# Oxidation of Some Primary Amines by Bromamine-B in Alkaline Medium: A Kinetic and Mechanistic Study

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## ABSTRACT

The kinetics of oxidation of the aliphatic primary amines, *n*-propylamine, *n*-butylamine, and isoamylamine, by sodium N-bromobenzenesulfonamide or bromamine-B (BAB) in sodium hydroxide medium has been studied at 35° C. The reaction rate shows a first-order dependence each on [BAB] and [amine], and fractional order on  $|OH^-|$ . Additions of halide ions and the reduction product of BAB (benzenesulfonamide), and variation of ionic strength and dielectric constant of the medium do not have any significant effect on the reaction rate. Activation parameters have been evaluated. A Taft linear free-energy relationship is observed for the reaction with  $\rho^* = -3.0$  and  $\delta = -2.0$  indicating that electron-donating groups enhance the rate. An isokinetic relationship is observed with  $\beta = 393$  K indicating that enthalpy factors control the rate. The existence of the relationship has been supported by the Exner criterion. Mechanisms consistent with the observed kinetic data have been proposed. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

A literature survey shows that the kinetic studies of reactions of some aromatic amines and their derivatives with chloramine-T (CAT) have been reported by Ramaiah and Rao [1] and Radhakrishnamurthi and Rao [2]. These studies show that the aromatic amine

Received January 12, 1996; accepted April 6, 1996 \* Authors to whom correspondence should be addressed. International Journal of Chemical Kinetics, Vol. 28, 873–878 (1996) oxidations are independent of the variation in  $[OH^-]$ . Gupta and Agrawal [3] have shown that the kinetics of S-butylamine oxidation by CAT involves a retarding influence of alkali. To our knowledge, there is no information available on the oxidation of aliphatic amines by bromamines. The present studies were undertaken to investigate the kinetic and mechanistic aspects of the oxidation of three aliphatic primary amines, *n*-propylamine (*n*PA), *n*-butylamine (*n*BA), and isopentylamine or isoamylamine (iAA), by bromamine-B (PhSO<sub>2</sub>NBrNa 1.5 H<sub>2</sub>O or BAB) in NaOH medium.

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#### EXPERIMENTAL

The oxidant, BAB, was prepared and purified using the methods reported elsewhere [4,5]. Its purity was checked iodometrically and through IR and <sup>13</sup>C NMR spectral data [4]. Aqueous solutions of BAB were prepared, standardized by the iodometric method, and preserved in amber colored bottles. Aqueous solutions of *n*-propylamine (E. Merck), *n*-butylamine (E. Merck), and isoamylamine (Fluka) were prepared. All other chemicals used were of analytical grade. Triply distilled water was used for preparing aqueous solutions.

#### **Kinetic Measurement**

The reaction was carried out in stoppered pyrex glass tubes whose outer surfaces were coated black to eliminate photochemical effects. Requisite amounts of the amine substrate, NaClO<sub>4</sub>, and NaOH solutions, and water (to maintain a constant total volume for all runs) were taken in the tubes and thermally equilibrated in a water bath set at a given temperature (e.g.,  $35 \pm 0.1^{\circ}$ C). To this solution, was added a measured amount of BAB solution, also preequilibrated at the same temperature, to initiate the reaction. The reaction mixture was 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. The pseudo-first-order rate constants, k', calculated were reproducible within  $\pm 3\%$ . Regression analysis of the experimental data was carried out on an EC-75 Statistical Calculator to obtain the regression coefficient 'r'.

## **Stoichiometry and Product Analysis**

Reaction mixtures containing [amine]  $\gg$  [BAB] and  $5 \times 10^{-3}$  mol dm<sup>-3</sup> NaOH were equilibrated with occasional shaking at 35°C for 24 h. The iodometric determination of unreacted BAB in the reaction mixture showed that one mole of BAB was consumed per mole of the amine substrate according to eq. (1).

$$R-CH_2NH_2 + PhSO_2NBrNa + H_2O \longrightarrow R-CHO + PhSO_2NH_2 + NH_3 + Na^+ + Br^- (1)$$

where  $\mathbf{R} = \mathbf{CH}_{3}\mathbf{CH}_{2^{-}}$  for *n*-propylamine (*n*PA),  $\mathbf{CH}_{3}\mathbf{CH}_{2}\mathbf{CH}_{2^{-}}$  for *n*-butylamine (*n*BA), and  $(\mathbf{CH}_{3})_{2}\mathbf{CH}\mathbf{CH}_{2^{-}}$  for isoamylamine (iAA).

The presence of the aldehydes, which are oxidation products of the amines, in the reaction mixtures was detected by preparing their 2,4-dinitrophenylhydrazone derivatives and by using Tollens' and chromic acid tests [6]. The other product, ammonia, was quantitatively estimated by the standard micro-Kjeldahl procedure. The reduction product of BAB, PhSO<sub>2</sub>NH<sub>2</sub>, was identified by TLC using petroleum ether-chloroform-1-butanol (2:2:1 V/V) solvent system with ascending irrigation and using iodine as the developing reagent ( $R_f = 0.88$ ) [7].

### RESULTS

Under pseudo-first-order conditions of  $[amine]_0 \gg [BAB]_0$  in the presence of a known [NaOH], plots of log [BAB] vs. time were linear (r > 0.9978) indicating a first-order dependence of the reaction rate on [BAB] (plots not shown). The pseudo-first-order rate constants, k', obtained at 35°C are listed in Table I.

**Table I** Effect of Varying Reactant Concentrations on the Rate  $[NaOH] = 5.0 \times 10^{-3} \text{ mol} dm^{-3}$ ;  $\mu = 0.40 \text{ mol} dm^{-3}$ ; and Temp. =  $35 \pm 0.1^{\circ}$ C

		$k' \times 10^4 ({\rm s}^{-1})$			
$[BAB]_0 \times 10^4$ (mol dm <sup>-3</sup> )	$\begin{array}{c} \left[\text{Amine}\right]_0 \times 10^2\\ \text{(mol dm}^{-3}) \end{array}$	<i>n</i> -propyl- amine	<i>n</i> -butyl- amine	isoamyl- amine	
6.0	7.5	1.13	4.16	7.29	
7.0	7.5	1.12	4.14	7.24	
8.0	7.5	1.12	4.12	7.21	
9.0	7.5	1.12	4.11	7.21	
10.0	7.5	1.11	4.11	7.19	
11.0	7.5	1.10	4.10	7.17	
9.0	2.5	0.38	1.30	2.35	
9.0	5.0	0.72	2.70	4.84	
9.0	7.5	1.12	4.11	7.21	
9.0	12.5	2.12	6.90	11.98	
9.0	22.0	3.51	10.71	21.38	
9.0	30.0	4.82	14.92	_	
9.0	40.0	6.23	-	-	

$[NaOH] \times 10^{3}$ (mol dm <sup>-3</sup> )		$k' \times 10^4  (s^{-1})$	
	n-propylamine	n-butylamine	isoamylamine
2.0	0.73	2.80	
3.0	_		5.21
4.0	_	_	6.38
5.0	1.12	4.11	7.21
6.0	_		8.18
10.0	1.58	5.36	_
15.0	1.93	6.92	_
20.0	2.23	8.43	-
30.0	3.28	10.20	-

**Table II** Effect of Varying Hydroxide Concentration on the Rate  $|BAB|_0 = 9.0 \times 10^{-4} \text{ mol} \text{ dm}^{-3}$ ;  $|Amine|_0 = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $\mu = 0.40 \text{ mol dm}^{-3}$ ; and Temp =  $35 \pm 0.1^{\circ}\text{C}$ 

Under the same experimental conditions, an increase in [amine] increased the k' values. Plots of log k' vs. log [amine] were linear (r > 0.9978) with unit slopes, showing a first-order dependence of the rate on [substrate] (Table I) (plots not shown). At constant [BAB]<sub>0</sub>, [substrate]<sub>0</sub>, and temperature, the rate increased with increase in [NaOH] yielding linear plots of log k' vs. log [NaOH] (r > 0.9986) (plots not shown). These plots with slopes less than unity show positive fractional orders in [NaOH] (Table II). Addition of Cl<sup>-</sup> or Br<sup>-</sup> ions in the form of NaCl or NaBr at fixed [OH<sup>-</sup>] and ionic strength did not affect the rate (results not shown). Addition of the reduction product, benzenesulfonamide or PhSO<sub>2</sub>NH<sub>2</sub> (2 ×  $10^{-4}$ -8 × 10<sup>-4</sup> mol dm<sup>-3</sup>), or the variation of ionic strength of the medium  $(0.09-0.40 \text{ mol } \text{dm}^{-3})$  had no effect on the reaction rate. The variation of the solvent composition using MeOH (0-15%) did not affect the rate (see k' values in Table I).

The reaction was studied at varying temperatures, 298 K to 313 K. The activation parameters, namely energy of activation  $(E_a)$ , enthalpy of activation  $(\Delta H\neq)$ , entropy of activation  $(\Delta S\neq)$ , and free energy of activation  $(\Delta G\neq)$ , were obtained from the Arrhenius plots of log k' vs. (1/T) and the Eyring plots of log (k'/T) vs. (1/T) which were linear (plots not shown). The kinetic and activation parameters obtained are presented in Table III. Additions of the reaction mixtures to aqueous acrylamide monomer solutions, in the dark, did not initiate polymerization indicating the absence of the in situ formation of free radical species in the reaction sequence (proper control experiments were also run simultaneously).

#### MECHANISMS AND DISCUSSION

Pryde and Soper [8], Morris et al. [9], and Bishop and Jennings [10] have shown the existence of similar equilibria in acid and alkaline solutions of *N*-metallo-*N*-haloarylsulfonamides. Bromamine-B (PhSO<sub>2</sub>NBrNa 1.5 H<sub>2</sub>O) which is similar to its chlorine analogues, such as chloramine-T, behaves as a strong electrolyte in aqueous solutions forming different species as in eqs. (2-6).

$$PhSO_{3}NBrNa \Longrightarrow PhSO_{3}NBr^{-} + Na^{-}$$
(2)

$$PhSO_2NBr^- + H^+ \Longrightarrow PhSO_2NHBr$$
 (3)

 $PhSO_2NHBr + H_2O \Longrightarrow PhSO_2NH_2 + HOBr$  (4)

2 PhSO<sub>2</sub>NHBr 
$$\stackrel{K'_{d}}{\longleftarrow}$$
 PhSO<sub>2</sub>NH<sub>2</sub> + PhSO<sub>2</sub>NBr<sub>2</sub>  
( $K'_{d} = 1.13 \times 10^{-2} \text{ at } 25^{\circ}\text{C}$ ) (5)

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

**Table III** Temperature Dependence and Activation Parameters for the Oxidation of Primary Amines by BAB in Alkaline Medium  $[BAB]_0 = 9.0 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[Amine]_0 = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[NaOH] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ; and  $\mu = 0.40 \text{ mol dm}^{-3}$ 

	$k' \times 10^4/\mathrm{s}^{-1}$			ΛH≠	۸۶≠	٨G≠	F	
Substrate	298 K	303 K	308 K	313 K	$(kJ mol^{-1})$	$(JK^{-1} mol^{-1})$	$(kJ mol^{-1})$	$(kJ mol^{-1})$
<i>n</i> -propylamine	0.44	0.70	1.12	1.81	70.5	-87.9	98.5	73.1
n-butylamine	1.69	2.58	4.11	6.03	63.9	-102.8	95.3	66.5
isoamylamine	3.38	4.94	7.21	10.18	54.6	-128.1	93.9	57.2

In acidic medium, the probable oxidizing species are the free acid (PhSO<sub>2</sub>NHBr), dibromamine-B  $(PhSO_2NBr_2)$ , HOBr or  $H_2OBr^+$ . In alkaline medium, in which PhSO<sub>2</sub>NBr<sub>2</sub> and H<sub>2</sub>OBr<sup>+</sup> do not exist, the expected reactive species are PhSO<sub>2</sub>NHBr, HOBr, and PhSO<sub>2</sub>NBr<sup>-</sup>. Hardy and Johnston [11] have reported the following equilibria in alkaline solutions of BAB:

$$PhSO_2NBr^{-} + H_2O \Longrightarrow PhSO_2NHBr + OH^{-} (7)$$

$$PhSO_2NHBr + H_2O \xleftarrow{K_h} PhSO_2NH_2 + HOBr (K'_h = 4.21 \times 10^{-3} \text{ at } 25^{\circ}C) (8)$$

As eq. (8) indicates a slow hydrolysis, if HOBr were the primary oxidizing species, a first-order retardation of the rate by the added PhSO<sub>2</sub>NH, would be expected, which is contrary to the experimental observations. If PhSO<sub>2</sub>NHBr were the reactive species, a retardation of the rate by [OH<sup>-</sup>] would be expected (eq. (7)), which is also contrary to the experimental observations. It is, therefore, likely that the anion, PhSO<sub>2</sub>NBr<sup>-</sup>, itself acts as the reactive species responsible for the oxidation of amines. Based on the preceding discussion of the experimental data, the following mechanism (Scheme I) is proposed for the reaction:

$$PhSO_2NHBr + OH^{-} \xrightarrow{k_1} PhSO_2NBr^{-} + H_2O \quad fast \quad (i)$$

$$PhSO_2NBr^{-} + S \xrightarrow{k_2} X' + PhSO_2NH^{-} \quad slow \quad (ii)$$

slow (ii)

$$X' + H_2O \rightarrow products fast$$
 (iii)  
Scheme I

where S is the amine substrate, nPA or nBA or iAA and X' is an intermediate species, for each amine, whose structure is shown in Scheme III.

The total effective concentration of BAB, from Scheme I, is as in eq. (9)

$$[BAB]_{t} = [PhSO_{2}NHBr] + [PhSO_{2}NBr^{-}] \quad (9)$$

This equation leads to the following rate law:

$$-d[BAB]_{t}/dt = \frac{K_{1}k_{2}[BAB]_{t}[S][OH^{-}]}{K_{1}[OH^{-}] + [H_{2}O]}$$
(10)

This rate law (eq. (10)) is in agreement with the experimental data including a first-order each in [BAB] and [amine], and a fractional order in [OH<sup>-</sup>].

Since rate =  $k_{obs}[BAB]$ , eq. (10) can be transformed into the following forms:

$$\frac{1}{k_{\rm obs}} = \frac{K_1[\rm OH^-] + [\rm H_2O]}{K_1k_2[\rm S][\rm OH^-]}$$
(11)

OT

$$\frac{1}{k_{\rm obs}} = \frac{[\rm H_2O]}{K_1 k_2 [\rm S][\rm OH^-]} + \frac{1}{k_2 [\rm S]}$$
(12)

The double reciprocal plots of  $1/k_{obs}$  vs.  $1/[OH^-]$  at constant [S], from eq. (12), were found to be linear (r > 0.9993). The values of  $K_1$  and  $k_2$  were calculated from the slope and intercept, respectively, of the plots for the standard runs with  $[BAB]_0 = 9.0 \times 10^{-4} \text{ mol}$  $dm^{-3}$  and [S or amine]<sub>0</sub> = 7.5 × 10<sup>-2</sup> mol dm<sup>-3</sup> at 308 K (Table IV). The constancy of  $K_1$  values and the near constancy of  $k_2$  values form a strong support for the proposed mechanism of the amine oxidation by BAB (Scheme I).

The fractional order dependence of the rate on  $[OH^-]$  shows that rate =  $k_0 + k_{OH^-}[OH^-]$  indicating an alkali-dependent pathway (Scheme I) and an alkali-independent pathway as in Scheme II, the latter pathway involving a direct interaction between the acid form of BAB, PhSO<sub>2</sub>NHBr, and the amine.

$$PhSO_2NHBr + S \xrightarrow{k_1^{\prime}} X'' slow$$
 (iv)

$$X'' + H_2O \xrightarrow{k'_2}$$
 products fast (v)  
Scheme II

where S represents the amine substrates as in Scheme I and X" represents an intermediate complex species, for each amine, whose anion structure is shown as X in Scheme III.

The magnitudes of  $k_0$  and  $k_{OH^-}$  were computed from the linear plots of k' vs.  $[OH^-]: k_0 = 5.9 \times$  $10^{-5} \text{ s}^{-1} \text{ and } k_{\text{OH}^-} = 8.84 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for}$   $n\text{PA}; k_0 = 2.68 \times 10^{-4} \text{ s}^{-1} \text{ and } k_{\text{OH}^-} = 2.64 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for } n\text{BA}; \text{ and } k_0 = 2.83 \times 10^{-4} \text{ s}^{-1} \text{ and} k_{\text{OH}^-} = 8.54 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for iAA}.$ The blank experiments performed with the amines and BAB in the absence of NaOH yielded the rate

Table IV Equilibrium and Rate Constant Data from Eq. (12)<sup>a</sup>

Substrate	$K_1 \times 10^{-4}$	$k_2 \times 10^3 (\mathrm{dm^3 \ mol^{-1} \ s^{-1}})$
<i>n</i> -propylamine	1.03	3.10
n-butylamine	0.980	13.6
isoamylamine	1.05	19.7

<sup>a</sup> Calculated from the plots of  $\frac{1}{k_{obs}}$  vs.  $\frac{1}{[OH^-]}$ .



Here  $R = CH_3CH_2$ - for nPA,  $CH_3CH_2CH_2$ - for nBA, and  $(CH_3)_2CHCH_2$ - for iAA, as in eq. (1).

Scheme III

constants for the alkali-independent pathway ( $k_0 = 6.1 \times 10^{-5} \text{ s}^{-1}$  for *n*PA; 2.61 × 10<sup>-4</sup> s<sup>-1</sup> for *n*BA; and 2.97 × 10<sup>-4</sup> s<sup>-1</sup> for iAA) which compare well with those obtained from the intercepts of above plots of k' vs. [OH<sup>-</sup>].

A detailed mechanistic interpretation of the amine oxidation by BAB in NaOH medium is presented in Scheme III. An electrophilic attack by the positive bromine of the oxidizing species,  $(PhSO_2NBr)^-$ , at the amino nitrogen atom of the substrate forms the complex species X (step i) which leads to the formation of the intermediate X' and  $PhSO_2NH^-$  (step ii). Step iii involves a nucleophilic attack on X' by H<sub>2</sub>O, followed by intramolecular rearrangement, forming an *N*-protonated amine and a bromide ion. In the next step, the *N*-protonated amine species interacts with the hydroxide ion and eliminates an ammonia molecule to form the aldehyde and water (step iv).

Attempts were made to arrive at a linear free energy relationship for the oxidation of primary amines by BAB [12]. Tests of the complete Taft equation as well as single parameter correlations with polar substitution constant  $\sigma^*$  and steric substitution constant  $E_s$  were made by plotting,  $(\log k' \cdot E_s)$  vs.  $\sigma^*$ ,  $\log k'$  vs.  $\sigma^*$ , and  $\log k'$  vs.  $E_s$ . The following regression equations were found:

$$(\log k' \cdot E_s) = -3.0 \ \sigma^* - 4.1 \ (r = 0.9998) \ (13)$$

$$\log k' = -7.1 \ \sigma^* - 4.46 \ (r = 0.8269) \ (14)$$

$$\log k' = -2.0 E_{\rm s} - 4.1 \quad (r = 0.9999) \quad (15)$$

A good correlation of log k' with  $E_s$  in eq. (15) implies that steric effects play a dominant role in determining the rate. The implication of the electronic effects on the rate is not clear from eq. (14). However, the good correlation in eq. (13) shows that both steric and electronic factors have a synergistic effect in determining the rate. The negative values of reaction constant  $\rho^*$  indicate that the presence of electrondonating groups in the substrate increases the reaction rate.

It is seen from the data in Tables I and II that the rate of oxidation of the amines by BAB increases in the order: nPA < nBA < iAA, indicating the combined effects of the inductive and steric factors of the alkyl groups in the amines.

The relative magnitudes of energies of activation for the oxidation of three amines, in Table III, which support the above trend, indicate that the reactions are enthalpy controlled. This is verified by calculating the isokinetic temperature ( $\beta$ ) from the slope of the plot of  $\Delta H^{\neq}$  vs.  $\Delta S^{\neq}$  (plot not shown, r = 0.9987). The  $\beta$ value of 393 K, which is higher than the experimental temperature range used in the present study, indicates that the substrate oxidation is enthalpy controlled. Similar kinetic results were observed in the osmium(VIII) catalyzed oxidation of indoles by aryl-N-haloamines in alkaline medium [13]. The further confirmation of the existence of isokinetic relationship was done by the Exner criterion [14] by plotting  $\log k'_{(313K)}$  vs.  $\log k'_{(298K)}$  which is linear (r = 0.9992). The Exner slope ( $\beta$ ) gave a value of 443 K. The fairly negative values of entropy of activation indicate the formation of a rigid transition state in each case. The near constancy of  $\Delta G^{\neq}$  values indicates that the three primary amines react with BAB via the same mechanism.

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