Kinetic and Mechanistic Studies of Some Aliphatic Amines' Oxidation by Sodium N-bromo-*p*-toluenesulfonamide in Hydrochloric Acid Medium

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ABSTRACT: Oxidations of *n*-propyl, *n*-butyl, isobutyl, and isoamyl amines by bromamine-T (BAT) in HCl medium have been kinetically studied at 30°C. The reaction rate shows a first-order dependence on [BAT], a fractional-order dependence on [amine], and an inverse fractional-order dependence on [HCl]. The additions of halide ions and the reduction product of BAT, *p*-toluenesulfonamide, have no effect on the reaction rate. The variation of ionic strength of the medium has no influence on the reaction. Activation parameters have been evaluated from the Arrhenius and Eyring plots. Mechanisms consistent with the preceding kinetic data have been proposed. The protonation constant of monobromamine-T has been evaluated to be 48 ± 1. A Taft linear free-energy relationship is observed for the reaction with $\rho^* = -12.6$, indicating that the electron-donating groups enhance the reaction rate. An isokinetic relationship is observed with $\beta = 350$ K, indicating that enthalpy factors control the reaction rate. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 776–783, 2000

INTRODUCTION

Aromatic *N*-halosulfonamides are mild oxidants containing a strongly polarized *N*-linked halogen in its +1 oxidation state. The prominent member of this group, chloramine-T (CAT), is a well-known analytical reagent and the mechanistic aspects of many of its reactions have been documented [1,2]. The bromine analogue, bromamine-T (BAT), is a better oxidizing agent than CAT. However, meager information exists in the literature on BAT reactions [3–6].

Aliphatic amines are nitrogen-containing bases that find wide applications in industry as additives in plating complex baths, as reagents in the synthesis of dyes and polymeric materials, and as potential ligands for metal complexes used in heterogeneous catalysis. They also play an important role in biological systems. Oxidation of primary amines is of importance, as it adds to the body of knowledge on redox chemistry. The products of oxidation depend on the type of oxidant, on the reaction medium, and on the nature of the

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alkyl groups present. Because of these, amines have been oxidized by a number of oxidizing agents under various experimental conditions.

Radhakrishriamurthi and Rao [7] have studied the kinetics of oxidation of aniline and substituted anilines by CAT in alkaline medium and observed a first-order dependence of the rate on both CAT and aniline concentrations and a zero-order dependence on $[OH^-]$. The reactivity order shows that electron-withdrawing groups retard the reaction. A mechanism leading to the formation of azobenzene is postulated through a rate-determining radical formation. The kinetics of oxidation of benzoyl hydrazines by CAT [8] in the alkaline pH 8.9–11.5 have shown a first-order dependence on both [CAT] and [substrate] and a zero-order dependence on $[H^+]$. The reaction is accelerated by electron-withdrawing groups. Gupta and Agarwal [9] have reported the oxidation kinetics of *S*-butylamine by CAT in alkaline medium and the rate is first-order in [CAT], [amine], and $[OH^-]$. Jabbar and Rao [10] have oxidized methylamine, *n*-butylamine, diethylamine, and triethylamine with *N*-bromophthalamide (NBP) in the presence of $Hg(OAc)_2$. The reaction rate shows a first-order dependence on [NBP] and a fractional-order on [amine] and $[H^+]$. Saxena et al. [11] have studied the oxidation of ethylamine, diethylamine, and triethylamine by *N*-bromosuccinimide (NBS) catalyzed by palladium(II) in perchloric acid medium. Shukla and Upadhyay [12] have investigated the mechanism of the $PdCl_2$-catalyzed oxidation of amines and amino alcohols by hexacyonoferrate(III) in alkaline medium. A mechanism involving $[Pd(II) - A_1]$ or $[Pd(II) - A_2]$ (where A_1 represents amines and A_2 represents amino alcohols) as the intermediate complex is proposed. Ananda et al. have reported the kinetics of uncatalyzed [13] and Os(VIII)-catalyzed [14] oxidations of *n*-propyl, *n*-butyl, and isoamyl amines by bromamine-B (BAB) in alkaline medium. The rate laws for the two paths are: rate $= k\,[BAB]\,[amine]\,[OH^-]^x$ and rate $= k\,[BAB]\,[Os(VIII)]\,[OH^-]^y$, where x and y are less than unity.

Most of the investigations reported on the oxidation of amines with different oxidants were carried out in alkaline medium. The literature reports are lacking on the oxidation kinetics of amines in acid medium, especially using BAT as oxidant. For these reasons, in the present communication we report the kinetics of oxidation of four aliphatic primary amines, *n*-propylamine (*n*PA), *n*-butylamine (*n*BA), isobutylmine (*i*BA), and isopentyl or isoamylamine (*i*AA), by BAT (p-CH_3-C_6H_4-$SO_2NBrNa \cdot 3H_2O$) in HCl medium. It is interesting to note that the present study involves oxidation kinetics showing a different mechanism and a different rate law. Attempts have been made to arrive at a LFER through the Taft treatment and an isokinetic relationship with the computed activation parameters.

EXPERIMENTAL

The oxidant, bromanine-T, was prepared by a standard procedure and its purity was checked iodometrically and through UV, IR, and ^{13}C-NMR spectral data [15,16]. Aqueous solutions of BAT were prepared, standardized by the iodometric method and preserved in amber-colored bottles until use, to prevent its photochemical deterioration.

Aqueous solutions of analar grade *n*-propylamine (E. Merck), *n*-butylamine (E. Merck), isobutylamine (Sisco Chem.), and isoamylamine (Fluka) were prepared and used. All other chemicals used were of acceptable grades of purity. A constant ionic strength of the reaction mixture was maintained at 0.30 M by adding a required amount of a concentrated $NaClO_4$ solution. Triply distilled water was used for preparing aqueous solutions.

Kinetic Measurement

The kinetic runs were performed under pseudo-first-order conditions of $[amine]_0 \gg [BAT]_0$. Requisite amounts of solutions of the amine, $NaClO_4$, and HCl were taken in stoppered Pyrex glass tubes whose outer surfaces were coated black to eliminate photochemical effects. A required amount of water was added to maintain a constant total volume for all runs. The tube was thermostated in a water bath set at a given temperature (30°C for most runs). To this solution was added a measured amount of preequilibrated BAT solution to give a known concentration. The reaction mixture was periodically shaken for uniform concentration. The progress of the reaction was monitored iodometrically for two half-lives by withdrawing aliquots of the reaction mixture at regular time intervals. Under pseudo-first-order conditions, rate constants, k', were reproducible within $\approx 3\%$. The regression analysis of experimental data was carried out on an EC-75 statistical calculator.

Stoichiometry and Product Analysis

Reaction mixtures containing different compositions of amine, BAT, and 5.00×10^{-2} M HCl were equilibrated with occasional shaking at 30°C for 24 h. The iodometric titration of unreacted BAT in the reaction mixture showed that one mole of BAT was consumed per mole of the amine.

Table I Effects of Varying Reactant Concentrations on the Reaction Rate. $[HCl]_0 = 0.0500$ mol dm^{-3}; $\mu = 0.30$ mol dm^{-3}; temp = 30°C.

$10^4[BAT]_0$ (mol dm^{-3})	$10^2[amine]_0$ (mol dm^{-3})	$k' \times 10^5$ (s^{-1})			
		*n*PA	*n*BA	*i*BA	*i*AA
8.00	5.00	7.15	7.66	8.06	8.38
9.00	5.00	7.10	7.50	8.02	8.30
10.00	5.00	7.05	7.58	8.10	8.32
11.00	5.00	7.12	7.44	8.15	8.38
12.00	5.00	7.02	7.48	8.12	8.30
13.00	5.00	7.08	7.56	8.08	8.40
10.00	1.00	2.00	2.15	2.35	2.60
10.00	2.00	3.35	3.75	4.10	4.45
10.00	5.00	7.05	7.58	8.10	8.32
10.00	8.00	9.74	10.20	10.60	10.90
10.00	10.00	12.30	12.40	12.50	12.90

$$R{-}CH_2NH_2 + TsNBrNa + H_3O^+ \longrightarrow R{-}CHO + TsNH_2 + NH_4^+ + Na^+ + Br^- \quad (1)$$

where R = CH_3CH_2 for *n*-propylamine (*n*PA), $CH_3CH_2CH_2$ for *n*-butylamine (*n*BA), $(CH_3)_2CH$ for isobutylamine (*i*BA), and $(CH_3)_2CHCH_2$ for isoamylamine (*i*AA).

The presence of the corresponding aldehyde products of the amines in the reaction mixture was detected by preparing their 2,4-dinitrophenylhydrazone derivatives and by using Tollen's and chromic acid tests [17]. The other product, ammonia, was quantitatively estimated by the standard micro-Kjeldahl procedure. The reduction product of BAT, p-$CH_3C_6H_4SO_2NH_2$ or $TsNH_2$, was identified by paper chromatography using benzyl alcohol saturated with water as the solvent system using 0.5% vanillin in 1% HCl in EtOH as the spray reagent ($R_f = 0.905$) [18].

RESULTS

Effects of Varying Reactant Concentrations

The stoichiometry of the amine-BAT reaction was found to be of 1 : 1 ratio. The reaction performed in the presence of HCl, under pseudo-first-order conditions of $[amine]_0 \gg [BAT]_0$, gave linear plots of log [BAT] vs. time ($r > 0.9985$). The linearity of these plots, together with the constancy of the slope for various $[BAT]_0$, indicates a first-order dependence of the reaction rate on [BAT]. The pseudo-first-order rate constants, k', obtained at 30°C are listed in Table I. Under the same experimental conditions, an increase in $[amine]_0$ increased the rate. Plots of log k' vs. log $[amine]_0$ were linear ($r > 0.9989$) with slopes of 0.74 (*n*PA), 0.64 (*n*BA), 0.62 (*i*BA), and 0.65 (*i*AA), thus indicating a fractional-order dependence on [amine].

Effect of HCl

At constant $[BAT]_0$, $[amine]_0$, and temperature, the rate of the reaction decreased with increase in $[HCl]_0$ (Table II). The plots of log k' vs. log $[HCl]_0$ were linear, with negative fractional slopes indicating an inverse fractional-order of approximately -0.5 in [acid].

Effects of Halide Ions, $TsNH_2$, and Ionic Strength

The addition of Cl^- or Br^- ions in the form of NaCl or NaBr at constant $[H^+]$ and ionic strength did not affect the rate. Hence the dependence of the rate on [HCl] reflected the effect of $[H^+]$ only on the reaction. The variation of ionic strength of the medium using $NaClO_4$ (0.12–0.30 M overall) had no effect on the

Table II Effect of Varying [HCl] on the Reaction Rate. $[BAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}; $[amine]_0 = 5.00 \times 10^{-2}$ mol dm^{-3}; $\mu = 0.30$ mol dm^{-3}; temp = 30°C.

$10^2[HCl]_0$ (mol dm^{-3})	$k' \times 10^5$ (s^{-1})			
	*n*PA	*n*BA	*i*BA	*i*AA
1.00	13.00	13.30	13.70	14.00
3.00	9.00	9.30	9.70	10.50
5.00	7.05	7.58	8.12	8.38
8.00	5.60	6.10	6.65	6.90
10.00	4.82	5.26	5.90	6.14

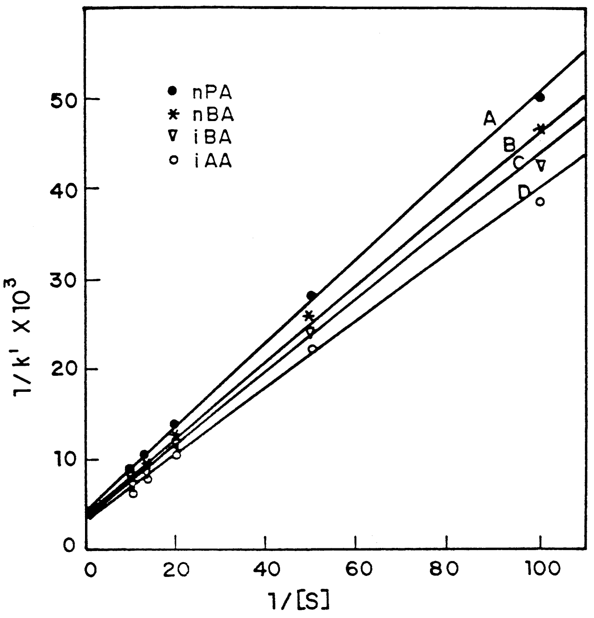


Figure 1 Plots of $1/k'$ vs. $1/[S]$: (A) *n*PA, (B) *n*BA, (C) *i*BA, and (D) *i*AA. $[BAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}; $[HCl] = 5.00 \times 10^{-3}$ mol dm^{-3}; $\mu = 0.30$ mol dm^{-3}; temp = 30°C.

rate. The addition of *p*-toluenesulfonamide or $TsNH_2$ ($2.0 \times 10^{-4} - 1.0 \times 10^{-3}$ M) had no effect on the rate, indicating that it is not involved in a preequilibrium to the rate-determining step.

Effect of Temperature on the Rate

The reaction was studied by varying $[amine]_0$ at each temperature, in the range of 298 K to 313 K. From the linear plots of $1/k'$ vs. $1/[S]$ (Fig. 1) at each temperature, the rate constants k_3 for the rate-determining step of the reaction were obtained from the values of intercept. The activation parameters, namely energy of activation (E_a), enthalpy of activation ($\Delta H^{\neq}$), and entropy of activation ($\Delta S^{\neq}$), were obtained from the Arrhenius and Eyring plots of $\ln k_3$ vs. $1/T$ and $\ln k_3/T$ vs. $1/T$, respectively. The kinetic and activation parameters obtained are presented in Table III.

Test for Free Radicals

The addition of the reaction mixtures to aqueous acrylamide monomer solutions, in the dark, did not initiate polymerization, indicating the absence of *in situ* formation of free-radical species in the reaction sequence. The control experiments were also performed under the same reaction conditions.

DISCUSSION AND MECHANISM

Pryde and Soper [19], Morries et al. [20], and Bishop and Jennings [21] have shown the existence of similar equilibria in acid and alkaline solutions of *N*-metallo-*N*- haloarylsulfonamides. Bromamine-T (TsNBrNa or *p*-$CH_3C_6H_4SO_2NBrNa$), like its chlorine analog chloramine-T, behaves as a strong electrolyte in aqueous solutions, forming different species as shown in Eqs. (2)–(6):

$$TsNBrNa \rightleftharpoons TsNBr^- + Na^+ \qquad (2)$$

$$TsNBr^- + H^+ \rightleftharpoons TsNHBr \qquad (3)$$

$$TsNHBr + H_2O \rightleftharpoons TsNH_2 + HOBr \qquad (4)$$

$$2TsNHBr \overset{K_d'}{\rightleftharpoons} TsNH_2 + TsNBr_2 \qquad (5)$$

$$HOBr + H^+ \rightleftharpoons H_2OBr^+ \qquad (6)$$

In acid medium, the probable oxidizing species are the free acid (TsNHBr), dibromamine-T ($TsNBr_2$), HOBr, and H_2OBr^+. The involvement of $TsNBr_2$ in the mechanism leads to a second-order rate law according to Eq. (5), which is contrary to the experimental observations. As Eq. (4) indicates a slow hydrolysis, if HOBr were the primary oxidizing species, a first-order retardation of the rate by the added $TsNH_2$ would be expected, contrary to the observed results. Hardy and Johnston [22], who have studied the pH-dependent relative concentrations of the species present in acidified haloamines' solutions of compa-

Table III Temperature Dependence of k_3 and Activation Parameters.

	$k_3 \times 10^4$ (s^{-1})				$\Delta H^{\neq}$	$\Delta S^{\neq}$	E_a
Substrate	298 K	303 K	308 K	313 K	(kJ/mol)	(J/K mol)	(kJ/mol)
*n*PA	1.56	2.42	3.55	5.25	59.5	−118	62.1
*n*BA	1.69	2.48	3.70	5.37	57.2	−125	59.7
*i*BA	1.85	2.55	3.85	5.52	54.6	−134	57.2
*i*AA	1.95	2.62	3.92	5.65	52.7	−139	55.3

rable molarities, have shown that TsNHBr is the likely oxidizing species in acid medium. Narayanan and Rao [23] and Subhashini et al. [24] have reported that monohalomines can be further protonated at pH < 2, as shown in the following Eqs. (7) and (8) for chloramine-T (CAT) and chlorarnine-B (CAB), respectively:

$$\underset{\text{(CAT)}}{p\text{-}\mathrm{CH_3C_6H_4SO_2NHCl}} + \mathrm{H^+} \rightleftharpoons p\text{-}\mathrm{CH_3C_6H_4SO_2\overset{+}{N}H_2Cl} \tag{7}$$

$$\underset{\text{(CAB)}}{\mathrm{C_6H_5SO_2NHCl}} + \mathrm{H^+} \rightleftharpoons \mathrm{C_6H_5SO_2\overset{+}{N}H_2Cl} \tag{8}$$

The second protonation constants for CAT and CAB are 102 and 61 ± 5, respectively, at 25°C. Gupta [25] believes that the values could be lower than those reported by the above workers [23,24]. In the present case, the inverse fractional order in $[\mathrm{H^+}]$ suggests that the deprontonation of $\mathrm{Ts\overset{+}{N}H_2Br}$ results in the regeneration of TsNHBr, which is likely to be the active oxidizing species involved in the mechanism of the amine oxidation. Based on the preceding discussion, a mechanism (Scheme I) is proposed for the reaction.

$$\mathrm{Ts\overset{+}{N}H_2Br} \underset{\text{(fast)}}{\overset{K_1}{\rightleftharpoons}} \mathrm{TsNHBr} + \mathrm{H^+} \tag{i}$$

$$\mathrm{TsNHBr} + \mathrm{S} \underset{\text{(fast)}}{\overset{K_2}{\rightleftharpoons}} \underset{\text{(complex)}}{\mathrm{X}} \tag{ii}$$

$$\mathrm{X} \underset{\text{(slow)}}{\xrightarrow{k_3}} \underset{\text{(complex)}}{\mathrm{X'}} + \mathrm{TsNH_2} \tag{iii}$$

$$\mathrm{X'} + \mathrm{H_2O} \underset{\text{(fast)}}{\longrightarrow} \underset{\text{(complex)}}{\mathrm{X''}} + \mathrm{H_3O^+} + \mathrm{Br^-} \tag{iv}$$

$$\mathrm{X''} + \mathrm{H_2O} \underset{\text{(fast)}}{\longrightarrow} \longrightarrow \underset{\text{(fast)}}{\longrightarrow} \text{products} \tag{v}$$

Scheme I

In Scheme I, S represents the amine substrate, *n*PA or *n*BA or *i*BA or *i*AA, and X, X′, and X″ represent the complex intermediates, which are defined in Scheme II.

A detailed mechanistic interpretation of the amine-BAT reaction in hydrochloric acid medium is presented in Scheme II. An initial equilibrium involves deprotonation of $\mathrm{TsNH_2Br^+}$, forming the active oxidizing species of BAT, TsNHBr (step i in Scheme I, not shown in Scheme II). In the next fast preequilibrium, an electrophilic attack of the positive bromine species ($\mathrm{Br^+}$) of the oxidant at the nitrogen atom of the substrate amine leads to the formation of an *N*-bromo species, X′, and the reduction product $\mathrm{TsNH_2}$ (steps i and ii of Scheme II). In step iii, a nucleophilic attack by $\mathrm{H_2O}$ on the α-C$^{\partial+}$ atom of the C—N bond of the neutral species, X′, and intramolecular rearrangements result in the formation of an imine intermediate, X″, along with the elimination of $\mathrm{H_3O^+}$ and $\mathrm{Br^-}$. In step iv, the electrophilic α-C center of the imine intermediate undergoes a fast nucleophilic attack by $\mathrm{H_2O}$ followed by intramolecular rearrangements, forming an α-hydroxyamine intermediate. This step is consistent with the observed negative reaction constant ρ^* (-0.06 and -12.6), suggesting a positive charge development in the intermediate. This unstable α-hydroxyamine in the presence of acid disproportionates into the products aldehyde and ammonia, where the latter forms an ammonium ion (step v).

From Scheme I,

$$\text{rate} = -d[\mathrm{BAT}]_t/dt = k_3[\mathrm{X}] \tag{9}$$

Then

$$[\mathrm{TsNHBr}] = \frac{[\mathrm{X}]}{K_2[\mathrm{S}]} \tag{10}$$

$$[\mathrm{TsNH_2Br^+}] = \frac{[\mathrm{TsNHBr}]\,[\mathrm{H^+}]}{K_1} \tag{11}$$

$$[\mathrm{TsNH_2Br^+}] = \frac{[\mathrm{X}]\,[\mathrm{H^+}]}{K_1K_2\,[\mathrm{S}]} \tag{12}$$

The total effective concentration of BAT, from Scheme I, is given by Eq. (13):

$$[\mathrm{BAT}]_t = [\mathrm{TsNH_2Br^+}] + [\mathrm{TsNHBr}] + [\mathrm{X}] \tag{13}$$

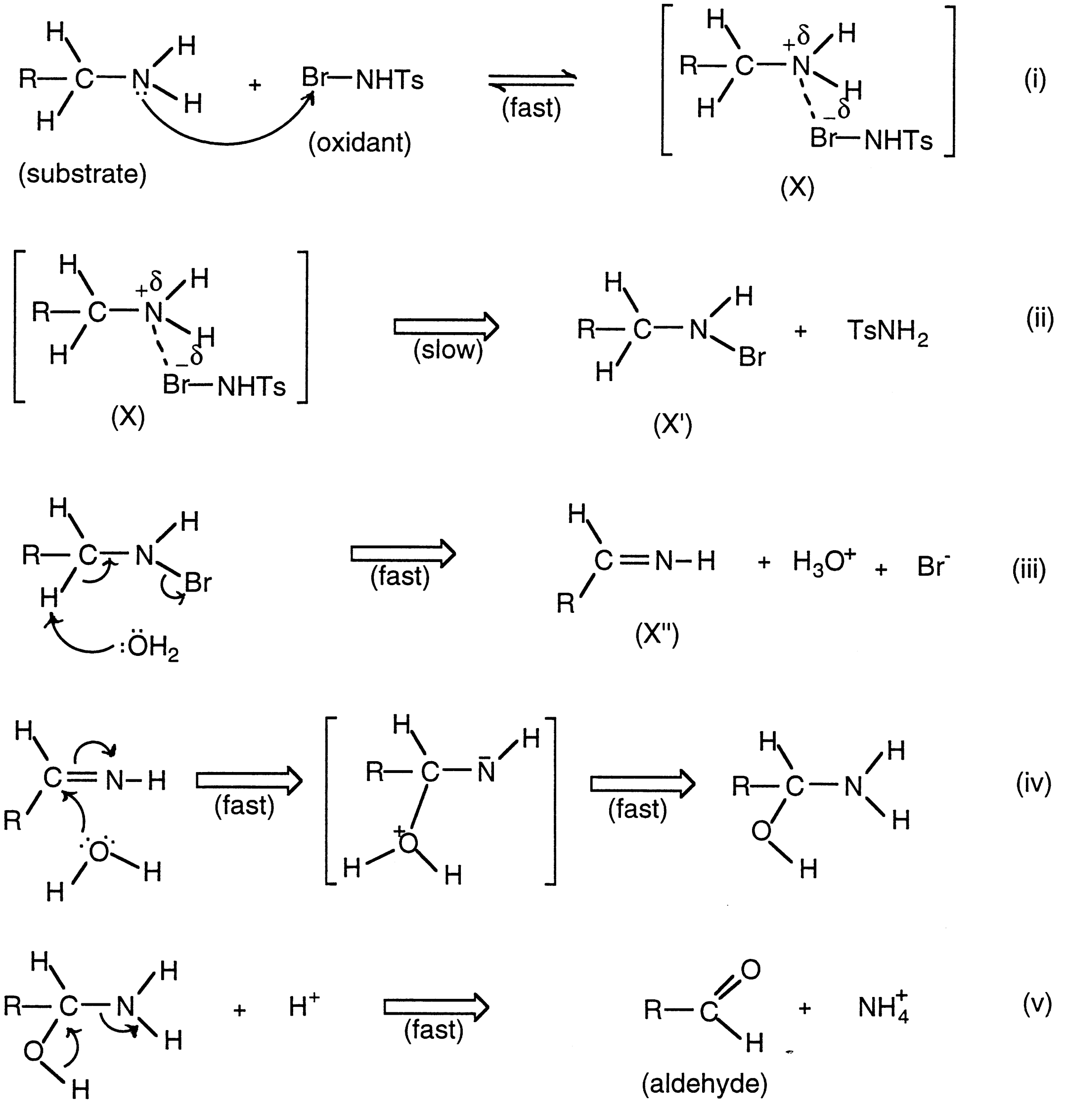
By substituting for [TsNHBr] from Eq. (10) and for $[\mathrm{TsNH_2Br^+}]$ from Eq. (12) into Eq. (13) and solving for [X], one gets

$$[\mathrm{X}] = \frac{K_1K_2\,[\mathrm{BAT}]_t[\mathrm{S}]}{[\mathrm{H^+}] + K_1 + K_1K_2\,[\mathrm{S}]} \tag{14}$$

The substitution for [X] in Eq. (9) leads to the following rate law [Eq. (15)]:

$$\text{rate} = -d[\mathrm{BAT}]_t/dt = \frac{K_1K_2k_3\,[\mathrm{BAT}]_t[\mathrm{S}]}{K_1 + [\mathrm{H^+}] + K_1K_2\,[\mathrm{S}]} \tag{15}$$

The rate law is consistent with the experimental data, including a first-order dependence of the rate on



Here, Ts = p-CH_3-$C_6H_4SO_2$- and R = CH_3CH_2- for *n*PA, $CH_3CH_2CH_2$- for *n*BA, $(CH_3)_2CH$- for *i*BA, and $(CH_3)_2CHCH_2$- for *i*AA, as in Eq. (1).

Scheme II

[BAT], fractional-order dependence on [S or amine], and a negative fractional-order dependence on [acid].

Since the rate = k' $[\text{BAT}]_t$, under pseudo-first-order conditions of $[\text{amine}]_0 \gg [\text{BAT}]_0$, the rate equation (15) can be transformed into Eqs. (16)–(19).

$$k' = \frac{K_1K_2k_3\,[\text{S}]}{K_1 + [\text{H}^+] + K_1K_2\,[\text{S}]} \tag{16}$$

or

$$\frac{1}{k'} = \frac{1}{K_2k_3\,[\text{S}]} + \frac{[\text{H}^+]}{K_1K_2k_3\,[\text{S}]} + \frac{1}{k_3} \tag{17}$$

or

$$\frac{1}{k'} = \frac{1}{K_2k_3\,[\text{S}]}\left\{\frac{K_1 + [\text{H}^+]}{K_1}\right\} + \frac{1}{k_3} \tag{18}$$

or

$$\frac{1}{k'} = \frac{[\text{H}^+]}{K_1K_2k_3\,[\text{S}]} + \left\{\frac{1}{K_2k_3\,[\text{S}]} + \frac{1}{k_3}\right\} \tag{19}$$

Based on Eq. (18), a plot of $1/k'$ vs. $1/[\text{S}]$ (Fig. 1) at constant $[\text{H}^+]$, $[\text{BAT}]_0$, and temperature was found to

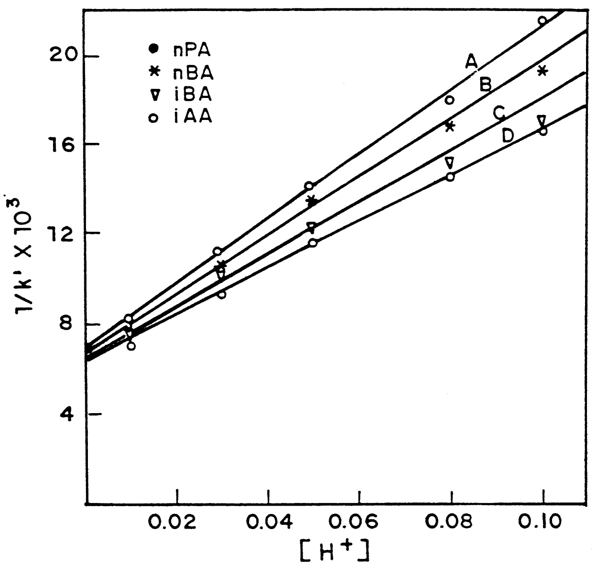


Figure 2 Plots of $1/k'$ vs. $[H^+]$: (A) *n*PA, (B) *n*BA, (C) *i*BA, and (D) *i*AA. $[BAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}; [S or amine] $= 5.00 \times 10^{-2}$ mol dm^{-3}; $\mu = 0.30$ mol dm^{-3}; temp = 30°C.

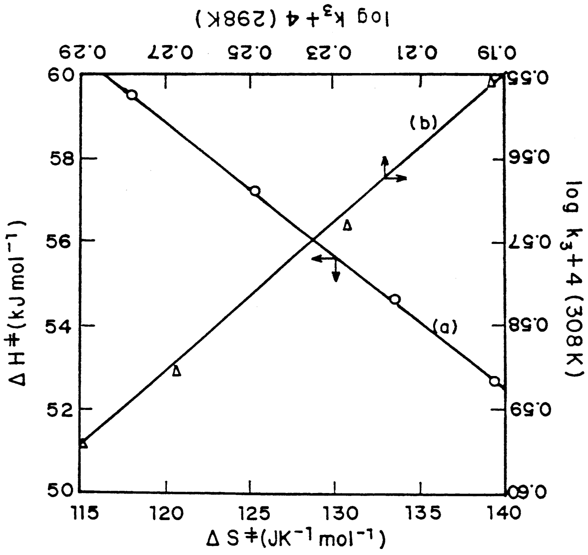


Figure 3 (a) A plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ and (b) an Exner plot of log k_3 (308 K) vs. log k_3 (298 K).

be linear ($r > 0.9989$) for each amine. Similarly, from Eq. (19), a plot of $1/k'$ vs. $[H^+]$ (Fig. 2) at constant [S] or $[\text{amine}]_0$, $[BAT]_0$, and temperature was linear for each amine. The values of K_1, K_2, and k_3 were calculated from the slopes and intercepts of the plots. The protonation constant, $Kp = 1/K_1$, of TsNHBr can be evaluated from Eqs. (18) and (19); the data of K_1, K_2, k_3, and Kp are presented in Table IV. The constancy of Kp or K_1 values forms strong indirect evidence for the existence of the reactive species $TsNH_2Br^+$ of the oxidant, supporting the proposed mechanism of oxidation of amines by BAT (Scheme I).

The existence of a linear free-energy relationship for the oxidation of primary amines by BAT has been evaluated [26]. Tests of the complete Taft equation as well as single-parameter correlations with polar substitution constant σ^* and steric substitution constant E_s were made by plotting log $(k_3 - E_s)$ vs. σ^*, log k_3 vs. σ^*, and log k_3 vs. E_s. The following regression equations were found:

$$\log(k_3 - E_s) = -12.6\sigma^* - 5.2 \quad (r = 0.8987) \quad (20)$$

$$\log k_3 = -1.8\sigma^* - 3.6 \quad (r = 0.8567) \quad (21)$$

$$\log k_3 = -0.06E_s - 3.6 \quad (r = 0.9976) \quad (22)$$

A good correlation of log k_3 with E_s in Eq. (22) implies that steric effects play a dominant role in determining the reaction rate. The implication of the electronic effects on the rate is not clear from Eq. (21). However, a reasonable correlation in Eq. (20) shows that both steric and electronic factors have a synergistic effect in determining the rate. The negative values of the reaction constant ρ^* (−0.06 and −12.6) suggest that the presence of electron-donating groups in the amine substrate increases the reaction rate.

The data in Tables I and II show that the rate of

Table IV The Equilibrium and Protonation Constants Calculated from Eqs. (18) and (19).

Substrate or S	$k_3 \times 10^4$ (s^{-1})	K_2 (dm^3/mol)	$10^2 \times K_1$ (mol/dm^3) a	b	$1/K_1 = Kp$ (dm^3/mol) a	b
*n*PA	2.42	32.0	2.07	2.04	48.3	49.0
*n*BA	2.48	31.6	2.12	2.11	47.2	47.4
*i*BA	2.55	31.2	2.13	2.12	47.0	47.2
*i*AA	2.62	30.8	2.14	2.12	46.7	47.2

[a] The values of K_1 and Kp calculated from the plot of $1/k'$ vs. $1/[S]$.

[b] The values of K_1 and Kp calculated from the plot of $1/k'$ vs. $[H^+]$.

oxidation of the amines by BAT increases in the order *n*PA < *n*BA < *i*BA < *i*AA, indicating a combined effect of the electronic and steric factors of the alkyl groups in amines.

The relative magnitudes of activation energies for the oxidation of the amines, in Table III, which support the preceding trend, indicate that the reactions are enthalpy controlled. This is verified by calculating the isokinetic temperature (β) from the slope of a linear plot of $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ (Fig. 3, $r = 0.9999$). The β value of 350 K, which is higher than the experimental range used in the present study, implies that the substrate oxidation is enthalpy controlled. A further confirmation of the existence of the isokinetic relationship was inferred from the Exner criterion [27], by plotting log k_3 (308 K) vs. log k_3 (298 K), which yielded a linear plot ($r = 0.9973$). The Exner slope gave a value of β 347 K. The fairly negative values of $\Delta S^{\neq}$ indicate the formation of a rigid associative transition state in each case.

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