

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

S. Ananda¹, T. Demappa¹, and Puttaswamy²

¹Department of Studies in Chemistry
University of Mysore

Manasagangothri, Mysore 570 006, INDIA

²Department of Studies in Chemistry
Central College

Bangalore University, Bangalore 560 001, INDIA

and

N. M. Made Gowda*

Department of Chemistry
Western Illinois University
1 University Circle
Macomb, IL 61455, USA

*corresponding author

ABSTRACT

The kinetics of oxidation of the aliphatic primary amines, *n*-propylamine, *n*-butylamine, and *n*-hexylamine, by sodium *N*-bromo-*p*-toluenesulfonamide or bromamine-T (BAT) in sodium hydroxide medium has been studied at 308 K. The reaction rate shows a first-order dependence on [BAT] and fractional-order each on [amine] and [OH⁻]. Additions of halide ions and the reduction product of BAT (*p*-toluenesulfonamide) have no effect on the reaction rate. Also, the variation of ionic strength and dielectric constant of the medium does not have any significant effect on the reaction. Activation parameters have been evaluated. A Taft linear free-energy relationship is observed for the reaction with $\rho^* = -0.44$ and $\delta = -1.76$ indicating that electron-donating groups enhance the rate. An isokinetic relationship is observed with $\beta = 355$ K indicating that enthalpy factors control the rate. Mechanisms consistent with the observed kinetic data have been proposed. The average value of deprotonation constant of monobromamine-T forming TsNBr⁻ has been evaluated as $3.3 \pm 0.1 \times 10^3$ M at 308K.

INTRODUCTION

A literature search shows that the kinetic studies of reactions of some aromatic amines and their derivatives with chloramine-T (CAT) have been reported by Ramaiah¹ and

Rao². In these studies, the aromatic amine oxidation is independent of the variation in $[\text{OH}^-]$. Gupta and Agrawal³ have shown that the kinetics of *S*-butylamine reaction with CAT involves a retarding effect of alkali. To our knowledge, there is no study reported on the oxidation of aliphatic amines by bromamines. We report here our investigations of the kinetic and mechanistic aspects of the oxidation of three aliphatic primary amines, *n*-propylamine (*n*PA), *n*-butylamine (*n*BA), and *n*-hexylamine (*n*HA), by bromamine-T ($p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NbrNa}\cdot 3\text{H}_2\text{O}$ or BAT or TsNBrNa) in NaOH medium.

MATERIALS AND METHODS

Bromamine-T (BAT) was prepared by a standard procedure^{4,5} and its purity was checked by iodometry and by its mass spectrum, UV, IR, ^1H and ^{13}C NMR spectra. An aqueous solution of BAT was prepared, standardized, and preserved in brown bottles to prevent photochemical effects.

Analar grade *n*-propylamine (E.Merck), *n*-butylamine (E.Merck) and *n*-hexylamine (Fluka) were used and their solutions were prepared in water. All other chemicals used were of accepted grades of purity. Triply distilled water was used for preparing aqueous solutions. The ionic strength of the reaction mixture was kept at a high value using concentrated solution of NaClO_4 .

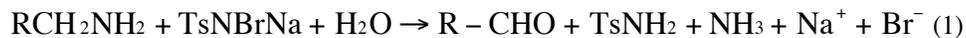
Kinetic Measurements

Mixtures containing requisite amounts of solutions of the amine, NaClO_4 , NaOH, and MeOH (10% v/v) were equilibrated at 308 K. To this mixture was added a measured amount of pre-equilibrated (308 K) standard solution of BAT. 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 calculated were reproducible within $\pm 3\%$.

A regression analysis of the experimental data was carried out on an EC-72 Statistical Calculator, to get the regression coefficient r .

Stoichiometry and Product Analysis

Reaction mixtures containing different compositions of the amine and BAT and 5.00×10^{-3} M NaOH were equilibrated with occasional shaking at 308 K for 24 hr. The iodometric determination of unreacted BAT in the reaction mixture showed that one mole of BAT was consumed per mole of the amine substrate as represented by equation (1).



where R = CH_3CH_2- for *n*-propylamine (*n*PA), $\text{CH}_3\text{CH}_2\text{CH}_2-$ for *n*-butylamine (*n*BA), and $\text{CH}_3(\text{CH}_2)_4-$ for *n*-hexylamine (*n*HA).

The reaction product, *p*-toluenesulfonamide (TsNH_2), was detected by paper chromatography⁴. Benzyl alcohol, saturated with water, was used as the solvent with 0.5% vanillin in 1% HCl in EtOH as spray reagent ($R_f = 0.905$). The presence of the aldehydes, which are the oxidation products of the amines, in the reaction mixtures was detected by preparing their 2,4-dinitrophenylhydrazone derivatives and by using Tollens' and chro-

mic acid tests⁶. The product ammonia was quantitatively determined by the standard micro-Kjeldahl procedure.

RESULTS

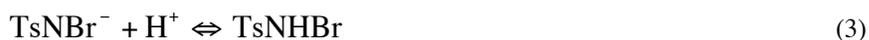
Under the condition of $[\text{amine}]_0 \gg [\text{BAT}]_0$, plots of $\log [\text{oxidant}]$ vs. time were linear ($r > 0.9983$) showing a first order dependence of the reaction rate on $[\text{oxidant}]$. The pseudo-first order rate constants, k' , are given in Table 1. Under the same experimental conditions, an increase in $[\text{amine}]_0$ increased the k' values. Plots of $\log k'$ vs. $\log [\text{amine}]_0$ were linear (Fig. 1; $r > 0.9978$) with slopes less than unity, showing fractional-order dependencies on $[\text{amine}]$ (Table 1). At constant $[\text{BAT}]_0$, $[\text{amine}]_0$, and temperature, the rate increased with increase in $[\text{NaOH}]$ yielding linear plots of $\log k'$ vs. $\log [\text{NaOH}]$ (Fig. 2; $r > 0.9987$). These plots with slopes less than unity show positive fractional-orders in NaOH (Table 2). Addition of Cl^- or Br^- ions in the form of NaCl or NaBr at fixed $[\text{OH}^-]$ and the variation of ionic strength did not affect the rate. Furthermore, the addition of the reduction product, TsNH_2 (2.0×10^{-4} - 8.0×10^{-4} M), and ionic strength of the medium (0.090 - 0.40 M) had no effect on the reaction rate. The variation of the solvent composition using MeOH (0-15% v/v) did not affect the rate.

The reaction was studied by varying the amine concentration at different temperatures, in the range of 298 K to 313 K. From the plots of $1/k'$ versus $1/[\text{amine}]_0$ and $1/k'$ vs. $1/[\text{OH}^-]$, the decomposition constant (k_3) of the amine-BAT complex was determined (Table 3). The activation parameters, namely energy of activation (E_a), enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger), and free energy of activation (ΔG^\ddagger) were obtained from the Arrhenius and Eyring plots. ($r > 0.9921$). The activation parameters obtained are presented in Table 4.

Additions 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.

DISCUSSION

Pryde and Sope⁸, Morris et al.⁹, and Bishop and Jennings¹⁰ have shown the existence of similar equilibria in acid and alkaline solutions of N-metallo-N-haloarylsulfonamides. Bromamine-T (TsNBrNa) which is similar to its chloramine analogues, such as chloramine-T, behaves as a strong electrolyte in aqueous solutions forming different species as in equations (2)-(6).





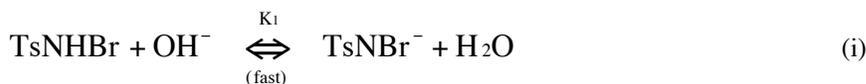
In acidic medium, the probable oxidizing species are TsNHBr, dibromamine-T (TsNBr₂), HOBr, and H₂OBr⁺. In alkaline medium, in which TsNBr₂ and H₂OBr⁺ do not exist, the expected reactive species are TsNHBr, HOBr and TsNBr⁻. Hardy and Johnston¹¹ have reported the following equilibria in alkaline solutions of bromamine-B (BAB):



(8)

Assuming the toluene derivative to be similar to the benzene analogue, equation (8) indicates a slow hydrolysis. If HOBr were the primary oxidizing species, a first-order retardation of the rate by the added *p*-toluenesulfonamide would be expected, which is contrary to the experimental observations. If TsNHBr were the reactive species, a retardation of the rate by [OH⁻] would be expected [equation. (7)], which is also contrary to the experimental observations. It is, therefore, likely that the anion, TsNBr⁻, 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:

Scheme I

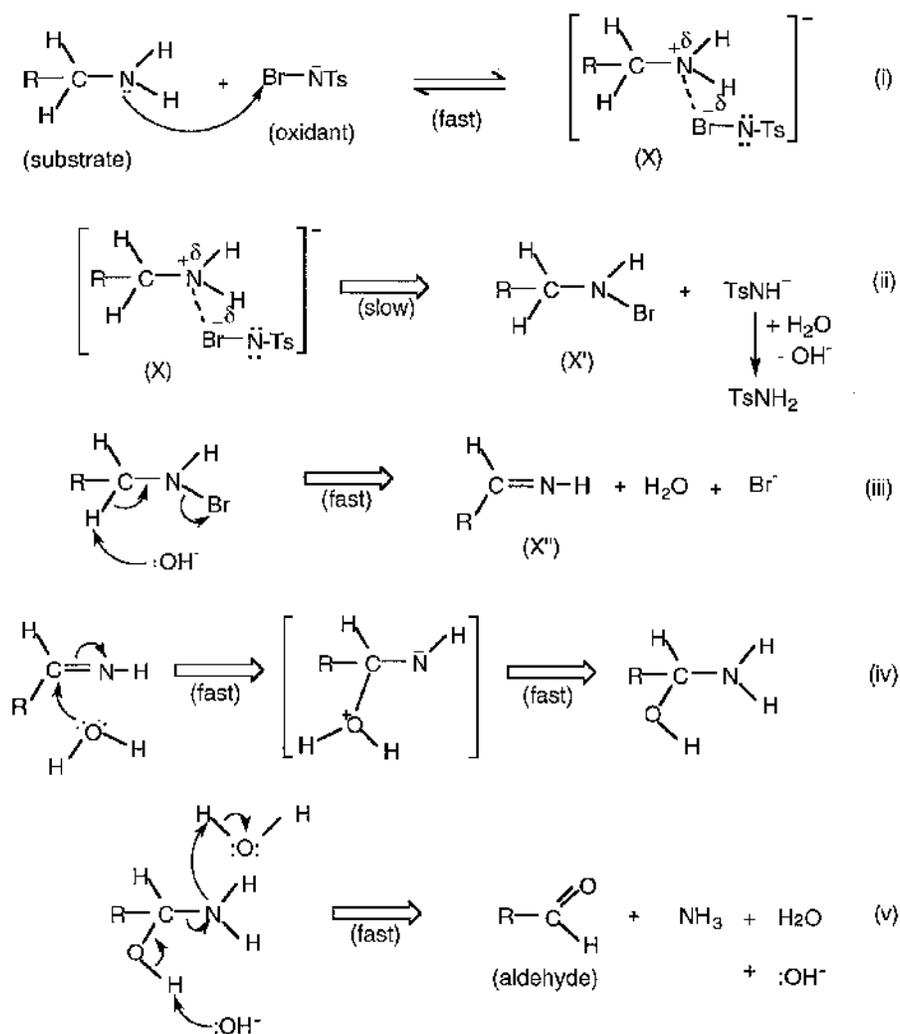


Here S is the amine substrate, *n*PA or *n*BA or *n*HA and X and X' are intermediate complex species, whose structures are shown in Scheme II.

A detailed mechanistic interpretation of the amine oxidation by BAT in NaOH medium is presented in Scheme II. An electrophilic attack by the positive bromine of the oxidizing species, (*p*-CH₃C₆H₄SO₂NBr⁺), 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 TsNH⁻ or *p*-CH₃C₆H₄SO₂NH⁻ (step ii). In Step iii, X' undergoes an α-hydrogen abstraction by OH⁻ forming an imine intermediate X'', a water molecule and a bromide

ion. In the next step, imine intermediate X'' undergoes a nucleophilic attack on α -carbon by water to form an α -hydroxyamine which on nucleophilic attacks by OH^- and H_2O forms the aldehyde and ammonia (step v).

Scheme II



Here Ts = $p\text{-CH}_3\text{-C}_6\text{H}_4\text{SO}_2^-$ and R = CH_3CH_2^- for *n*PA, $\text{CH}_3(\text{CH}_2)_2^-$ for *n*BA, and $\text{CH}_3(\text{CH}_2)_4^-$ for *n*HA as in equation (1).

If $[\text{BAT}]_t$ represents total $[\text{BAT}]$, then

$$[\text{BAT}]_t = [\text{TsNHBr}] + [\text{TsNBr}^-] + [\text{X}] \quad (9)$$

and
$$[\text{X}] = \frac{K_1 K_2 [\text{BAT}]_t [\text{S}] [\text{OH}^-]}{[\text{H}_2\text{O}] + K_1 [\text{OH}^-] \{1 + K_2 [\text{S}]\}} \quad (10)$$

Scheme I leads to the rate law [eq. (12)], since $\text{rate} = k_3 [\text{X}]$ (11)

$$\frac{-d}{dt} [\text{BAT}]_t = \frac{K_1 K_2 k_3 [\text{BAT}]_t [\text{S}] [\text{OH}^-]}{[\text{H}_2\text{O}] + K_1 [\text{OH}^-] \{1 + K_2 [\text{S}]\}} \quad (12)$$

This rate law [eq. (12)] is in agreement with the experimental data including a first-order in $[\text{BAT}]$ and a fractional-order each in $[\text{amine}]$ and $[\text{OH}^-]$.

Since $\text{rate} = k_{\text{obs}} [\text{BAT}]_t$, equation (12) can be transformed into equations (13) and (14).

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}_2\text{O}]}{K_1 K_2 k_3 [\text{OH}^-] [\text{S}]} + \frac{\{1 + K_2 [\text{S}]\}}{K_2 k_3 [\text{S}]} \quad (13)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_2 k_3 [\text{S}]} \left\{ \frac{[\text{H}_2\text{O}]}{K_1 [\text{OH}^-]} + 1 \right\} + \frac{1}{k_3} \quad (14)$$

A plot of $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ at constant $[\text{S}]$, from equation (13), is linear ($r > 0.9950$) with

$$\text{slope} = \frac{[\text{H}_2\text{O}]}{K_1 K_2 k_3 [\text{S}]} \quad \text{and} \quad \text{intercept} = \frac{1 + K_2 [\text{S}]}{K_2 k_3 [\text{S}]}$$

From equation (14), a plot of $1/k_{\text{obs}}$ vs. $1/[\text{S}]$ at constant $[\text{OH}^-]$ is linear ($r > 0.9938$) with

$$\text{slope} = \frac{1}{K_2 k_3} \left\{ \frac{[\text{H}_2\text{O}]}{K_1 [\text{OH}^-]} + 1 \right\} \quad \text{and} \quad \text{intercept} = \frac{1}{k_3}$$

Values of the formation constants K_1 and K_2 and of the decomposition rate constant (k_3) of the amine-BAT complex have been determined from the above double reciprocal plots. The data are presented in Tables 3 and 5. It may be seen that K_1 can be determined from both the equations. The results in Table 5 show that there is good agreement

between values of K_1 obtained from the two equations and the near constancy of K_1 values strongly supports the proposed mechanism of oxidation of amines by BAT.

Attempts were made to arrive at a linear free energy relationship for the oxidation of primary amines by BAT. Tests of the complete Taft equation¹² and the single parameter correlations with polar substitution constant (σ^*) and steric substitution constant (E_s) have been made with the plots: $\log(k_3 - E_s)$ vs. σ^* , $\log k_3$ vs. σ^* , and $\log k_3$ vs. E_s . The following regression equations were found:

$$\log k_3 = -0.63\sigma^* - 2.19 \quad (r = 0.9814) \quad (15)$$

$$\log k_3 = -1.76E_s - 6.0 \quad (r = 0.8966) \quad (16)$$

$$(\log k_3 - E_s) = -0.44\sigma^* - 1.5 \quad (r = 0.9911) \quad (17)$$

A good correlation of $\log k_3$ with σ^* implies that electronic effects play a dominant role in determining the rate. The implication of the steric effect on the rate is not too significant as revealed by equation (16). The negative values of reaction constant ρ^* (-0.63 and -0.44) indicate that the presence of electron-donating groups in the amine increases the reaction rate. However equation (17) implies that both steric and electronic effects play a role in determining the rate.

It is seen from the data in Tables 1 and 3 that the rate of oxidation of the amines by BAT increases in the order: $nPA < nBA < nHA$, 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 4, which support the above trend, indicate that the reactions are enthalpy controlled. This is verified by calculating the isokinetic temperature (β) from the slope of the plot of ΔH^\ddagger vs. ΔS^\ddagger (Fig. 3). The β value of 355 K, which is higher than the experimental temperature range used in the present study, indicates that the amine oxidation is enthalpy controlled. A further confirmation of the existence of isokinetic relationship was done by the Exner criterion¹³ by plotting $\log k'_{(313K)}$ vs. $\log k'_{(298K)}$ which is linear ($r = 0.9985$). The Exner slope gave a β value of 338 K. The fairly negative values of entropy of activation indicate the formation of a rigid associative transition state in each case. The near constancy of ΔG^\ddagger values indicates that the three primary amines react with BAT via the same mechanism.

CONCLUSION

The kinetics of oxidation of selected aliphatic primary amines by bromamine-T in alkaline medium leads to the following important conclusions. The linear free energy relationship shows that an increase in chain length of the electron-donating alkyl group, CH_3CH_2 , $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2CH_2$, increases the rate of reaction as supported by the negative value of the reaction constant ($\rho^* = -0.44$). The value of isokinetic temperature obtained indicates that the oxidation of amines with BAT is an enthalpy controlled reaction. The average deprotonation constant of monobromamine-T, a reac-

tive species of BAT, in alkaline medium has been evaluated at 303 K ($K = 3.3 \pm 0.1 \times 10^3 M$).

LITERATURE CITED

- [1] A. K. Ramaiah and P. V. K. Rao, *Indian J. Chem.*, 19A, 1120 (1980)
- [2] P. S. Radhakrishnamurthi and M. D. P. Rao, *Indian J. Chem.*, 14B, 790 (1976).
- [3] J. Gupta and M. C. Agrawal, *Indian J. Chem.*, 28A, 1100 (1989).
- [4] M.S. Ahmed and D.S. Mahadevappa, *Talanta*, 27, 669 (1980).
- [5] C. G. R. Nair and P. Indrasenan, *Talanta*, 23, 239 (1976).
- [6] F. Feigl, *Spot Tests in Organic Analysis*, Elsevier, Amsterdam, 1975.
- [7] S. Ananda, B. M. Venkatesha, D. S. Mahadevappa, and N. M. Made Gowda, *Int. J. Chem. Kinet.*, 25, 755 (1993); S. Ananda, M. B. Jagadeesha, L. Rai, and N. M. Made Gowda, *Synth. React. Inorg. Met.-Org. Chem.*, 29, 1-21 (1999).
- [8] F. G. Soper, *J. Chem. Soc. Trans.*, 125, 1899 (1924).
- [9] J. C. Morris, J. A. Salazar, and M. A. Wineman, *J. Am. Chem. Soc.*, 70, 2036 (1948).
- [10] E. Bishop and V. J. Jennings, *Talanta*, 1, 197 (1958).
- [11] F. F. Hardy and J. P. Johnston, *J. Chem. Soc. Perkin Trans. II*, 742 (1973).
- [12] R. D. Gilliom, *Introduction to Physical Organic Chemistry*, Addison-Wesley, London, 1970, pp. 156-160, 224.
- [13] O. Exner, *Coll. Czech. Chem. Commun.*, 29, 1094 (1964).

Table 1. Effects of varying reactant concentrations on the rate.
 $[\text{NaOH}] = 5.00 \times 10^{-3} \text{ M}$; $\mu = 0.400 \text{ M}$ and $\text{Temp} = 308 \text{ K}$

$[\text{BAT}]_0 \times 10^4$ (M)	$[\text{Amine}]_0 \times 10^2$ (M)	$k' \times 10^4 \text{ (s}^{-1}\text{)}$		
		<i>n</i> PA	<i>n</i> BA	<i>n</i> HA
6.00	7.50	2.02	2.41	2.74
7.00	7.50	2.02	2.41	2.72
8.00	7.50	2.01	2.40	2.74
9.00	7.50	2.01	2.41	2.75
10.0	7.50	1.98	2.39	2.73
11.0	7.50	1.95	2.38	2.73
9.00	2.50	1.11	1.23	1.37
9.00	5.00	1.67	1.92	2.15
9.00	7.50	2.01	2.41	2.75
9.00	9.00	2.17	2.63	3.03
9.00	10.0	2.27	2.70	3.17

Table 2. Effects of varying hydroxide concentrations on the rate.
 $[\text{BAT}]_0 = 9.00 \times 10^{-4} \text{ M}$; $[\text{Amine}]_0 = 7.50 \times 10^{-2} \text{ M}$; $\mu = 0.400 \text{ M}$; and $\text{Temp} = 308 \text{ K}$

$[\text{OH}]_0 \times 10^3$ (M)	$k' \times 10^4 \text{ (s}^{-1}\text{)}$		
	<i>n</i> PA	<i>n</i> BA	<i>n</i> HA
3.00	1.57	1.82	2.00
4.00	1.79	2.19	2.51
5.00	2.01	2.41	2.75
6.00	2.22	2.75	3.24
10.0	2.67	3.37	4.18
15.0	2.94	3.98	4.65
20.0	3.31	4.42	5.29
30.0	3.71	4.97	5.93

Table 3 Rate constants (k_3) for the decomposition of the amine-BAT complex determined from double reciprocal plots* at different temperatures.

Temp (K)	$k_3 \times 10^4 \text{ (s}^{-1}\text{)}$		
	<i>n</i> PA	<i>n</i> BA	<i>n</i> HA
298	1.62	2.11	2.69
303	2.05	2.93	3.71
308	3.43	4.57	5.56
313	5.12	6.25	7.89

* A plot of $1/k'$ vs. $1/[\text{OH}^-]$ at constant $[\text{S}]$ at each temperature based on equation (13)

Table 4. Activation parameters for the decomposition of the amine-BAT complex determined from the values of k_3 at different temperatures.

Parameter	<i>n</i> PA	<i>n</i> BA	<i>n</i> HA
$E_a/\text{kJ mol}^{-1}$	60.1	56.8	55.0
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	57.5	54.3	52.4
$\Delta S^\ddagger/\text{JK}^{-1} \text{ mol}^{-1}$	-126	-133	-138
$\Delta G^\ddagger/\text{kJ mol}^{-1}$	95.7	95.0	94.5

Table 5. Equilibrium and formation constants of the amine-BAT complex determined from the double reciprocal plots.

Amine	$K_1 \times 10^{-3}$		$K_2 (M^{-1})$
	(a)	(b)	
n-Propylamine	3.10	2.00	86.5
n-Butylamine	3.40	2.20	63.1
n-Hexylamine	3.40	2.20	54.5

(a) From the plot of $1/k'$ vs. $1/[S]$ at constant $[OH^-]$ and temperature of 308 K based on equation (14)

(b) From the plot of $1/k'$ vs. $1/[OH^-]$ at constant $[S]$ and temperature of 308 K based on equation (13)

Figure 1. Plots of $\log k'$ vs. $\log [S]_0$ where S = amine.

$[\text{BAT}]_0 = 9.00 \times 10^{-4} \text{ M}$; $[\text{NaOH}]_0 = 5.00 \times 10^{-3} \text{ M}$; $\mu = 0.400 \text{ M}$; and $\text{Temp} = 308 \text{ K}$

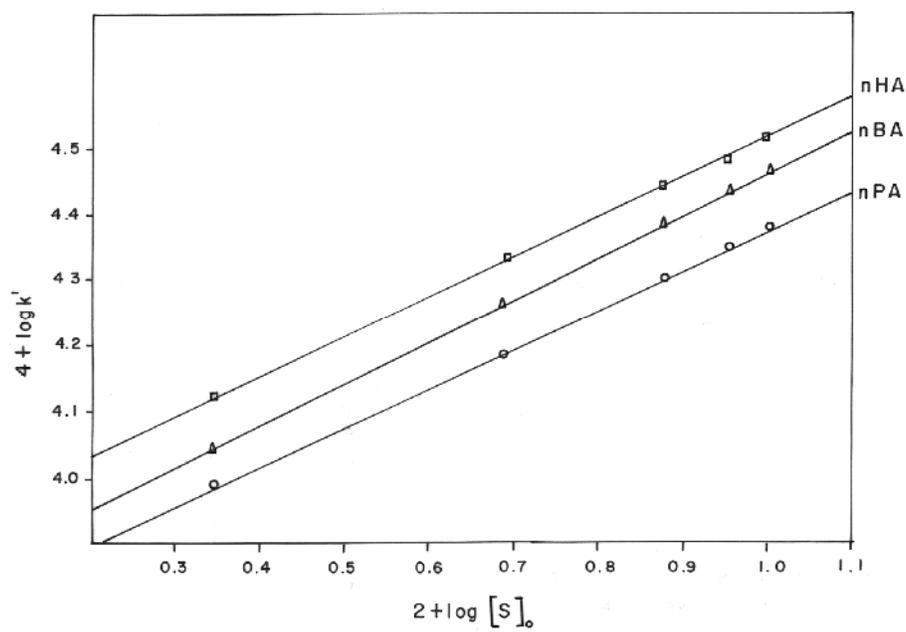


Figure 2. Plots of $\log k'$ vs. $\log [\text{OH}]_o$.

$[\text{BAT}]_o = 9.00 \times 10^{-4} \text{ M}$; $[\text{Amine}]_o = 7.50 \times 10^{-2} \text{ M}$; $\mu = 0.400 \text{ M}$; and $\text{Temp} = 308 \text{ K}$

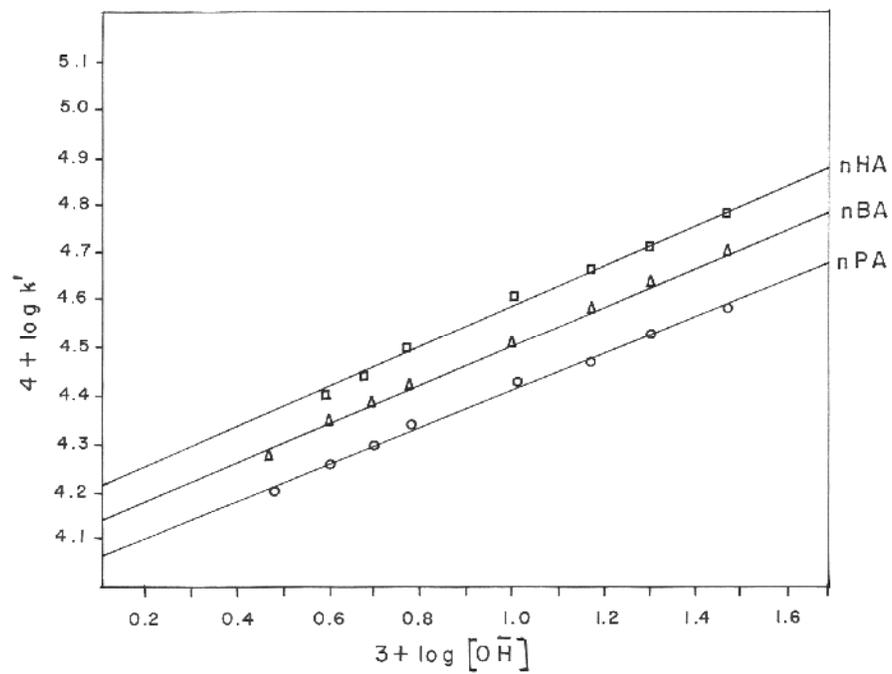


Figure 3. A plot of ΔH^\ddagger vs. ΔS^\ddagger .