Kinetic Study of the Formation of *N*-Chloramines

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Abstract

We studied the kinetics of the chlorination of amines by sodium hypochlorite in strongly alkaline aqueous solution. A reaction mechanism compatible with experimental results is proposed and discussed. © 1995 John Wiley & Sons, Inc.

Introduction

During chlorination of waters intended for the public water supply, combination of chlorine with nitrogen-containing compounds may lead to the formation of *N*-chloramines, which have quite different oxidation and disinfection properties to hypochlorite. Moreover, any free chlorine present in drinking water comes into contact with a variety of nitrogen-containing organic compounds during the various stages of ingestion, and may react with these biomolecules (e.g., in the saliva or gastric fluids) to give *N*-chlorinated products.

Because of the need to evaluate the possible effects of water chlorination on human health, knowledge of the rates and mechanisms of these reactions is of great interest. Although several studies on the chlorination of nitrogen-containing compounds have been carried out [1–7], as yet no definitive mechanism has been established.

In this work we undertook a kinetic study of the formation of *N*-chloramines and *N*-chloroalcoholamines in strongly basic solution, and obtained kinetic and mechanistic data which may be useful for predicting the processes occurring during the ingestion of chlorinated water.

Experimental

N-chloramines are formed by reaction of sodium hypochlorite with amines in alkaline solution,

$$\text{(1)} \qquad OCl^- + Na^+ + RNH_2 \longrightarrow RNHCl + Na^+ + OH^-$$

Sodium hypochlorite was obtained by bubbling chlorine (generated by oxidation of conc. HCl by potassium permanganate) through a 0.5 M solution of sodium hydroxide. The final hypochlorite concentration was calculated from measurements of the solution absorbance ($\lambda(OCl^-) = 292$ nm, $\varepsilon = 350\ M^{-1}\ cm^{-1}$) [8]. To prevent decomposition of the hypochlorite, the solution was brought to pH > 11 and placed in a UV-opaque flask.

Amine solutions were prepared by direct weighing of Merck p.a. products: 4-amino-1-butanol (4A1B), 2-amino-1-butanol (2A1B), 2-amino-2-methyl-1-propanol (AMP), methylamine (MA), ethylamine (EA), *n*-propylamine (*n*PA), and isopropylamine

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(*iso*PA). A sodium chloride solution was also prepared and used to maintain the ionic strength of the solutions used in the experiments. Sodium hydroxide solutions were prepared from Merck p.a., and titrated with a primary standard of known concentration to obtain their exact concentrations.

Reactions were followed by spectrophotometrically monitoring the progressive degeneration of the UV absorption band due to the hypochlorite, and the simultaneous development of a band at 250 nm due to the *N*-chloramine (Fig. 1). Firstly, each amine was mixed with hypochlorite and allowed to react until the absorption band at 250 nm reached a constant absorbance value. Calculation of the molar extinction coefficient at this wavelength gave the values listed in Table I.

Owing the rapidity of the reactions, kinetic studies were carried out by means of the stopped-flow technique (Applied Photophysics Spectrophotometer). Solutions of sodium hypochlorite and at least a ten-fold excess of the amine (the isolation method) were prepared with concentrations and alkalinities selected to give specific reaction conditions; they were mixed at 25 ± 0.1°C and degeneration of the absorption band at $\lambda = 292$ nm was monitored.

Kinetic data were obtained as empirical values of absorbance A at reaction time t and were analyzed by fitting them to the expression

$$A_t = A_\infty + (A_0 - A_\infty)e^{(-k_{obs}t)} \tag{2}$$

(where A_t, A_0 y A_∞ are the absorbance values at time t, zero, and infinity, respectively, and k_{obs} is the observed first-order rate constant ($v = k_{obs}$ [NaOCl]).

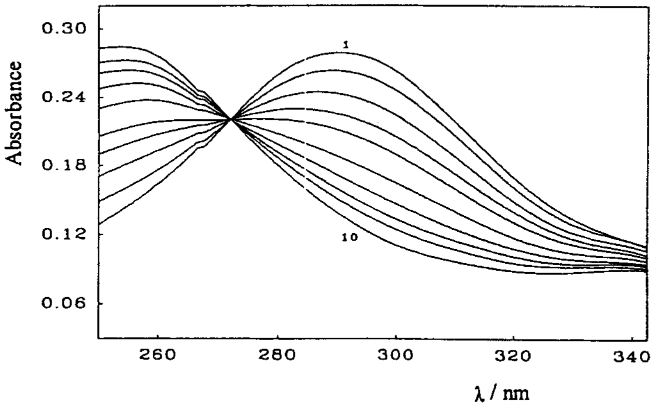

Figure 1. Ten UV absorption spectra corresponding to a reaction mixture containing [NaClO] = 0.0006 M, [NaOH] = 0.1 M, and [2A1B] = 0.01 M at 25°C. t_r = 0.05 s.

TABLE I. Molar extinction coefficients of the *N*-chloramines.

N-chloramine	ε/M^{-1} cm^{-1}
4-amino-1-butanol	350 ± 2
2-amino-1-butanol	347 ± 1
2-amino-2-methyl-1-propanol	350 ± 2
methylamine	360 ± 2
ethylamine	367 ± 1
n-propylamine	377 ± 8
isopropylamine	371 ± 4

Results

Reaction Order with Respect to Hypochlorite

Ten experiments were carried out at each of several concentrations of hypochlorite, but with fixed concentrations of each amine (at least a ten-fold excess) and sodium hydroxide. In every case, the reaction reached in excess of 90% completion and the values of k_{obs} measured for each amine were reproducible to within ±5%. The fitting of the above expression to each set of data gave a regression coefficient greater than 0.999, confirming that the reaction was first-order with respect to hypochlorite. Ten experiences were carried out to get the rate constant and a media value of them was obtained. Table II lists the mean values of k_{obs} obtained in the concentration range studied, together with the corresponding standard deviations.

Influence of the Concentration of Amine and Sodium Hydroxide

The remaining terms of the rate law were also determined by means of the isolation method: a constant but deficient hypochlorite concentration was maintained while amine and alkali concentrations were varied in separate series of experiments, so determining their effects on the reaction rate. Table III lists the values of k_{obs} which were obtained for each amine and the corresponding experimental conditions.

These k_{obs} showed a linear relationship with amine concentration, and also with reciprocal sodium hydroxide concentration, which suggest the rate law:

$$\text{v} = k_r \frac{[\text{Amine}]}{[\text{OH}^-]}[\text{NaOCl}] \tag{3}$$

$$k_{obs} = k_r \frac{[\text{Amine}]}{[\text{OH}^-]} \tag{4}$$

Figure 2 shows how well this rate law fits the experimental data, with the regression lines passing through the origin in all cases. The slope of each plot was the rate constant k_r for the formation of each amine (Table IV).

In order to calculate the experimental activation energy (E_a) for formation of the *N*-chloramines, the effects of temperature on the reaction rates was studied. The Arrhenius equation was fitted to the rate constants obtained and E_a was calculated, which then enabled calculation of the experimental activation enthalpy, $\Delta H^{\#}$ and, by means of the absolute rate equation the experimental entropy of activation $\Delta S^{\#}$ for each *N*-chloramine (Table V).

TABLE II. Influence of NaOCl concentration on the formation of *N*-chloramines observed first-order rate constants k_{obs}. T = 25°C.

N-chloramine	10^3 [NaOCl]/M	[Amine]/M	[OH$^-$]/M	k_{obs}/s^{-1}
N—Cl-4A1B	0.37 – 1.35	0.010	0.051	5.6 ± 0.2
N—Cl-2A1B	0.31 – 1.19	0.020	0.032	8.9 ± 0.1
N—Cl-AMP	0.31 – 1.19	0.010	0.016	5.61 ± 0.07
N—Cl-EA	0.31 – 1.19	0.010	0.090	4.1 ± 0.2
N—Cl-*n*PA	0.15 – 0.45	0.010	0.050	3.09 ± 0.06
N—Cl-*iso*PA	0.33 – 1.35	0.015	0.051	5.40 ± 0.06

TABLE III. Influence of amine and alkali concentrations on the formation of *N*-chloroalcoholamines observed first-order rate constants k_{obs}. $T = 25°C$.

10^3 [NaOCl]/M	[Amine]/M	[OH$^-$]/M	N—Cl-4A1B k_{obs}/s^{-1}	N—Cl-2A1B k_{obs}/s^{-1}	N—Cl-AMP k_{obs}/s^{-1}
0.63	0.010	0.010	27.70		9.03
0.63	0.010	0.012			7.29
0.63	0.010	0.016			5.61
0.63	0.010	0.017	16.70		
0.63	0.010	0.025	11.05		3.51
0.63	0.010	0.050			2.13
0.63	0.010	0.051	5.71		
0.63	0.010	0.102	2.71		
0.63	0.010	0.190			0.57
0.63	0.010	0.203	1.66		
0.61	0.020	0.020		14.10	
0.61	0.020	0.023		12.30	
0.61	0.020	0.032		8.83	
0.61	0.020	0.060		4.67	
0.61	0.020	0.100		2.92	
0.65	0.026	0.051	15.4		
0.65	0.020	0.051	12.15		
0.65	0.015	0.051	8.89		3.35
0.65	0.0035	0.051	1.94		
0.65	0.0020	0.051	1.15		0.44
0.65	0.006	0.051			1.40
0.65	0.025	0.051			5.55
0.65	0.030	0.051			6.39
0.50	0.0020	0.030		1.02	5.55
0.50	0.0035	0.030		1.58	6.39
0.50	0.005	0.030		2.47	
0.50	0.015	0.030		7.40	
0.50	0.020	0.030		15.19	

TABLE III. Influence of amine and alkali concentrations on the formation of *N*-chloramines observed first-order rate constants k_{obs}. $T = 25°C$.

10^3 [NaOCl]/M	[Amine]/M	[OH$^-$]/M	N—Cl-EA k_{obs}/s^{-1}	N—Cl-*n*PA k_{obs}/s^{-1}	N—Cl-*iso*PA k_{obs}/s^{-1}
0.45	0.0100	0.030	11.90		9.03
0.45	0.0100	0.050	7.46		7.29
0.45	0.0100	0.070	5.10		5.61
0.45	0.0100	0.090	3.92		
0.45	0.0100	0.010	36.00		3.51
0.25	0.0050	0.050		3.28	2.13
0.25	0.0050	0.125		1.35	
0.25	0.0050	0.200		0.87	
0.25	0.0050	0.275		0.66	0.57
0.25	0.0050	0.350		0.64	
0.25	0.0050	0.030		5.85	
0.63	0.0050	0.100	1.86		
0.63	0.0125	0.100	5.31		
0.63	0.0200	0.100	9.37		
0.63	0.0300	0.100	15.60		
0.63	0.0250	0.100	11.79		

TABLE III. (continued)

10^3 [NaOCl]/M	[Amine]/M	[OH^-]/M	N—Cl-EA k_{obs}/s^{-1}	N—Cl-*n*PA k_{obs}/s^{-1}	N—Cl-*iso*PA k_{obs}/s^{-1}
0.25	0.0025	0.030		2.83	
0.25	0.0042	0.030		5.15	
0.25	0.0075	0.030		8.81	
0.25	0.0150	0.030		17.02	
0.25	0.0175	0.030		21.24	
0.25	0.0225	0.030		26.80	
0.28	0.0020	0.051			0.76
0.28	0.0062	0.051			2.40
0.28	0.0100	0.051			3.69
0.28	0.0124	0.051			4.57
0.28	0.0150	0.051			5.39
0.28	0.0175	0.051			6.32
0.28	0.0195	0.051			7.06

Influence of pH

In order to study the influence of pH on the kinetics of the reaction of formation of *N*-chloramines, experiments were carried out in media whose pH was controlled using buffer solutions (NaH_2PO_4/Na_2HPO_4 and H_3BO_3/NaH_2BO_3). The relation-

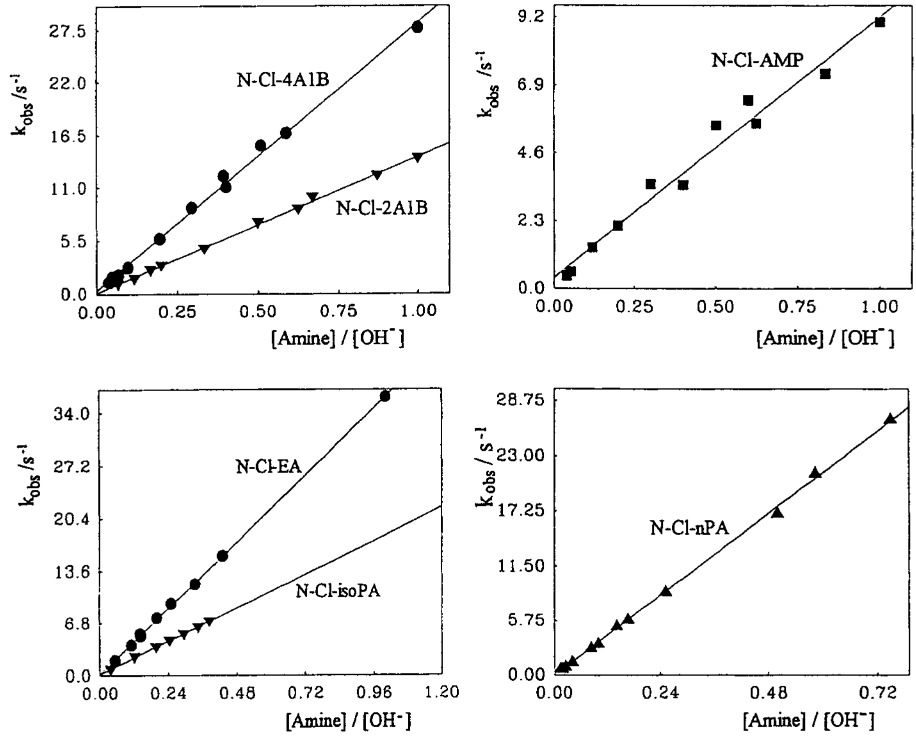

Figure 2. Plots of k_{obs} as a function of the quotient [amine]/[OH^-] (for slopes and standard deviations, see Table IV).

TABLE IV. Values of k_r and standard deviations obtained from the plots in Figure 2.

N-Chloramine	k_r/s^{-1}	pK_a
N—Cl-AMP	9.4 ± 0.3	9.694
N—Cl-2A1B	14.3 ± 0.1	9.516
N—Cl-*iso*PA	18.6 ± 0.1	10.67
N—Cl-4A1B	28.5 ± 0.4	10.38
N—Cl-*n*PA	35.5 ± 0.3	10.566
N—Cl-EA	36.1 ± 0.2	10.636

TABLE V. Experimental activation energies, enthalpies, and entropies (E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$, respectively) for formation of the N-chloramines.

	N—Cl-4A1B	N—Cl-2A1B	N—Cl-AMP	N—Cl-EA	N—Cl-*n*PA	N—Cl-*iso*PA
E_a/kJmol^{-1}	60 ± 3	51 ± 3	61 ± 3	53 ± 2	46 ± 1	43 ± 1
$\Delta H^{\#}/\mathrm{kJmol}^{-1}$	57 ± 3	49 ± 3	59 ± 3	50 ± 3	44 ± 1	40 ± 1
$\Delta S^{\#}/\mathrm{Jmol}^{-1}\mathrm{K}^{-1}$	−26 ± 1	−60 ± 9	−30 ± 1	−46 ± 9	−69 ± 3	−84 ± 5

ship between k_{exp} and pH was nonlinear, exhibiting a maximum characteristic of each amine.

Table VI list the experimental rate constants in the range of pH studied for N—Cl-2A1B and N—Cl-*s*BA (N—Cl-sec-butilamine) and Figures 3 and 4 show the results together with the curve deduced from the proposed mechanism. The corresponding curves fit the data reasonably well and the marked influence of pH upon the rate of formation of N-chloramines must be noted.

Discussion

Reaction Mechanism

The reaction mechanism we propose takes into account existing information about N-chlorination, and the chlorine species possibly present in solution and any equilibria in which they may be involved. The following series of equilibria illustrate the

TABLE VI. Influence of pH on the formation rate constants. [NaClO$_4$] = 0.30 M. T = 25°C. N—Cl-2A1B. [2A1B] = 0.007 M, [NaOCl] = 0.0008 M. N—Cl-*s*BA. [*s*BA] = 0.007 M, [NaOCl] = 0.0008 M.

N—Cl-2A1B		N—Cl-*s*BA	
$k_{\mathrm{obs}}/\mathrm{s}^{-1}$	pH	$k_{\mathrm{obs}}/\mathrm{s}^{-1}$	pH
66 ± 1	6.26	23.4 ± 0.4	7.15
178 ± 2	6.84	40.0 ± 0.3	7.35
423 ± 3	7.33	64.0 ± 1.4	8.00
745 ± 5	8.03	70.0 ± 1.0	8.30
840 ± 5	8.38	80.0 ± 1.5	8.76
755 ± 5	8.98	80.0 ± 0.4	9.20
536 ± 4	9.59	76.4 ± 1.3	9.73
578 ± 3	9.39	73.0 ± 0.9	9.84

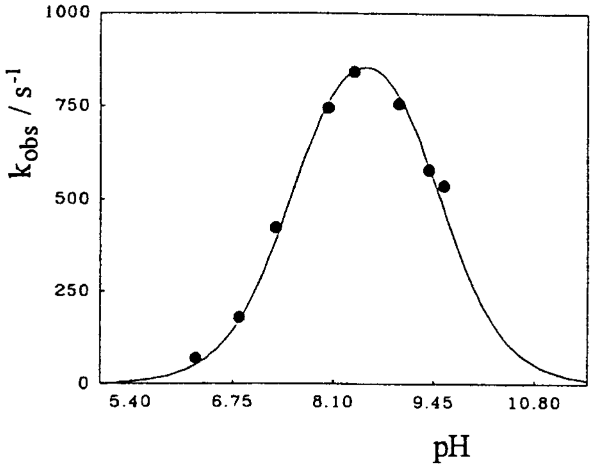

Figure 3. Influence of pH on the formation rate constants of N—Cl-2A1B. The symbols represent the experimental data while the theoretical dependence is shown by the solid line.

general case of RNH_2:

(5) $$HOCl \overset{K_1}{\rightleftharpoons} OCl^- + H^+$$

(6) $$RNH_3^+ \overset{K_2}{\rightleftharpoons} RNH_2 + H^+$$

(7) $$RNH_2 + HOCl \rightleftharpoons X_3^{\neq} \xrightarrow{k_3} RNHCl + H_2O$$

(8) $$RNH_3^+ + HOCl \rightleftharpoons X_4^{\neq} \xrightarrow{k_4} RNHCl + H_3O^+$$

(9) $$RNH_2 + OCl^- \rightleftharpoons X_5^{\neq} \xrightarrow{k_5} RNHCl + OH^-$$

(10) $$RNH_3^+ + OCl^- \rightleftharpoons X_6^{\neq} \xrightarrow{k_6} RNHCl + H_2O$$

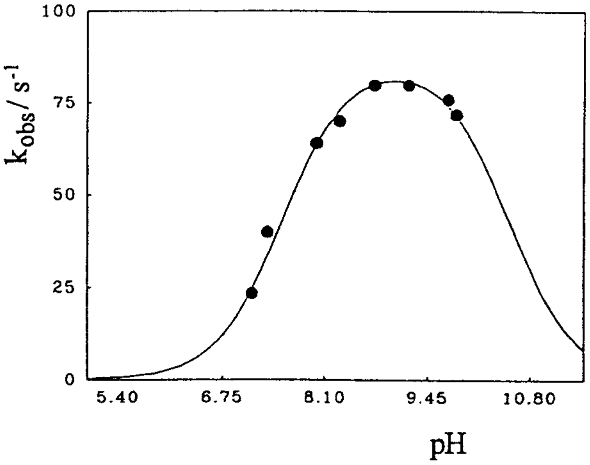

Figure 4. Influence of pH on the formation rate constants of N—Cl-*s*BA. The symbols represent the experimental data while the theoretical dependence is shown by the solid line.

If formation of the N-chloramine were to occur solely via reaction 7, the rate law would be

$$\text{v} = \frac{d[\text{RNHCl}]}{dt} = k_3[\text{RNH}_2][\text{HOCl}] \tag{11}$$

Taking into account the acid-base equilibria occurring in solution (reactions 5 and 6 above), and assuming that they proceed much more rapidly than the reaction of interest, the reaction rate can be expressed as

$$\text{v} = k_3[\text{Cl}_T][\text{Am}]\frac{[\text{H}^+]}{(K_1 + [\text{H}^+])}\frac{K_2}{(K_2 + [\text{H}^+])} \tag{12}$$

$$k_{\text{obs}} = k_3[\text{Am}]\frac{[\text{H}^+]}{(K_1 + [\text{H}^+])}\frac{K_2}{(K_2 + [\text{H}^+])} \tag{13}$$

where

$$[\text{Am}] = [\text{RNH}_3{}^+] + [\text{RNH}_2] \tag{14}$$

and

$$[\text{Cl}_T] = [\text{HOCl}] + [\text{OCl}^-] \tag{15}$$

Using eq. (13) to fit the observed rate constants against the different proton concentrations, the absolute rate constants to the molecular and ionic mechanisms, k_3 and k_6, respectively, were obtained. If the inverse process is realized, replacing k_3 and K_2 values in eq. (13), the theoretical curve shown in Figures 3 and 4 can be drawn. The same procedure can be used to the ionic mechanism. These curves reproduce satisfactorily the experimental behavior, which confirm the proposed mechanism.

Since, in reaction 5 above, the acid dissociation constant $pK_1 = 7.54$ [9] at 25°C and, in reaction 6, pK_2 ranges from 9–11 for the amines under study [10], under the conditions of $\text{pH} > 12$, both K_1 and K_2 will be $\gg [\text{H}^+]$, and the reaction rate expression simplifies to

$$\text{v} = k_3\frac{K_w}{K_1}[\text{Cl}_T]\frac{[\text{Amine}]}{[\text{OH}^-]} = k_{\text{obs}}[\text{Cl}_T] \tag{16}$$

$$k_{\text{obs}} = k_3\frac{K_w}{K_1}\frac{[\text{Amine}]}{[\text{OH}^-]} = k_r\frac{[\text{Amine}]}{[\text{OH}^-]} \tag{17}$$

where K_w is the ionic product of water.

This process was repeated for reactions 8, 9, and 10, and it was shown that under the conditions employed only reactions 7 and 10 gave reaction rate expressions consistent with the experimental observations. For reaction 10 the reaction rate is expressed as follows:

$$\text{v} = k_6\frac{K_w}{K_2}[\text{Cl}_T]\frac{[\text{Amine}]}{[\text{OH}^-]} = k_{\text{obs}}[\text{Cl}_T] \tag{18}$$

$$k_{\text{obs}} = k_6\frac{K_w}{K_2}\frac{[\text{Amine}]}{[\text{OH}^-]} = k_r\frac{[\text{Amine}]}{[\text{OH}^-]} \tag{19}$$

These reaction rate expressions correspond to a molecular (k_3) and an ionic reaction mechanism (k_6), either of which could be occurring and both of which could account for the kinetic data obtained in this work. Moreover, if the above equations are redefined in terms of activities, e.g., for k_3 in reaction 7.

$$k_3 = k_3^0\frac{K_w}{K_1}\frac{\gamma_{\text{OCl}^-}\gamma_{\text{A}^-}}{\gamma_3{}^{\neq}\gamma_{\text{OH}^-}} \tag{20}$$

(where k_3^0 is the rate constant at zero ionic strength and $\gamma_3{}^{\#}$ is the activity coefficient of the activated complex $X_3{}^{\#}$), by considering the solution to be sufficiently dilute for the Debye-Hückel limiting law to be applicable and the overall charge of the activated complex to be the sum of the charges of the ions which comprise it, it can be shown that the rate law is independent of the activity coefficient (and similarly for k_6):

$$k_3 = k_3^0 \frac{K_w}{K_1} \tag{21}$$

$$k_6 = k_6^0 \frac{K_w}{K_2} \tag{22}$$

This is in keeping with the observation that, under the conditions employed (pH > 12), the observed rate in this work was independent of ionic strength.

It can be easily demonstrated that the rate law established for chlorination at pH values 5–10 is valid in strongly alkaline solution, with only the proposed mechanisms (reactions 7 or 10) accounting for the experimental results. The fact that both mechanisms are apparently valid is explained by the acid-base equilibria occurring in the aqueous solution: these involve very rapid proton transfer between the reactant species, and as a result the precise mechanism cannot be determined by studying the reaction kinetics [11].

Influence of the Substituent

From the experimental data the rate constant k_3 (k_{HOCl}) for molecular mechanism (reaction 7) of each amine can be calculated, the logarithm of which shows a linear relationship with the pK_2 of the amine, as shown in Figure 5 (which also includes some values taken from the literature [2]). Linear regression yields the equation

$$\log k_{\mathrm{HOCl}} = (2.9 \pm 0.5) + (0.48 \pm 0.05)pK_2 \tag{23}$$

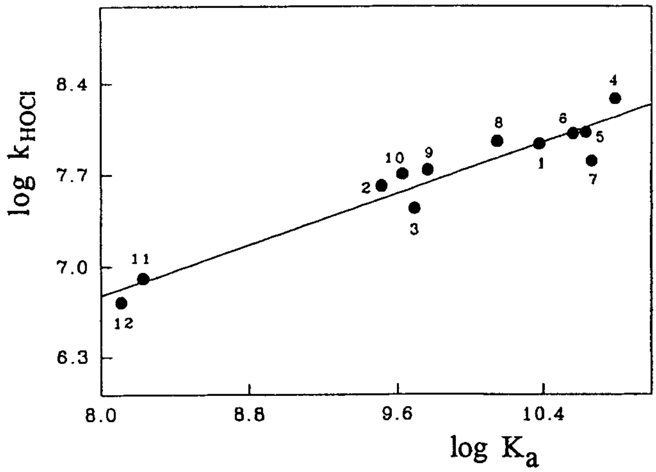

Figure 5. Plot of the log of the rate constant for the molecular mechanism, k_{HOCl} (k_3) as function of pK_2 of amines: 4A1B (1); 2A1B (2); AMP (3); MA (4); EA (5); *n*PA (6); *iso*PA (7); β-alanine (8); alanine (9); glycine (10); 2-amino-2-(hydroxymethyl)-1,3-propandiol (11); and glycylglycine (12).

and analogous equations were obtained by using k_6 (k_{OCl^-}) or k_r. Since k_r is independent of reagent concentrations, and therefore constant for a given reaction at a given temperature, its value or logarithmic relation to pK_2 can be compared with those of other amines regardless of any differences in mechanism (molecular or ionic).

The above relationship clearly establishes the dependence of the rate on the pK_2 of the amine, which is in turn dependent on the nature of the substituent group. Overall substituent constants $\sum\sigma^*$ have been used [12] to establish a Taft relationship between the nature of the substituent and the pK_2, and a similar relationship was found for log k_{HOCl} (Fig. 6), described by the equation:

$$\log k_{\mathrm{HOCl}} = (7.2 \pm 0.2) + (0.7 \pm 0.3)\sum\sigma^* \tag{24}$$

and similar relationships were again obtained for k_{OCl^-} or k_r.

The above equations can be used to calculate a value of k_{HOCl} (or k_{OCl^-} or k_r) from amine pK_2 values or substituent constants σ^*, which together with K_w, amine and hypochlorous acid concentrations and pH, could then be used to predict the rate of formation of *N*-chloramines.

Activation Parameters

From the results of our studies of the influence of temperature on the observed rates activation enthalpy and entropy values, ($\Delta H^{\#}$ and $\Delta S^{\#}$), can be calculated for both the proposed mechanisms by means of the appropriate equations: for the molecular mechanism (reaction 7)

$$\Delta H_3{}^{\neq} = \Delta H^{\neq} - \Delta H_w + \Delta H_1 \tag{25}$$

$$\Delta S_3{}^{\neq} = \Delta S^{\neq} - \Delta S_w + \Delta S_1 \tag{26}$$

and for the ionic mechanism (reaction 10)

$$\Delta H_6{}^{\neq} = \Delta H^{\neq} - \Delta H_w + \Delta H_2 \tag{27}$$

$$\Delta S_6{}^{\neq} = \Delta S^{\neq} - \Delta S_w + \Delta S_2 \tag{28}$$

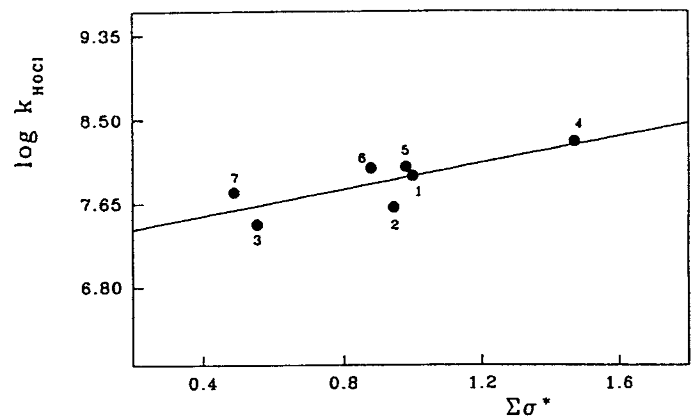

Figure 6. Taft correlation plot of log k_{HOCl} (k_3) as a function of the overall substituent constants $\sum\sigma^*$ of amines: 4A1B (1); 2A1B (2); AMP (3); MA (4); EA (5); *n*PA (6); and *iso*PA (7).

TABLE VII. Calculated activation enthalpies and entropies for formation of the *N*-chloramines formed by the molecular mechanism ($\Delta H_3{}^{\#}$ and $\Delta S_3{}^{\#}$, respectively) or the ionic mechanism ($\Delta H_6{}^{\#}$ and $\Delta S_6{}^{\#}$, respectively).

	N—Cl-4A1B	N—Cl-2A1B	N—Cl-AMP	N—Cl-EA	N—Cl-*n*PA	N—Cl-*iso*PA
$\Delta H_3{}^{\#}$/kJmol^{-1}	19	11	21	12	6	2
$\Delta S_3{}^{\#}$/Jmol^{-1}K^{-1}	−30	−64	−34	−50	−73	−88
$\Delta H_6{}^{\#}$/kJmol^{-1}		46	58	53	47	44
$\Delta S_6{}^{\#}$/Jmol^{-1}K^{-1}		17	49	26	5	9

where ΔH_2 and ΔS_2 are the enthalpies and entropies of activation, respectively, corresponding to the protonation of the amines studied, and ΔH_1 and ΔS_1, and ΔH_w and ΔS_w are the equivalent quantities for the dissociations of hypochlorous acid and water, respectively.

For the molecular mechanism calculated enthalpy values (Table VII) are all below 20 kJ/mol, which is considered the upper limit for diffusion controlled reactions; while $\Delta S_3{}^{\#}$ values are all negative, suggesting a transition state with a higher degree of organization than that of the reactants. If the molecular mechanism were to proceed via nucleophilic attack of the hypochlorous acid by amine, with a water molecule assisting the displacement of −OH (a rather poor leaving group), a cyclic transition state [1] stabilized by hydrogen bonds might result, which would account for the low enthalpies of activation and relatively low rate constants.

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