JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 447–454 (1996)

KINETIC STUDY OF THE DECOMPOSITION OF *N*-CHLORAMINES

J. M. ANTELO, F. ARCE AND M. PARAJÓ

Departamento de Química Física, Facultad de Química, Universidad de Santiago, E- Santiago de Compostela, Spain

The decomposition of various *N*-chloroalkylamines and *N*-chloroalcoholamines was investigated kinetically at pH 4–12 and in strongly alkaline media. The rate of *N*-chloramine decomposition increased with increasing pH above pH 10, remained virtually constant over the pH range 7–10 and again increased with decreasing pH in the acidic zone. The results are described by a rate equation involving general base catalysis terms. Experimental evidence suggests that the decomposition of *N*-haloamines proceeds via an elimination mechanism that yields an imine. This β-elimination process is a non-synchronized concerted mechanism where cleavage of the N—X bond has progressed to a greater extent than that of the C_α—H by the time the transition state is reached, which is therefore '*E*1-like' (i.e. with a transition state having a certain nitrenium character).

INTRODUCTION

The large amount of nitrogen-containing compounds present in natural waters[1] endows the decomposition of *N*-chloramines with great practical interest as it is one of the reactions involved in water purification by treatment with chlorine or hypochlorite ion.

This type of reaction has been the object of kinetic studies aimed at elucidating its mechanism. Antelo and co-workers[2,3] studied the reactions of *N*-chloro-*N,N*-dimethylammonium ion and *N*-chlorodiethanolamine with hypochlorite ion and other chlorinating agents over the pH range 6·55–12·01. More recently, the decomposition of various secondary *N*-chloramines was also investigated.[4]

The stability of *N*-chloramines derived from amino acids has also been the subject of several kinetic studies in the light of which potential reaction mechanisms in aqueous solution have been discussed. Thus, Fox and Bullock[5] put forward a mechanism involving the loss of an α-proton to yield a carbanionic intermediate as the rate-determining step; subsequently, the intermediate releases a chlorine atom and produces an imine which is rapidly hydrolysed. Stambro and Smith[6] studied the decomposition of *N*-chloroalanine. Also, Hand *et al.*[7] and Awad *et al.*[8] investigated the kinetics and mechanism of the decomposition of various amino acids, and found the rate constant to depend on the amino acid structure. Abia *et al.*[9] studied the kinetics of decomposition of *N*-chlorovaline in aqueous solution using sodium hypochlorite as the chlorinating agent. Finally, the stability of some *N*-chloropeptides has also been studied in this context.[10,11]

This paper summarizes the results obtained in a study of the decomposition of various chloramines, namely *N*-chloromethylamine (*N*-C1-MA), *N*-chloroethylamine (*N*-Cl-EA), *N*-chloro-*n*-propylamine (*N*-Cl-nPA), *N*-chloroisopropylamine (*N*-Cl-iPA), *N*-chloro-*n*-butylamine (*N*-Cl-*n*BA), *N*-chloroisobutylamine (*N*-Cl-iBA), *N*-chloro-*sec*-butylamine (*N*-Cl-sBA), *N*-chloro-4-aminobutan-1-ol (*N*-Cl-4AlB), *N*-chloro-2-aminobutan-1-ol (*N*-Cl-2AlB), *N*-chloro-2-amino-2-methylpropan-1-ol (*N*-Cl-AMP), *N*-chloro-2-aminopropan-1-ol (*N*-Cl-2A1Pr) and *N*-chloroethanolamine (*N*-C1-ETA).

EXPERIMENTAL

All reagent solutions were made by weighing the required amount of commercially available chemical (Merck, p.a. grade) and dissolving it in doubly distilled water. Boric acid–sodium borate and sodium carbonate–sodium hydrogencarbonate buffers were also prepared by weighing, from boric acid and sodium hydrogencarbonate (all Merck p.a. reagents), to which the required volume of sodium hydroxide at an appropriate concentration was added in order to adjust the pH to the desired value. Acetic acid–sodium acetate buffer solutions were made by weighing from commercially available chemicals (Merck, p.a. grade). Phosphate buffers were prepared from Na_2HPO_4 and NaH_2PO_4 (Merck, p.a grade) and supplied with an appropriate volume of sodium hydroxide at the required concentration.

Sodium hypochlorite was obtained by dropwise addition of concentrated hydrochloric acid over potassium permanganate solution, which produced a stream of

CCC 0894–3230/96/070447–08

Received 20 June 1995
Revised 22 January 1996

gaseous chlorine. The chlorine was first passed through potassium permanganate solution in order to oxidize residual HCl and then bubbled through 0·5 M sodium hydroxide. The solution thus obtained was kept in a UV-opaque flask at pH > 11 in order to avoid decomposition. The concentrations of these solutions were determined spectrophotometrically by measuring their absorbance at 292 nm (the absorption maximum for sodium hypochlorite, where its molar absorptivity coefficient[12] is $\varepsilon = 350\ \mathrm{l\,mol^{-1}\,cm^{-1}}$). The sodium hypobromite used to prepare the *N*-bromamines was obtained from commercial-grade bromine in an alkaline medium.[13]

Spectrophotometric measurements were made on a Kontron 930 instrument, the cuvette holder of which was thermostatted by circulating water from a thermostatic bath.

N-Chloramine decay products were analysed by HPLC using a Beckman chromatograph furnished with a C_{18} column and using acetonitrile-water (50:50) as the mobile phase.

pH measurements were made with a Radiometer PHM82 pH meter equipped with a GK2401C combined glass/KCl-saturated calomel electrode, also from Radiometer. The pH meter was calibrated with commercially available buffers of pH 4·01, 7·00, 10·01 and 12·45.

N-Chloramines were obtained *in situ* by reaction of the corresponding amine with sodium hypochlorite.[14] In order to establish the optimum conditions for monitoring the reaction, their decomposition was preliminarily studied using a spectrophotometric procedure. *N*-Chloramines exhibit an absorption maximum at *ca.* 250 nm, the height of which decreases with time. Figure 1 shows the spectrum for the decomposition of *N*-Cl-2A1B. Both the spectral maximum and the molar absorption coefficient were found to be pH independent at the wavelength of maximum absorption for the compound. Below pH 4, the absorbance decreased with decreasing pH owing to protonation and disproportionation of the *N*-chloramine. The spectrophotometric study revealed 250 nm to be a suitable wavelength for monitoring the reaction as no other reactant was found to absorb appreciably at this value.

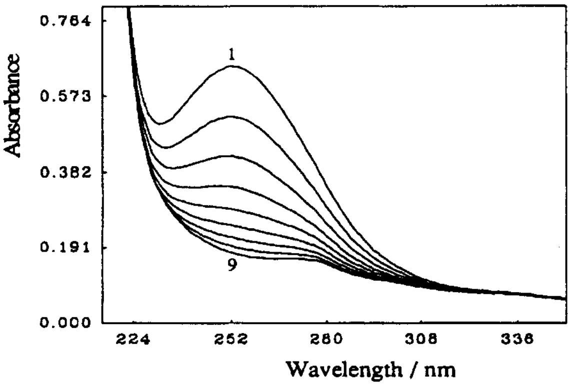


Figure 1. Absorption spectrum obtained during the decomposition of *N*-chloroaminobutan-1-ol. $[2A1B] = 5 \times 10^{-2}$ M; $[NaOCl] = 9 \times 10^{-4}$ M, $[NaOH] = 0{\cdot}1$ M; $[NaCl] = 0{\cdot}49$ M; $T = 25$ °C; $t_i = 10$ s; $\Delta t = 5$ min

N-bromamines were obtained by reaction between the parent amines and sodium hypobromite. Their kinetics of decomposition were monitored similarly to the *N*-chloramines.

The reaction order was determined by fitting absorbance-time data to the integrated first-order rate equation:

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - kt$$

where A_0, A_t and A_∞ are the absorbance at time zero, t and infinity, respectively. The equation was solved by using a computational program based on the Davies-Swan-Campey algorithm.[15] The reaction was monitored to at least 80% completion in every case and the correlation coefficient was always greater than 0·999.

The good fit obtained confirms the assumed order for the process. Preliminary studies on this type of reaction below pH 11 revealed that the decomposition is very slow under these conditions. This necessitated the use of the initial-rate method in the kinetic analysis of the data obtained.

Product analysis

According to the previous results,[16] the decomposition of *N*-chloramines yields an aldehyde (or ketone) and ammonia. Aldehydes and ketones can be identified by a general test for carbonyl compounds[17] using 2,4-dinitrophenylhydrazine (which forms a dinitrophenylhydrazone). Addition of a few drops of this reagent to our reaction mixture produced a crystalline precipitate that revealed the presence of carbonyl compounds in the reaction medium.[18] However, this test does not allow one to distinguish between aldehydes and ketones, or to determine them quantitatively. The most frequently used method for measuring small amounts of these carbonyl compounds involves the formation of the corresponding 2,4-dinitrophenylhydrazone and its analysis by HPLC. Hydrazones exhibit an absorption band at 337 nm, the wavelength at which they were studied here.

The hydrazones were then determined using a Beckman reversed-phase 5 mm Ultrasphere C_{18} column, using a acetonitrile/water (50:50, v/v) as the mobile phase and peak detection at 337 nm with two internal standards (formaldehyde and acetaldehyde). The flow rate was 1 $\mathrm{ml\,min^{-1}}$. Peak areas for 2,4-dinitrophenylhydrazones of carbonyl compounds were obtained by electronic integration of the absorbance at this wavelength.

We found formaldehyde to be formed in the decomposition of *N*-Cl-2AlB, *N*-Cl-AMP and *N*-Cl-2AlPr, with yields of 70%, 60% and 41%, respectively, and acetaldehyde to be obtained from *N*-Cl-2AlPr in 51% yield.

RESULTS

The concentrations of sodium hypochlorite, amine and sodium chloride (the supporting electrolyte used to adjust the ionic strength) were found not to have any appreciable influence on the rate of *N*-chloramine decomposition.

The results of a series of experiments carried out in strongly basic media using various concentrations of sodium hydroxide and constant concentrations of all other reagents showed the rate constant to increase with increasing NaOH concentration. Figures 2 and 3 show that both the *N*-chloroalkylamines and the *N*-chloroalcoholamines complied with the equation:

$$\log k_{obs} = \text{constant} + H_-$$

where H_- is Yagil's[19] acidity function (a more appropriate measure of basicity than pH for these media).

The reaction of *N*-chloroalkylamines was slower than that of *N*-chloroalcoholamines, probably owing to the absence of an OH^- group (Figures 2 and 3).

To study the influence of the reagents on the rate of *N*-chloramine decomposition in the pH range 4–12, experiments were carried out in acetic acid–sodium acetate, boric acid–sodium borate, sodium carbonate–sodium hydrogencarbonate, disodium hydrogenphosphate–sodium hydroxide and sodium dihydrogenphosphate–sodium hydroxide buffers. Several different buffer concentrations were used, and since the decomposition rates increased linearly with increasing buffer concentration [Figure 4(a)–(e)], rate constants at zero buffer concentration were calculated as the *y*-intercepts of the straight lines fitted to these data. The decomposition rates increased with increasing pH above pH 10, remained virtually constant over the pH range 7–10 and then increased again with decreasing pH in the acidic region (Figure 5 shows the results for *N*-Cl-2AlB).

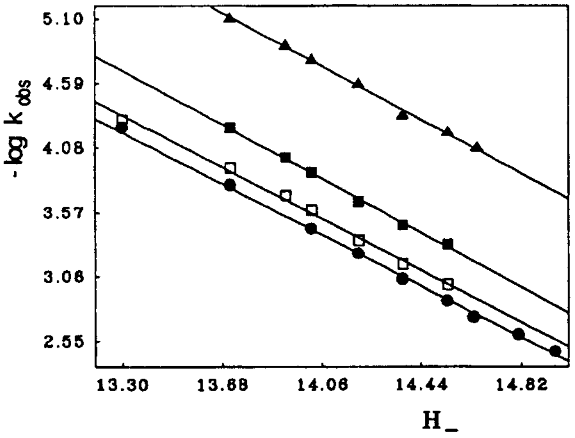


Figure 2. Influence of pH on the rate of decomposition of aliphatic *N*-chloramines in a strongly alkaline media. (▲) *N*-Cl-MA ($\log k = 20{\cdot}33 - 1{\cdot}10\,H_-$); (■) *N*-Cl-EA ($\log k = 19{\cdot}72 - 1{\cdot}12\,H_-$); (●) *N*-Cl-nPA ($\log k = 18{\cdot}61 - 1{\cdot}05\,H_-$); (□) *N*-Cl-iPA ($\log k = 18{\cdot}65 - 1{\cdot}07\,H_-$)

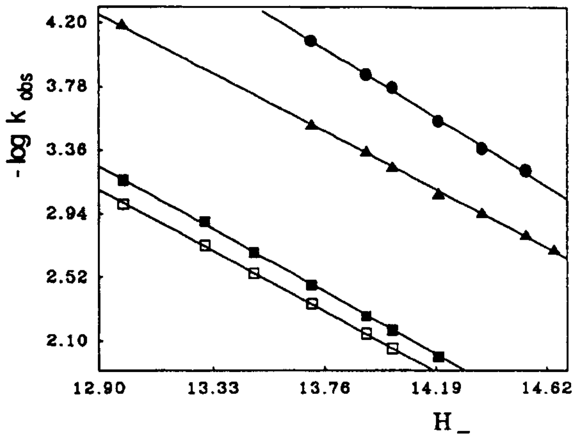


Figure 3. Influence of pH on the rate constant of decomposition of *N*-chloroalcoholamines in strongly alkaline media. (●) *N*-Cl-4AlB ($\log k = 16{\cdot}76 - 1{\cdot}05\,H_-$); (Δ) *N*-Cl-2AlB ($\log k = 15{\cdot}18 - 0{\cdot}94\,H_-$); (■) *N*-Cl-2AlPr ($\log k = 15{\cdot}71 - 0{\cdot}97\,H_-$); (▲) *N*-Cl-ETA ($\log k = 15{\cdot}77 - 0{\cdot}90\,H_-$)

To study the effect of the leaving group on *N*-haloamine decomposition, we carried out experiments with *N*-bromamines under similar conditions. Table 1 gives the values of k_{Br}/k_{Cl}, the ratio of the corresponding observed rate constants.

Table 1. Values of k_{Br}/k_{Cl} for decomposition of *N*-haloalcoholamines and *N*-haloalkylamines at 25 °C.

N-Haloalcoholamine	k_{Br}/k_{Cl}	*N*-Haloalkylamine	k_{Br}/k_{Cl}
N-X-4AlB	12	*N*-X-iBA	11
N-X-ETA	20	*N*-X-EA	12
N-X-2AlPr	23	*N*-X-nBA	14
N-X-AMP	27	*N*-X-nPA	14
N-X-2AlB	31	*N*-X-iPA	24
		N-X-sBA	24
		N-X-MA	44

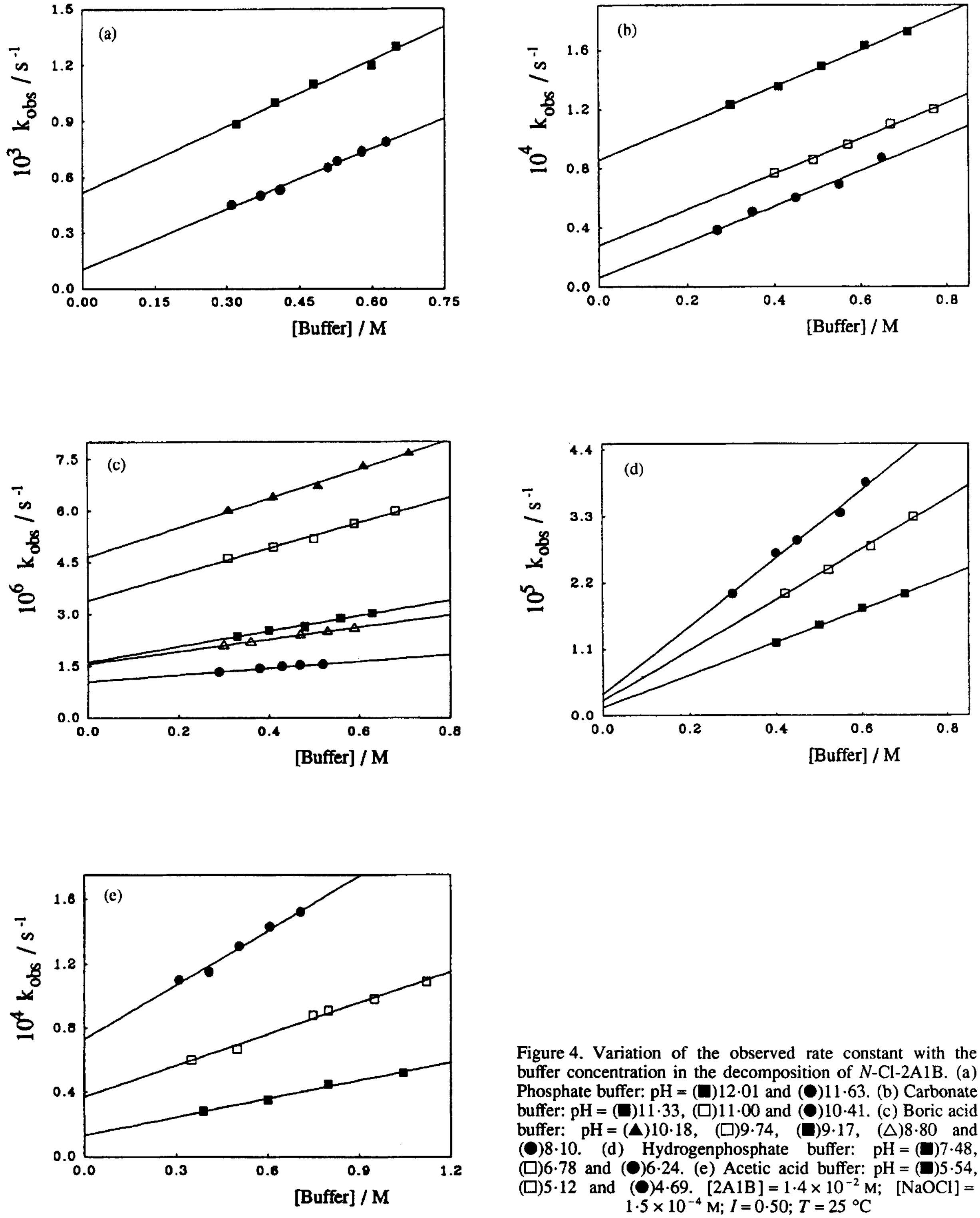


Figure 4. Variation of the observed rate constant with the buffer concentration in the decomposition of *N*-Cl-2A1B. (a) Phosphate buffer: pH = (■)12·01 and (●)11·63. (b) Carbonate buffer: pH = (■)11·33, (□)11·00 and (●)10·41. (c) Boric acid buffer: pH = (▲)10·18, (□)9·74, (■)9·17, (△)8·80 and (●)8·10. (d) Hydrogenphosphate buffer: pH = (■)7·48, (□)6·78 and (●)6·24. (e) Acetic acid buffer: pH = (■)5·54, (□)5·12 and (●)4·69. [2A1B] = $1{\cdot}4 \times 10^{-2}$ M; [NaOCl] = $1{\cdot}5 \times 10^{-4}$ M; $I = 0{\cdot}50$; $T = 25$ °C

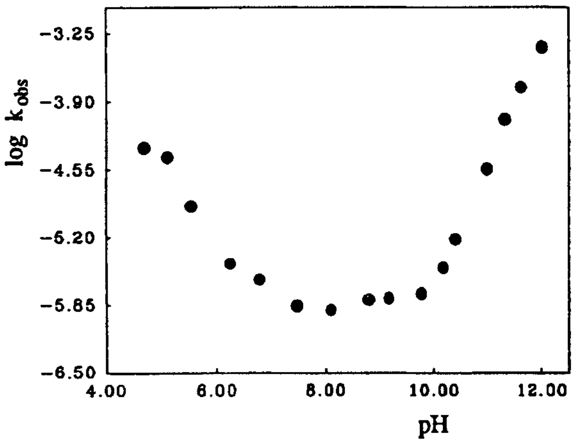


Figure 5. Influence of pH on the rate constant of decomposition of *N*-Cl-2A1B

DISCUSSION

When amine and hypochlorous or hypobromous acid solutions are mixed, on *N*-haloamine[14] is rapidly obtained:

$$\mathrm{HOX} \overset{K_1}{\rightleftharpoons} \mathrm{OX^-} + \mathrm{H^+} \quad (1)$$

$$\mathrm{RNH_2} + \mathrm{H^+} \overset{K_2}{\rightleftharpoons} \mathrm{RNH_3^+} \quad (2)$$

$$\mathrm{RNH_2} + \mathrm{HOX} \longrightarrow \mathrm{RNHX} + \mathrm{H_2O} \quad (3)$$

Our experimental results show that the decomposition of *N*-haloamines is a bimolecular process:

$$\mathrm{RNHX} + \mathrm{B} \longrightarrow \text{products} \quad (4)$$

where X is a Cl or Br atom and B is the base present in the medium.

The results obtained for *N*-chloramines in strongly alkaline media and in phosphate, carbonate and boric acid buffers [Figures 4(a)–(c) show the latter results for *N*-Cl-2A1B] are in keeping with a rate equation reflecting general base catalysis:

$$-\frac{\mathrm{d}[N\text{-chloramine}]}{\mathrm{d}t} = k_{obs}[N\text{-chloramine}] \quad (5)$$

where

$$k_{obs} = k_a + k_{OH}[\mathrm{OH^-}] + k_{cat}[\mathrm{B}] \quad (6)$$

k_a, k_{OH} and k_{cat} being the rate constants for the uncatalysed reaction, the $\mathrm{OH^-}$-catalysed reaction and the reaction catalysed by the basic form of the buffer (if present), respectively. In fact plotting k_{obs} against $[\mathrm{OH^-}]$ for the reactions carried out in highly alkaline media in the absence of buffer produced straight lines whose *y*-intercepts did not differ significantly from zero, showing that under these conditions the only operative reaction path involves surrender of a proton to $\mathrm{OH^-}$ (the values of k_{OH} given by the slopes of these plots are given in Table 2).

However, catalysis by the hydrogenphosphate and acetic acid buffers used at pH 4–7 was greater than expected at low pH [Figure 4(d) and 4(e)]; this behaviour, indicative of general acid catalysis ($k_{obs} = k_a + k_H[\mathrm{H^+}] + k_{cat}[\mathrm{A}]$, where A is the acid form of the buffer), suggests that in this pH range the buffers catalysed the disproportionation reactions by which *N*-chloramines decompose at low pH, which are known to be subject to general acid catalysis.[20,22] (The fact that the reaction rate at zero buffer concentration increased with decreasing pH in the pH range 4–7 is also attributed to increasing involvement of the disproportionation path.) Table 3 gives the values of k_{cat} obtained for *N*-Cl-2A1B from the slopes of the plots of Figure 4(a)–(e).

The general base catalysis observed in strongly alkaline media and in phosphate, carbonate and boric acid buffers is in keeping with the mechanism shown in Scheme 1: β-elimination leading to an imine that is rapidly hydrolysed to an aldehyde or a ketone.

In the case of *N*-chloroalcoholamines, an alternative possibility is for the group lost from the β-carbon to be a deprotonated form of the starting compound (Scheme 2).

Table 2. Values of k_{OH^-} for decomposition of *N*-chloroalcoholamines and *N*-chloroalkylamines at 25 °C.

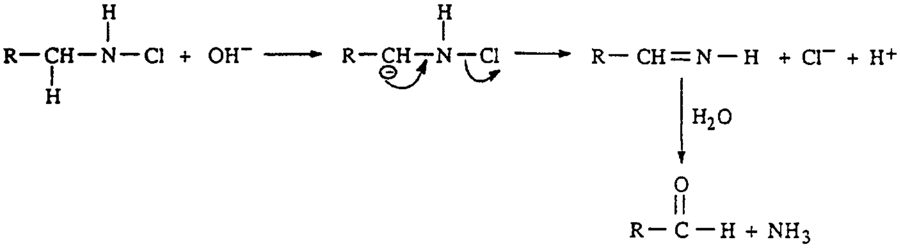
N-Chloroalcoholamines	$10^3\,k_{\mathrm{OH}^-}$/l mol^{-1} s^{-1}	*N*-Chloroalkylamine	$10^4\,k_{\mathrm{OH}^-}$/l mol^{-1} s^{-1}
N-Cl-4A1B	0·177 ± 0·005	*N*-Cl-MA	0·166 ± 0·003
N-Cl-ETA	0·57 ± 0·08	*N*-Cl-iBA	1·04 ± 0·03
N-Cl-2A1Pr	6·83 ± 0·03	*N*-Cl-nBA	1·19 ± 0·07
N-Cl-AMP	81·0 ± 0·02	*N*-Cl-EA	1·26 ± 0·03
N-Cl-2AlB	9·00 ± 0·06	*N*-Cl-nPA	1·30 ± 0·02
N-Cl-3AP	15·00 ± 0·05	*N*-Cl-iPA	2·50 ± 0·04
		N-Cl-sBA	3·50 ± 0·10

Table 3. Values of k_{cat} for base-catalysed decomposition of *N*-chloro-2-aminobutan-1-ol ([2A1B] = $1{\cdot}4 \times 10^{-2}$ M; [NaClO] = $1{\cdot}5 \times 10^{-3}$ M; $I = 0{\cdot}20$ M) of p*K*a and of *p* and *q* in the Brønsted relationship for each catalysing base

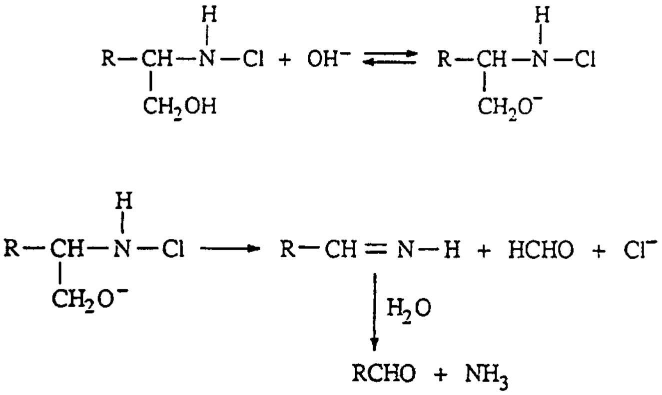
Base	pk_a	k_{cat}/l mol^{-1} s^{-1}	*p*	*q*
H_2O	−1·74	$2{\cdot}47 \times 10^{-8}$	3	1
AcO^-	4·75	$1{\cdot}50 \times 10^{-6}$	1	1
HPO_4^{2-}	7·21	$5{\cdot}20 \times 10^{-6}$	2	2
$BO_3H_2^-$	9·24	$4{\cdot}65 \times 10^{-6}$	3	1
CO_3^{2-}	10·25	$1{\cdot}21 \times 10^{-4}$	1	2
PO_4^{3-}	12·32	$1{\cdot}14 \times 10^{-3}$	1	3
OH^-	15·74	$9{\cdot}00 \times 10^{-3}$	2	2

Two questions therefore arise: (1) which path is more important for *N*-chloroalcoholamines, that of Scheme 1 or that of Scheme 2; and (2) is the β-elimination reaction (a) an *E*1 reaction involving the rate-controlling formation of a nitrenium ion and subsequent loss of the C_α substituent, (b) an *E*1*cB* reaction in which formation of a carbanion is followed by loss of the chloride ion or (c) a concerted (*E*2) reaction in which the N—Cl and C_α—H bonds are cleaved simultaneously? The three possible β-elimination mechanisms are illustrated in the More O'Ferrall–Jencks diagram[23,24] shown in Figure 6, which depicts the path of the reaction on a two-dimensional energy surface whose coordinates are the extent of C_α—H cleavage (horizontal axis) and the extent of N—Cl cleavage (vertical axis). The problem of distinguishing between *E*1, *E*1*cB* and *E*2 mechanisms has been extensively studied by Bordwell,[25] Saunders and Cockerill[26] and Cockerill and Harrison,[27] among others.

The *E*1 mechanism is immediately ruled out by the fact that the observed decomposition kinetics were bimolecular rather than unimolecular. An 'irreversible' *E*1*cB* mechanism can also be ruled out, because rate-controlling C_α—H cleavage is incompatible with the large increase in reaction rate when chlorine was replaced by the better leaving group bromine (Table 1), while a 'reversible' or 'pre-equilibrium' *E*1*cB* mechanism (postulating rate-controlling N—Cl cleavage) is unable to explain the observed general base catalysis. The reaction must therefore be of *E*2 type. To investigate whether N—Cl cleavage and C_α—H cleavages are exactly synchronized (as represented by the diagonal in Figure 6), or whether, in the transition state, N—Cl cleavage is more or less advanced than C_α—H cleavage (situations represented by curved paths lying in the



Scheme 1



Scheme 2

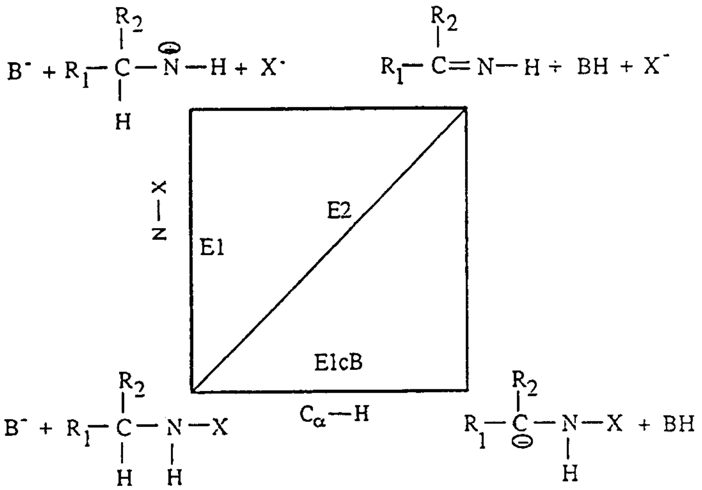


Figure 6. More O'Ferrall–Jencks diagram for the decomposition of *N*-chloramines showing the spectrum of bimolecular elimination mechanisms in terms of bond-breaking orders

upper left and lower right regions of the diagram, respectively),[28] we examined Brønsted plots and Taft correlations.

When the data obtained in the various media for each *N*-chloramine were fitted with Brønsted equations, i.e. equations of the form

$$\log\left(\frac{k_{cat}}{q}\right) = \log G_B + \beta\left[\log\left(\frac{p}{q}\right) + \mathrm{p}K_a\right] \qquad (7)$$

where q is the number of individual indistinguishable positions in a base where a proton can be accommodated and p is the number of equivalent dissociable protons in the conjugate acid form, the values of β so obtained ranged from 0·20 to 0·31. For example. the equation obtained for *N*-Cl-2A1B (Figure 7) using the data listed in Table 3 was

$$\log\left(\frac{k_{cat}}{q}\right) = -7{\cdot}35 + 0{\cdot}31\left[\log\left(\frac{p}{q}\right) + \mathrm{p}K_a\right] \qquad (8)$$

These values of β are within the range 0·2–0·8 associated with most cases of general catalysis (in fact, values close to zero or unity make general catalysis very difficult to observe, in the latter case because of the dominance of the proton or hydroxide ion due to their extreme $\mathrm{p}K_a$ values); and they are keeping with reported data for other *N*-chloramines.[29] Since β is usually taken to be a measure of the extent of proton transfer in the transition state (although known cases[30] in which β lies outside the range [0, 1] show that the assumptions underlying this interpretation are not always fulfilled), the values of β obtained in this work suggest that in the transition state of the β-elimination process, the C_α—H bond is relatively intact.

Figure 8 shows Taft plots of $-\log k_{exp}$ (measured at [NaOH] = 1 M and [*N*-chloramine] = 2×10^{-3} M) against the total electron-withdrawing capacity of the substituents borne by the α-carbon of the *N*-chloramine.[31] The substituent dependence of the *N*-chloroalcoholamines ($\log k_{exp} = -0{\cdot}078 + 2{\cdot}09\ \Sigma\sigma^*$, if *N*-Cl-4A1B is excluded from the analysis) clearly differs from that of *N*-chloroalkylamines ($\log k_{exp} = 2{\cdot}96 + 1{\cdot}15\ \Sigma\sigma^*$), which suggests that the

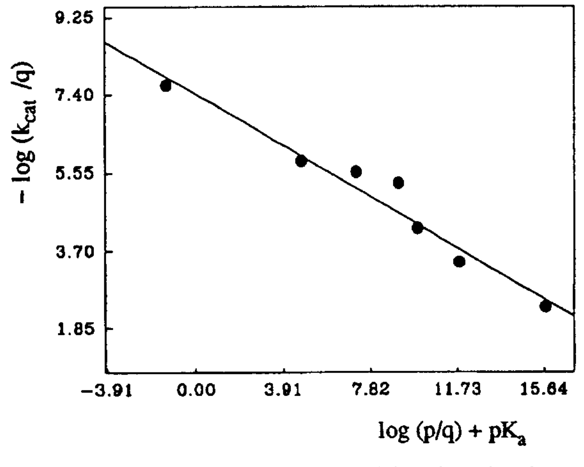


Figure 7. Brønsted plot for the general based-catalysed process in the decomposition of *N*-Cl-2A1B. Data from Table 3

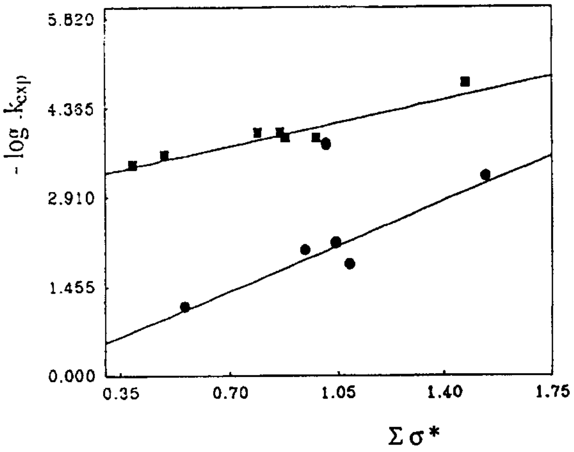


Figure 8. Substituent effects on the rate of decomposition of (■) *N*-chloroalkylamines and (●) *N*-chloroalcoholamines

two sets of *N*-chloramines must have different major decomposition paths. Specifically, the *N*-chloroalcoholamines in which a – CH_2OH group is borne by the α-carbon must decompose primarily via the mechanism shown in Scheme 2. *N*-Cl-4A1B, on the other hand, would appear to decompose primarily by the same mechanism as *N*-chloroalkylamines (Scheme 1), no doubt because its OH group is far from the amino group. This mechanistic difference is also reflected in the pH-dependence of the reaction with *N*-Cl-4A1B, which resembles that of the *N*-chloroalkylamines more than that of any other *N*-chloroalcoholamine.

The fact that the decomposition rates of both the *N*-chloroalkylamines and *N*-chloroalcoholamines decrease with increasing total electron-withdrawing capacity of the α-carbon substituents suggests that the nitrogen atom bears a strong positive charge in the transition state, and hence that N—Cl cleavage is well advanced at this point. Combined with the Brønsted plot results, this finding implies that, for *N*-chloramines, the β-elimination process is an '*E*1-like' mechanism, i.e. one in which the reaction path lies in the upper left region of Figure 6.

REFERENCES

1. A. I. Russell and J. C. Morris, *Environ. Sci. Technol.* **17**, 738–742 (1983).
2. J. M. Antelo, F. Arce, J. L. Armesto, J. Casado and A. Varela, *An. Quím.* **79**, 196–204 (1983).
3. J. M. Antelo, F. Arce, D. Casal, P. Rodríguez and A. Varela, *Tetrahedron* **45**, 3955–3966 (1989).
4. Ll. Abia, PhD Thesis, Universidad de La Coruña (1993).
5. S. W. Fox and M. W. Bullock, *J. Am. Chem. Soc.* **73**, 2754–2755 (1951).
6. W. D. Stambro and W. D. Smith, *Environ. Sci. Technol.*, **13**, 446–451 (1979).
7. V. C. Hand, M. P. Snyder and D. W. Margerum, *J. Am. Chem. Soc.*, **105**, 4022–4025 (1983).
8. R. Awad, A. Hussain and P. A. Crooks, *J. Chem. Soc., Perkin Trans. 2*, 1233–1238 (1990).
9. Ll. Abia, X. L. Armesto, M. Canle, M. V. García, M. Losada and J. A. Santaballa, *Int. J. Chem. Kinet.* **26**, 1041–1053 (1994).
10. D. H. Rosenblatt and E. P. Barrows, in *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives, Part 2*, edited by S. Patai, pp. 1085–1149. Wiley, Chichester (1982).
11. W. D. Stambro and M. J. Lenkevich, *Int. J. Chem. Kinet.* **17**, 401–411 (1985).
12. M. Anbar and I. Dostrovsky, *J. Chem. Soc.* 1105–1108 (1954).
13. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5 edn., Chapt. 14. Wiley, New York (1988).
14. J. M. Antelo, F. Arce and M. Parajó, *Int. J. Chem. Kinet.* **27**, 637–647 (1995).
15. J. Casado, M. Mosquera, M. F. Rodríguez Prieto and A. Santaballa, *Chem. Comput.* **7**, 209–213 (1983).
16. W. H. Dennis, L. A. Hull and D. H. Rosenblatt, *J. Org. Chem.* **32**, 3783–3787 (1967).
17. S. Selim, *J. Chromatog.* **136**, 271–277 (1977).
18. B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th ed. Longman, Harlow (1989).
19. G. J. Yagil, *Phys. Chem.* **71**, 1034–1045 (1967).
20. J. M. Antelo, F. Arce, M. Parajó, P. Rodríguez and A. Varela, *Int. J. Chem. Kinet.* **24**, 991–997 (1992).
21. J. M. Antelo, F. Arce, M. Parajó and P. Rodríguez, *Bull. Soc. Chim. Belg.* **101**, 1031–1036 (1992).
22. J. M. Antelo, F. Arce, M. Parajó and P. Rodríguez, *Gazz. Chim. Itali.* **123**, 549–552 (1993).
23. M. A. Alekserov, S. S. Yufit and V. K. Kucherov, *Russ. Chem. Rev.* **47**, 134 (1978).
24. R. A. More O'Ferrall, *J. Chem. Soc. B* 274–277 (1970).
25. F. G. Bordwell, *Acc. Chem. Res.*, **5**, 374–381 (1972).
26. W. H. Saunders, Jr, and A. F. Cockerill, in *Mechanisms of Elimination Reactions*, Chapt. 1. Wiley–Interscience, New York (1973).
27. A. F. Cockerill and R. G. Harrison, in *The Chemistry of Double-Bonded Functional Groups, Part I*, edited by S. Patai, pp. 155–189. Wiley, Chichester (1977).
28. J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.* 731–741 (1962).
29. W. P. Jencks, M. T. Haber, D. Herschleg and K. T. Nazaretian, *J. Am. Chem. Soc.* **108**, 479–483 (1986).
30. R. V. Hoffman, R. A. Bartsch and B. R. Cho, *Acc. Chem. Res.*, **22**, 211–217 (1989).
31. C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*. Wiley, New York (1979).