Kinetics and thermodynamics of the reaction of aliphatic N-bromamines with bromide ion in acid media, and the pK_a of N-bromamines†

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The kinetics of the oxidation of bromide ions by aliphatic N-bromamines in aqueous acid media were studied using a pH jump technique. The reaction is first order in both bromide ion and total bromamine concentrations, and takes place only through the protonated N-bromamine. For two of the N-bromamines studied (N-Br-dimethylamine and N-Br-diethylamine), hydrolysis competed with the reaction with bromide ions, whereas in all the other cases hydrolysis was too slow to be detected. The pK_a values obtained from the k_{obs} vs. [H$^+$] data at 25 °C are 2.88 for N-Br-dimethylamine, 3.24 for N-Br-diethylamine, 3.33 for N-Br-piperidine (all at $I = 0.1$ M), 2.26 for N-Br-iso-butylamine and 2.92 for N-Br-sec-butylamine (both at $I = 0.5$ M).

Introduction

The reactions of aqueous solutions of bromine and chlorine with organic nitrogenated compounds are of great importance in water quality control,[1,2] in the food industry[3] and in the anti-infection defense mechanisms of organisms.[4,5] While the reactions of aqueous chlorine with amines, amino acids and other nitrogen compounds have been widely studied,[6–10] mainly due to the important role of chlorine in water treatment, few of the analogous reactions of aqueous bromine have been investigated.[11–14] For this reason, in Haag and Lietzke's[15] model of the dynamics and equilibria of oxidants derived from chlorination in fresh water and sea water, most of the many constants for which estimates had to be used concerned the fundamental chemistry of organic and ammoniacal bromamines. These oxidants comprise aqueous chlorine and the N-chloramines formed by reaction of ammonia and other amines with aqueous chlorine, as well as hypobromite or hypobromous acid formed by oxidation of bromide ion (present in amounts of up to 65 mg L^{-1} in sea water) by these oxidizing chlorine compounds.[16,17]

When bromine or hypobromous acid is added to an aqueous solution of amine or ammonia, one or more bromamines† are rapidly formed. In the case of ammonia, monobromamine (NH$_2$Br), dibromamine (NHBr$_2$) and tribromamine (NBr$_3$) are formed sequentially in aqueous solution, their relative final concentrations depending on the initial bromine to ammonia ratio and the pH.[18,19] For [Br$_2$]/[NH$_3$] < 1 monobromamine is the predominant species in alkaline solution, mixtures of all three bromamines are obtained in neutral solution, and tribromamine is the main product in acidic media. Similarly, primary aliphatic amines and amino acids react with aqueous bromine to form variable proportions of the corresponding N-bromo and N,N-dibromo derivatives. Compounds bearing a secondary amino group can only form N-bromamines.[11,13]

The formation of N-bromo compounds is very fast, being complete a few seconds after aqueous bromine is mixed with the nitrogenous substrate in dilute aqueous solution.[11] However, these N-bromo amino compounds are not the final products of reaction: the ammonia derivatives, for example, decompose completely to N$_2$ and H$_2$O within hours or days, NHBr$_2$ being especially unstable,[18,20] and N-bromo amino acids

decompose within minutes to hours,[14,21] although N-bromo alkylamines are rather more stable, forming carboxylic acids or ketones only after several days.[22]

In the presence of bromide ion, the reactions involved in the decomposition of N-bromamines include the comproportionation reaction affording bromine and the corresponding amine. In this work we studied the kinetics and thermodynamics of the reactions of bromide ion with the N-monobromamines derived from dimethylamine, diethylamine, piperidine, iso-butylamine and sec-butylamine; for the reasons discussed below (Results and discussion), a pH jump technique was used. In addition, for the N-bromo derivatives of dimethyl-amine, diethylamine and piperidine, the pK_a values calculated from the observed pH dependence of the comproportionation reactions were corroborated by direct measurements which, because of the instability of the protonated N-bromamines, were likewise carried out using kinetic observations following pH jumps.

Experimental

Aqueous solutions of bromine were made up from reagent grade liquid bromine and their concentrations were determined as BrO$^-$ at 329 nm ($\varepsilon = 345$ M^{-1} cm^{-1})[19] or by iodometric titration. Dimethylamine, diethylamine, piperidine, isobutyl-amine and sec-butylamine were supplied by Aldrich, and were distilled before use. Sodium bromide, sodium perchlorate, perchloric acid and sodium hydroxide were reagent grade products and were used without further purification.

All pH jump experiments were carried out in an Applied Photophysics DX17MV sequential stopped flow apparatus. Aqueous bromine and amine solutions of pH ca. 7.0 were injected from separate syringes into the ageing loop (to prevent the formation of N,N-dibromamines, the amine was at least in 20-fold excess over bromine), and within 5 s the resulting N-bromamine solution was injected into the reaction cell together with phosphate buffer of the appropriate pH which, in the reactions of N-bromamines with bromide ion, contained NaBr at a known concentration; final concentrations in the reaction mixture were ca. 5×10^{-5} M for N-bromamine and 0.005–0.1 M for NaBr). The temperature of the solutions in the syringes and cell was kept constant to within ±0.1 °C by means of circulating water.

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† N-Bromamines = R^{1}R^{2}NBr.

For the reactions of *N*-bromamines with bromide ion, the adequacy of the pH jump proposed for each *N*-bromamine was first confirmed by obtaining spectra of the reaction mixtures at the high and low extremes of the jump; these spectra were run in Cary 219 or Kontron Uvikon 920 spectrophotometers. In the kinetic experiments, absorbance was monitored at 265 nm, the wavelength of the absorption maximum of Br_3^- ion ($\varepsilon_{Br_3^-} = 40900$ M^{-1} cm^{-1}),[23] formed in rapid establishment[24] of the equilibrium (1) by reaction of excess bromide with the bromine produced by the comproportionation reaction (2).

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad (1)$$

$$R^1R^2NBr + Br^- + H^+ \longrightarrow R^1R^2NH + Br_2 \qquad (2)$$
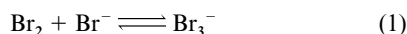
These reactions were followed until at least 95% complete, and the absorbance–time data were well fitted by first order integrated equations (3).

$$\ln(A_{inf} - A) = \ln(A_{inf} - A_o) - k_{obsd}t \qquad (3)$$

The observed rate constants used in further calculations were the means of 5–10 replicate experiments affording values differing from each other by no more than 3%.

Since protonated *N*-bromamines are rapidly hydrolysed in aqueous solution, direct measurements of their pK_a were carried out by measuring the absorbance of *N*-bromamine solutions (at the wavelength of the absorption maximum of the unprotonated species) immediately after being jumped from pH *ca.* 7 to various pH < 5, assuming instantaneous attainment of the protonation equilibrium. Specifically, for each pH value, the absorbance of the equilibrium mixture of unhydrolysed protonated and unprotonated *N*-bromamine was measured by linear extrapolation of the data for the first 5% of the hydrolysis reaction back to zero time, and a value of pK_a was calculated as usual[25] using the expression (4), where A_{max} is the absorbance at

$$pK_a = -\log[H^+] + \log[(A_{max} - A)/(A - A_{min})] \qquad (4)$$

pH *ca.* 7 and A_{min} the absorbance at a pH value low enough for the contribution of the unprotonated species to be negligible. The pK_a values reported below are the means of values obtained in two or three replicate experiments at each of 15–20 pH values. All these experiments were carried out at 25 °C and with an ionic strength of 0.1 M.

All pH values were measured with a Radiometer PHM 82 pH-meter equipped with a GK3401C combined glass electrode, and were converted to p[H$^+$] values on the basis of electrode calibrations carried out by titration of an HClO$_4$ standard with an NaOH standard at 25 °C and I = 0.1 or 0.5 M.

Results and discussion

Fig. 1 shows the percentage of the different "Br$^+$" species present in equilibrium mixtures of dimethylamine (0.02 M), bromine (5 × 10^{-5} M) and bromide ion (0.02 M) in water as a function of pH (these curves were calculated using the published equilibrium constants listed in Table 1). At pH values higher than about 5 the *N*-bromodimethylamine is the predominant species in the equilibrium mixture and therefore, its reaction with bromide to yield bromine and tribromide cannot be studied in this pH region. On the other hand, solutions of the *N*-bromamine have to be obtained at pH *ca.* 7, since at lower pH the comproportionation reaction is significant even when the only source of bromide is the bromine used to obtain the *N*-bromo compound. These two facts made it necessary to study the reaction by a pH jump method. The same is true of the other *N*-bromamines studied in this work, in which all kinetic experiments were performed using pH jumps from *ca.* pH 7 to pH < 3.5.

Table 1 Constants of the equilibria established in aqueous mixtures of dimethylamine and bromine

Reaction	pK	Ref.
$Br_2 + Br^- \rightleftharpoons Br_3^-$	−1.23	23
$Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HOBr$	8.21	23
$HOBr \rightleftharpoons BrO^- + H^+$	8.8	34
$(CH_3)_2NBr + H_2O \rightleftharpoons (CH_3)_2NH + HOBr$	11.66	13
$(CH_3)_2NH_2^+ \rightleftharpoons (CH_3)_2NH + H^+$	10.87	35
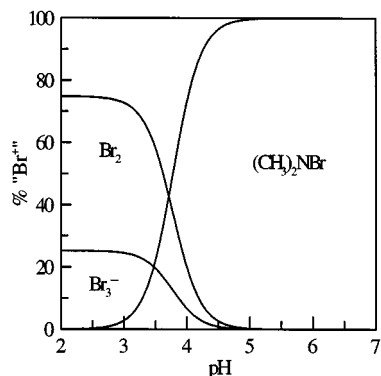
Fig. 1 Distribution of "Br$^+$" species in an aqueous solution of bromine (5 × 10^{-5} M), dimethylamine (0.02 M) and Br$^-$ (0.02 M), calculated from the data of Table 1.
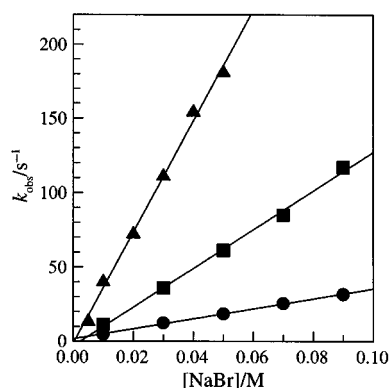
Fig. 2 Influence of bromide ion concentration upon the observed rate constant. $[Br_2]_0$ = 5 × 10^{-5} M, $[amine]_T$ = 3 × 10^{-3} M, I = 0.5 M and 25 °C. Circles stand for *N*-Br-dimethylamine (p[H$^+$] = 2.88), squares for *N*-Br-*sec*-butylamine (p[H$^+$] = 2.43) and triangles for N-Br-iso-butylamine (p[H$^+$] = 2.48).

The observed reaction rate k_{obs} was unaffected by varying the concentration of amine used to prepare the *N*-bromamines over one order of magnitude while all other reaction conditions were held fixed. This indicates that the reaction is not reversible. When the *N*-bromamine concentration was fixed while the NaBr concentration was varied, k_{obs} increased linearly with [Br$^-$] (Fig. 2 shows results for *N*-bromodimethylamine, *N*-bromo-*sec*-butylamine and *N*-bromo-isobutylamine). For *N*-bromodimethylamine and *N*-bromodiethylamine the regression lines fitted to the k_{obs} *vs.* [NaBr] data have *y*-intercepts differing significantly from zero, showing that, in these cases at least, the reaction mechanism must involve attack by the other nucleophiles present (H$_2$O and OH$^-$) as well as by Br$^-$.

When the pH of the lower end of the pH jump was varied while other conditions were held constant, k_{obs} was found to increase with [H$^+$] reaching a maximum value when all the bromamine is protonated. This behaviour is consistent with the protonated form of the *N*-bromamine being the only reactive species towards the nucleophile (Fig. 3 shows results for *N*-bromodimethylamine and *N*-bromo-*sec*-butylamine). The value of k_{obs} was unaffected by a 10-fold change in buffer concentration, showing that the reaction is not subject to general
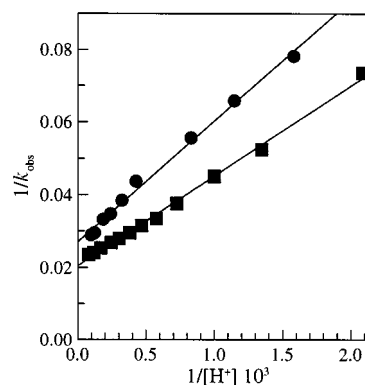
Table 2 Values of the rate constants of the slow steps of Scheme 1, and pK_a values for amines and the corresponding *N*-Br- and *N*-Cl-derivatives

N-Br-Amine	pK_a				k_1/M^{-1} s^{-1}	k_2/s^{-1}
	N-Br-Amine[a]	*N*-Br-Amine[b]	Amine[c]	*N*-Cl-Amine		
N-Br-Dimethylamine[d]	2.88 ± 0.09	2.67 ± 0.04	10.77	0.514[e]	8.2(±0.5) × 10^2	13.6 ± 0.8
N-Br-Dimethylamine[f]	2.91 ± 0.09		10.87	0.702[e]	4.9(±0.1) × 10^2	17 ± 3
N-Br-Diethylamine[d]	3.24 ± 0.05	3.28 ± 0.02	10.93	1.07[e]	3.1(±0.1) × 10^2	1.2 ± 0.2
N-Br-Piperidine[d]	3.3 ± 0.2	3.08 ± 0.02	11.12		35(±1)	Not detected
N-Br-Isobutylamine[f]	2.3 ± 0.1		10.57	1.52[g]	9.9(±0.3) × 10^3	Not detected
N-Br-*sec*-Butylamine[f]	2.92 ± 0.06		10.56	1.72[g]	1.78(±0.05) × 10^3	Not detected

[a] Obtained from the kinetic data. [b] Obtained directly (see Experimental). [c] Ref. 35. [d] $I = 0.1$ M (NaClO$_4$). [e] Ref. 36. [f] $I = 0.5$ M (NaClO$_4$). [g] Ref. 9.
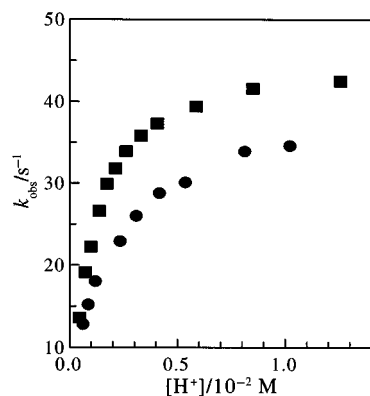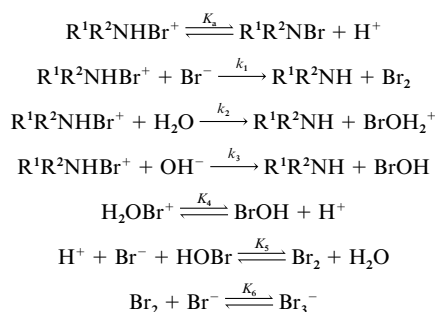

Fig. 3 Influence of hydrogen ion concentration upon the observed rate constant, [amine]$_T = 3 \times 10^{-3}$ M, [Br$_2$]$_0 = 5 \times 10^{-5}$ M, $I = 0.5$ M and 25 °C. Circles stand for *N*-Br-dimethylamine ([Br$^-$] = 0.05 M), squares for *N*-Br-*sec*-butylamine ([Br$^-$] = 0.03 M).

acid catalysis and hence that proton transfer is not involved in the slow step.

$$R^1R^2NHBr^+ \overset{K_a}{\rightleftharpoons} R^1R^2NBr + H^+$$

$$R^1R^2NHBr^+ + Br^- \overset{k_1}{\longrightarrow} R^1R^2NH + Br_2$$

$$R^1R^2NHBr^+ + H_2O \overset{k_2}{\longrightarrow} R^1R^2NH + BrOH_2^+$$

$$R^1R^2NHBr^+ + OH^- \overset{k_3}{\longrightarrow} R^1R^2NH + BrOH$$

$$H_2OBr^+ \overset{K_4}{\rightleftharpoons} BrOH + H^+$$

$$H^+ + Br^- + HOBr \overset{K_5}{\rightleftharpoons} Br_2 + H_2O$$

$$Br_2 + Br^- \overset{K_6}{\rightleftharpoons} Br_3^-$$

Scheme 1

The above findings can be explained by the reaction mechanism shown in Scheme 1, in which equilibria 4, 5 and 6 are all rapidly established following rate-controlling loss of "Br$^+$" to the nucleophile (disproportionation of the *N*-bromamines derived from primary amines to afford *N*,*N*-dibromamines will have been negligible under the conditions of this study and need not be considered).[13] Scheme 1 implies the relationship shown in eqn. (5), but the k_3[OH$^-$] term can be ignored: even if k_3 had the largest value known for a diffusion-controlled reaction in water, 10^{11} M^{-1} s^{-1},[26] this term would contribute less than 10% of k_{obs} under the working conditions ([OH$^-$] < 3 × 10^{11} M). Hence eqn. (5) may be simplified to eqn. (6), which can be linearized in the form of eqn. (7).

$$k_{obs} = \frac{(k_1[Br^-] + k_2 + k_3[OH^-])[H^+]}{K_a + [H^+]} \quad (5)$$

$$k_{obs} = \frac{(k_1[Br^-] + k_2)[H^+]}{K_a + [H^+]} \quad (6)$$

Fig. 4 Linearized plot of the k_{obs} *vs.* [H$^+$] data. Circles stand for *N*-Br-dimethylamine and squares for *N*-Br-*sec*-butylamine.

$$\frac{1}{k_{obs}} = \frac{K_a}{(k_1[Br^-] + k_2)} \frac{1}{[H^+]} + \frac{1}{(k_1[Br^-] + k_2)} \quad (7)$$

The linearity of plots of 1/k_{obs} against 1/[H$^+$] (Fig. 4 shows the data for *N*-bromodimethylamine and *N*-bromo-*sec*-butylamine) therefore supports the proposed reaction mechanism. Fitting eqn. (7) to these plots affords the values of pK_a that are listed in Table 2, and which allow eqn. (6) to be fitted to the k_{obs} *vs.* [Br$^-$] data to obtain values for k_1 and k_2 that are likewise listed in Table 2. For the *N*-bromamines for which direct measurements of pK_a were performed as described in the Experimental section, there is good agreement between the kinetically and spectrophotometrically determined values (also listed in Table 2).

Replacing an amino hydrogen with a chlorine or a bromine atom lowers the pK_a of the corresponding amine by 8 to 10 units (see Table 2), showing the large inductive effect of the halogen atom. The large pK_a difference between *N*-chloramines and *N*-bromamines (*ca.* 2 units for *N*-bromamines derived from secondary amines and *ca.* 1 unit for those derived from primary amines) does not agree with the very close values of the inductive parameter, σ_I, for the chloro and bromo substituents ($\sigma_I = 0.47$ and 0.45, respectively).[27] However, these σ_I substituent constants have been obtained for systems where the substituent is attached to a carbon atom and usually far from the reaction centre. For the *N*-haloamines, the substituent is directly bonded to the nitrogen atom, which is the protonation site. Furthermore, the halogen atom can act as an acceptor for the free electron pair on the nitrogen and bond orders larger than one have been found for the halogen–nitrogen bond of *N*-haloamines.[28,29] Therefore, the contribution of a resonance effect could be important for these systems and would probably be another reason for the lack of correlation between pK_a and σ_I values.

In experiments carried out at constant pH with *N*-bromo-dimethylamine and the two *N*-bromobutylamines, k_{obs} decreased as ionic strength, regulated with sodium perchlorate, was increased (Table 3). Although plots of k_{obs} against $\sqrt{I}/(1 + \sqrt{I})$ are linear (Fig. 5), the fact that k_{obs} is not the rate of an elementary

reaction step results in the slopes of the corresponding regression lines (-0.81 ± 0.05 for N-bromodimethylamine, -0.71 ± 0.03 for N-bromoisobutylamine and -0.80 ± 0.03 for N-bromo-sec-butylamine) being rather less steep than is predicted by eqn. (8).[30]

$$\log k = \log k_o + 1.02 Z_a Z_b \left(\frac{\sqrt{I}}{1 + \sqrt{I}} \right) \qquad (8)$$

Comparison of the results obtained for N-bromo-dimethylamine at $I = 0.1$ M and $I = 0.5$ M (Table 2) shows that
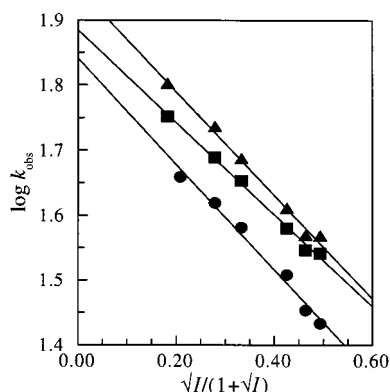
Fig. 5 Plot of k_{obs} against $\sqrt{I}/(1 + \sqrt{I})$. $[Br_2]_o = 5 \times 10^{-5}$ M, $[amine]_T = 3 \times 10^{-3}$ M, $T = 25$ °C. Circles stand for N-Br-dimethylamine ($[Br^-] = 0.05$ M, $p[H^+] = 2.2$), squares for N-Br-isobutylamine ($[Br^-] = 0.01$ M, $p[H^+] = 1.95$) and triangles for N-Br-sec-butylamine ($[Br^-] = 0.03$ M, $p[H^+] = 2.2$).

Table 3 Influence of ionic strength upon the observed rate constant. $[N\text{-Br-Amine}] = 5 \times 10^{-5}$ M, $[Phosphate]_T = 2 \times 10^{-3}$ M, $T = 25$ °C. The concentrations of NaBr were 0.05 M for the reaction of N-Br-dimethylamine, 0.01 M for that of N-Br-isobutylamine and 0.03 M for that of N-Br-sec-butylamine

	k_{obs}/M^{-1} s^{-1}		
I/M	N-Br-Dimethyl-amine	N-Br-Isobutyl-amine	N-Br-sec-Butyl-amine
0.05		56.5 ± 0.5	63.1 ± 0.4
0.07	45.6 ± 0.4		
0.15	41.6 ± 0.2	48.9 ± 0.6	54.2 ± 0.3
0.25	38.1 ± 0.2	45.0 ± 0.5	48.4 ± 0.2
0.55	32.2 ± 0.2	38.0 ± 0.2	40.6 ± 0.2
0.75	28.4 ± 0.3	35.2 ± 0.6	36.9 ± 0.3
0.95	27.1 ± 0.3	34.8 ± 0.4	36.8 ± 0.3

the effect of the ionic strength on the pK_a of the N-bromo compound is very small. The rate constant for the reaction of the protonated N-bramamine with water, k_2, increases slightly ($ca.$ 20%) upon increasing the ionic strength. However, this change is not significant if compared with the error in the k_2 values. Furthermore, no effect would be expected for a reaction in which one of the reagents bears no charge.[31] Therefore, if K_a and k_2 do not change significantly with the ionic strength, changes in k_{obs} (Table 3) can be attributed mainly to the effect of I on the rate constant for the reaction of the protonated N-bramamine with bromide ion, k_1. This rate constant decreases upon increasing the ionic strength (Table 2) and this I-dependence parallels that of k_{obs}. The negative slope of the plots shown in Fig. 5 provides further evidence for a charge neutralisation step, k_1, being rate determining.

For N-bromodimethylamine, K_a, k_1 and k_2 were determined as above over the temperature range 288–318 K; and for the N-bromobutylamines, for which k_2 is negligible, K_a and k_1 were determined over the same temperature range from k_{obs} $vs.$ $[H^+]$ data, using eqn. (7) with $k_2 = 0$ (Table 4). Plots of $\ln K_a$ or $\ln k/T$ against $1/T$ show excellent linearity, and the corresponding regression equations afford the thermodynamic and activation parameters listed in Table 5. Values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the ionisation equilibrium of the protonated form of the corresponding parent amines are also given in Table 5.

The fact that the enthalpy of dissociation of the protonated N-bramamines is lower than for the corresponding protonated amines[32] reflects the greater acidity of the former. The finding that the associated entropy change is more positive than that of the parent amines (although similar to that of amines of similar pK_a) is analogous to Snyder and Margerum's results for chloramine,[33] and suggests that N-bramamines are less well solvated than the parent amines.

The value of $\Delta S^\ddagger$ for the reaction of the protonated N-bromo-dimethylamine with water is negative, whereas that for the comproportionation reaction is positive or close to zero for the N-bramamines studied. Although there is a large experimental error associated with the value of $\Delta S_1^\ddagger$ for N-bromodimethyl-amine (see Table 5), the positive values obtained for the other N-bramamines seem to indicate that $\Delta S_1^\ddagger$ is close to zero for the former. This difference between the entropies of activation of the k_1 and k_2 reactions of N-bromodimethylamine is attributable to the fact that formation of the k_1 transition state by the bromide ion and the protonated N-bramamine involves both a reduction in the number of degrees of freedom (which contributes about -50 J mol^{-1} K^{-1} to $\Delta S^\ddagger$)[31] and partial charge neutralisation (which contributes about $-41 Z_A Z_B$ J

Table 4 Influence of temperature upon k_1, k_2, K_a (Scheme 1) for N-Br-dimethylamine, N-Br-isobutylamine and N-Br-sec-butylamine

	N-Br-Dimethylamine			N-Br-Isobutylamine		N-Br-sec-butylamine	
T/K	$10^{-2} k_1$/M^{-1} s^{-1}	k_2/M^{-1} s^{-1}	$10^3 K_a$/M	$10^{-3} k_1$/M^{-1} s^{-1}	$10^3 K_a$/M	$10^{-3} k_1$/M^{-1} s^{-1}	$10^3 K_a$/M
288	2.68(±0.09)	0.121(±0.009)	0.91(±0.02)	2.6(±0.1)	4.9(±0.2)	0.71(±0.03)	0.73(±0.02)
298	4.9(±0.4)	0.27(±0.02)	1.23(±0.04)	6.1(±0.6)	5.5(±0.3)	1.65(±0.06)	1.23(±0.03)
308	9.8(±0.4)	0.63(±0.02)	1.61(±0.05)	17(±3)	11(±1)	3.7(±0.1)	1.77(±0.06)
318	26(±2)	1.4(±0.1)	2.27(±0.09)	36(±1)	15(±1)	9.1(±0.8)	2.3(±0.1)

Table 5 Activation and thermodynamic parameters for the key steps in Scheme 1 and thermodynamic parameters for the equilibrium of ionization of the protonated parent amines. ΔH and ΔG in kJ mol^{-1}, ΔS in J mol^{-1} K^{-1}

	$\Delta H_1^\ddagger$	$\Delta S_1^\ddagger$	$\Delta G_1^\ddagger$	$\Delta H_2^\ddagger$	$\Delta S_2^\ddagger$	$\Delta G_2^\ddagger$	$\Delta H°$	$\Delta S°$	$\Delta G°$
N-Br-Dimethylamine	54 ± 6	−10 ± 9	57 ± 6	59 ± 1	−57 ± 4	76 ± 1	23 ± 1	21 ± 4	17 ± 1
N-Br-Isobutylamine	66 ± 2	49 ± 7	51 ± 2				31 ± 6	61 ± 19	12 ± 6
N-Br-sec-Butylamine	62 ± 2	25 ± 7	55 ± 2				29 ± 2	42 ± 8	17 ± 2
Dimethylamine[a]							50.3 ± 0.2	−36.4 ± 0.8	61.1 ± 0.3
Isobutylamine[a]							58.2 ± 0.3	−5.1 ± 0.8	59.7 ± 0.4
sec-Butylamine[a]							58.6 ± 0.2	−5.1 ± 0.8	60.1 ± 0.3

[a] Ref. 37.

mol^{-1} K^{-1}),[31] whereas formation of the k_2 transition state only reduces the number of degrees of freedom.

In conclusion, the experimental results presented above are consistent with a mechanism in which the rate-controlling step is nucleophilic attack of Br$^-$ or a water molecule on the bromine atom of the protonated *N*-bromamine to afford the neutral amine and Br$_2$ or BrOH as the immediate products. In the presence of excess Br$^-$, the latter then give rise to an equilibrium mixture in which the main species are Br$_2$ and Br$_3^-$. The proposed mechanism is supported by the good agreement between the pK_a values calculated for the *N*-bromamines from the kinetic data and those obtained by direct spectrophotometric means. The considerable increase in acidity brought about by replacement of an amino hydrogen by a bromine atom is attributable to the inductive effect of the latter.

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