. S.; Rangaswamy. Indian J Chem 1973, 11, 811; Rev. Roumaine de Chim 1977, 22, 1233.

25. Isaacs, N. S. Physical Organic Chemistry; Longman Scientific & Technical, UK, Copublished in the U.S. with John Wiley & Sons, Inc., New York, 1987, pp. 154–155.

26. Laidler, K. J. Chemical Kinetics; Tata McGraw Hill: Bombay, 1965, p. 474.

27. Exner, O. Collect Czech Chem Commun 1964, 29, 1094.

28. Amis, E. S. Solvent Effects on Reaction Rates and Mechanisms; Academic Press: New York, 1966.

29. Collins, C. J.; Bowman, N. S. Isotope Effect in Chemical Reactions; Van Nostrand Reinhold: New York, 1970, p. 267.