Tetrahedron Vol. 45, No. 12, pp. 3955 to 3966, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

INFLUENCE OF pH ON THE DECOMPOSITION OF N-CHLORODIETHANOLAMINE

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(*Received in UK* 29 *March* 1989)

SUMMARY

The kinetics of the decomposition of N-chlorodiethanolamine in water were studied over the range pH 6.55-12.01. Its coefficient of absorption in water at various pH and its protonation constant are reported, and the mechanism of its formation and decomposition is discussed. Comparison of the stabilities of various N-chloramines shows that the OH group of N-chloroalcoholamines makes them less stable than other N-chloramines and that the mechanism by which they react differs from that of aliphatic N-chloramines.

INTRODUCTION

The increasing use of synthetic organic compounds in industry, research and agriculture has in recent years led to an appreciable rise in their levels in both water supplies and wastewaters. It is therefore important to know the possible toxic effects of such substances, the degradation processes they undergo, and their behaviour in the presence of other chemicals found in the same waters. One group of potentially toxic organic substances comprises the secondary amines, which are known to be precursors of carcinogenic nitrosamines[1]. In the case of diethanolamine, the secondary amine involved in the study described in this paper, the results of laboratory biodegradation experiments suggest that its degradation in natural systems is probably slow[2].

An important source of chemicals in water supplies is the addition of disinfectants to natural waters. The most widely used method of disinfecting natural water supplies is treatment with chlorine or hypochlorite, which endows the medium with chlorination agents that react with other species present naturally or due to man-mediated causes. Chlorine itself reacts with amines to afford N-chloramines via a process involving hypochlorous acid and the free amine, but the chain of reactions does not necessarily terminate here, since N-chloramines differ widely as regards their stability in water (which also depends on the acidity of the medium) and can oxidize other species present. It is accordingly necessary to know the stability and reactivity of N-chloramines formed during water chlorination so as to be able to infer the secondary reactions that can take place. In this paper we report the influence of pH on the kinetics of the decomposition of N-chlorodiethanolamine obtained, in a reaction of half-life < 30 ms, by mixing aqueous solutions of sodium hypochlorite and diethanolamine[3].

EXPERIMENTAL

The decomposition of N-chlorodiethanolamine was followed spectrophotometrically by measuring the absorbance of the reaction mixture at 266 nm, the wavelength of maximum absorbance of the N-chloramine (the other components of the reaction mixture were found not to absorb appreciably at this wavelength). Absorbance-time data and the spectra of the reagents and reaction mixture were recorded in a Bausch&Lomb Spectronic 2000 spectrophotometer with a cell carrier thermostatted to within ±0.1°C by circulating water from a Heto 05-E-623 thermostat.

Hypochlorite solutions were prepared by bubbling chlorine through 0.5 M NaOH solution to saturation, after which NaOH was added to bring pH to about pH 11 and the solution was stored in the dark in an opaque flask to prevent decomposition of hypochlorite. The concentration of each stock solution was determined iodometrically and was redetermined during each working session by measuring its absorbance[4] at 292.5 nm.

N-chlorodiethanolamine was formed directly in the spectrophotometer cell by mixing appropiate quantities of hypochlorite, amine and buffer solutions. Rate constants k and the absorbance A_o at time t=0 were estimated by using the least squares method to fit first order integrated equations ($\ln A=\ln A_o-k\cdot t$) to the absorbance-time data for the first 70-80% of the reaction, correlation coefficients better than 0.9990 being obtained in all cases (the absorbance after 100% reaction was practically zero in all the many experiments in which this too was determined). All experiments were performed in triplicate, with results differing in no case by more than 2%.

All reagent solutions were prepared using Merck p.a. products. A Radiometer GK2401C electrode was used to measure the pH of the reaction mixtures.

RESULTS

Spectra of reagents and reaction mixtures. Suitable working conditions were determined by examining the absorption spectra of the reagents and the reaction mixture. Fig. 1 shows those of various sodium hypochlorite solutions in the range pH 3.97-12.05; the peak at 292.5 nm wanes as pH falls due to a shift to the left in the equilibrium

$$HClO \rightleftharpoons H^+ + ClO^-$$

since the molar absorptivity of HClO ($pK_a=7.54$)[5] is much less than that of ClO^- at 292.5 nm (26.9 as against 350 $M^{-1}\ cm^{-1}$)[4,5]. The spectra of diethanolamine and buffer solutions exhibited no absorption at all in the 240-340 nm region. The spectrum of the reaction mixture recorded one minute after the mixing of hypochlorite and diethanolamine solutions (Fig. 2) shows that the ClO^- band at 292.5 nm is replaced within the first minute by a band at 266 nm due to N-chlorodiethanolamine formed by the reaction

$$HClO + HN(CH_2CH_2OH)_2 \longrightarrow ClN(CH_2CH_2OH)_2 + H_2O$$

The waning of the 266 nm band in the spectra recorded at 5 minute intervals thereafter (Fig. 2) shows this initial product subsequently undergoes slow decomposition.

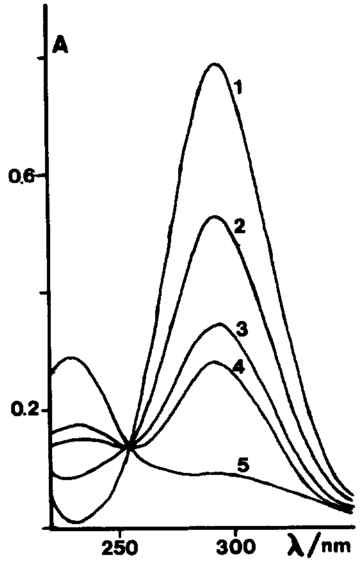

Fig.1. Spectra of NaClO solutions of various pH. [NaClO] = $2.05 \cdot 10^{-3}$ M (1)pH=12.5, (2)pH=8.03, (3)pH=7.44, (4)pH=7.25, (5)pH=3.97

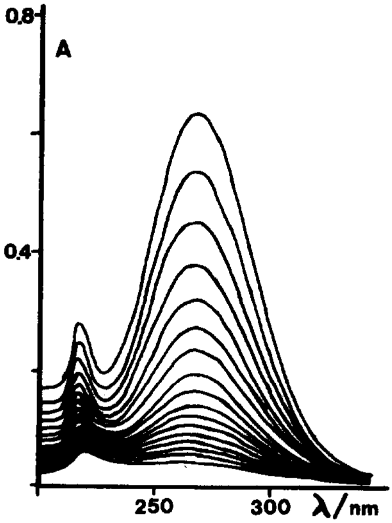

Fig.2. Spectra of a reaction mixture recorded one minute after initiation of the reaction and at 5-minute intervals thereafter.

Reaction products. According to the literature[6], the reaction products should be ethanolamine and formaldehyde:

$$ClN(CH_2CH_2OH)_2 \longrightarrow H_2NCH_2CH_2OH + 2HCHO + HCl$$

in the work described here, the presence of formaldehyde in the reaction mixture was confirmed by the chromotropic acid test[7] and by the agreement between the measured and published[8] melting points of the white precipitate obtained on addition of saturated dimedon solution (187°C and 188-189°C respectively). The 77% yield of formaldehyde calculated from the weight of precipitate in experiments in which 100 ml of 0.1 M NaClO was mixed with 100 ml of 1 M diethanolamine in the presence of 50 ml of boric acid/NaOH buffer (pH 9.50) is similar to published values[6].

Molar absorptivity of N-chlorodiethanolamine. At pH 4-8, the absorbance of the reaction mixture remained practically constant during the first 5 minutes of the reaction, and the molar absorptivity of N-chlorodiethanolamine was calculated from absorbance measurements performed during this period. At pH > 8, decomposition was rapid and molar absorptivity was calculated from initial absorbance values estimated as described in the Experimental section. The results of the two methods agree with each other and confirm compliance with Beer's law, the average molar absorptivity at 266 nm (the wavelength of maximum absorption by free N-chlorodiethanolamine) proving to be 298 M^{-1} cm^{-1} over the range pH 4-12.

pK_a of N-chlorodiethanolamine. The absorbances determined at 266 nm, where free N-chlorodiethanolamine absorbs much more than the protonated form, allow calculation[9,10] of the constant K_a of the equilibrium

$$BH^+ \rightleftharpoons B + H^+$$

where B is free N-chlorodiethanolamine. In terms of absorbances,

$$K_a = [H^+]\,(A-A_{BH})/(A_B-A)$$

where A is the absorbance of a mixture of free and protonated forms at the pH corresponding to $[H^+]$, A_B is the absorbance when only the free form is present and A_{BH} is the absorbance when only the protonated form is present. A_{BH} is difficult to determine directly because this would require measurements in strongly acid media. K_a and A_{BH} can nevertheless be estimated simultaneously by reformulating the above equation as

$$A=(A_B-A)K_a/[H^+] + A_{BH}$$

and fitting it to experimental absorbance-$[H^+]$ data. Good correlation was observed at all ionic strengths , I, and the linear dependence of the corresponding pK_a's on I (Table I) allows pK_0, the dissociation constant at zero ionic strength, to be calculated as -0.75 from the equation[11-13]

$$\log K_a = \log K_0 + c\cdot I$$

(where c is a constant).

Table I. Variation of the pKa of N-chlorodiethanolamine with ionic strength

I/M	pK_a	I/M	pK_a
0.5178	-0.633	1.7538	-0.335
0.8284	-0.577	2.0917	-0.289
1.0356	-0.530	2.6146	-0.120
1.3412	-0.447	3.1375	0.014
1.5475	-0.402	3.6604	0.141

λ_{max}= 266 nm ϵ_{266}= 23 $M^{-1}cm^{-1}$ pK_a^0= -0.75

Kinetics.

Reaction order. In all kinetic experiments, the absorbance-time data fitted a first order integrated equation

$$\ln(A_t-A) = \ln(A_0-A) - k\cdot t$$

showing that the decomposition reaction was of order one with respect to N-chlorodiethanolamine. Fig. 3 shows a typical example.

Influence of pH. Table II lists the rate constants and initial absorbances determined in the range pH 6.55-12.01 in the presence of suitable boric acid/NaOH or boric acid/HCl

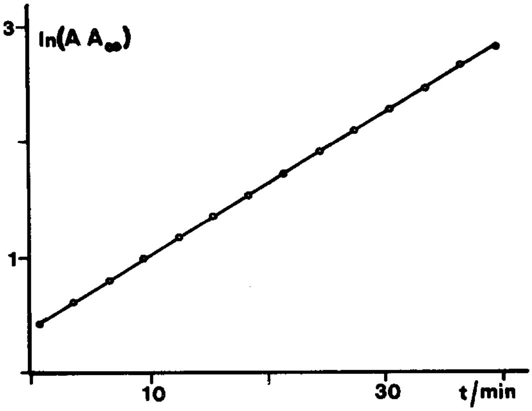

Fig.3. Typical experimental results fitting a first order integrated equation.
$[NaClO]=2.05\cdot10^{-3}$ M. $[DEA]=2.9\cdot10^{-3}$ M.
pH=10.94. T=298 K

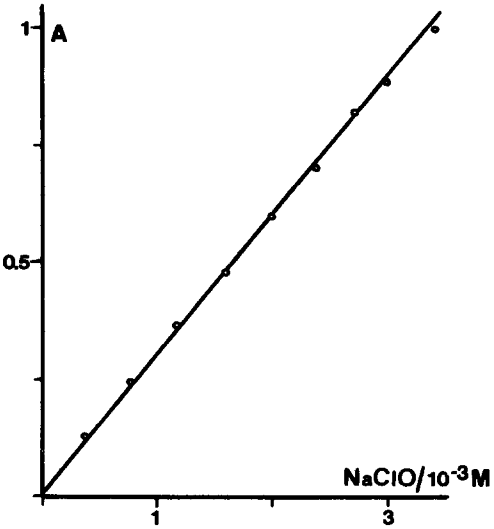

Fig.4. Compliance with Beer's Law (initial absorbances were calculated by fitting first order integrated equations to the experimental absorbance time data).
[DEA]=0.010 M. pH=10.20. T=298.3 K

Table II. Influence of pH on the rate of decomposition of N-chlorodiethanolamine
[NaClO]=0.00197 M [DEA]=0.010 M T=298 K

pH	$k/10^{-3}min^{-1}$	Ao
12.01	1360	0.606
11.76	760	0.592
11.38	197	0.592
11.02	90	0.573
10.77	56.2	0.604
10.38	20.5	0.610
9.99	8.53	0.592
9.65	3.93	0.594
9.31	2.50	0.602
8.96	1.12	0.585
8.52	0.413	0.576
8.15	0.199	0.580
7.67	0.0811	0.581
6.55	0.0119	0.569

buffers. The near constancy of Ao shows that under the conditions employed, acidity has no effect on the initial concentration of the species absorbing at 266 nm, i.e. the same forms of N-chlorodiethanolamine was predominant troughout the pH range considered. The increase in the reaction rate with pH obeys the empirical equation

$$\log k_{exp} = 0.930\ \text{pH} - 11.2 \qquad (r=0.9969)$$

Influence of the concentration of N-chlorodiethanolamine. Experiments carried out with various initial concentrations of N-chlorodiethanolamine at pH 10.2 (with concentrations $[H_3BO_3]=0.24$ M and $[NaOH]=0.22$ M in the reaction mixture) showed the reaction rate to be independent of N-chloramine concentration (Table III). The corresponding values of Ao comply with Beer's law (Fig. 4) and imply a molar absorptivity of 293±1 $M^{-1}cm^{-1}$.

Table III. Influence of the concentration of N-chlorodiethanolamine on the rate of decomposition.

[DEA]=0.010 M pH=10.20 T=298.3 K

$[NaClO]/10^{-3}$ M	k/min^{-1}	Ao
3.35	138	0.996
2.96	130	0.880
2.69	146	0.816
2.36	128	0.697
1.97	149	0.595
1.58	148	0.476
1.18	140	0.365
0.79	137	0.243
0.39	125	0.130

Influence of ionic strength and buffer and amine concentrations. The rate of decomposition of N-chlorodiethanolamine was found to be independent of the amount of excess amine used in its generation, ionic strength (which was controlled with NaCl), and the concentrations of the buffer reagents used (Table IV).

Influence of temperature. The rate constants determined at various temperatures in the range 286.8-304.9 K comply with Arrhenius' law and the equations of activated complex theory, implyng the thermodinamic activation parameters listed with them in Table V.

Stability of N-chloramines. To investigate possible correlations between the stability and other characteristics of N-chloramines derived from secondary amines, the decomposition of eight of those compounds was studied kinetically under the same pH and concentration conditions. The results (Table VI), show that those derived from secondary alcoholamines are much less stable than the derivatives of aliphatic secondary amines. The same tendency was found in a similar study of 12 N-chloramines derived from primary amines (Table VII), the dependence of the rate constant on σ^* being quite different for derivatives with and without an OH group. It is concluded that the mechanism of decomposition of alcoholamine derivatives must differ from that of derivatives of aliphatic amines (Fig. 5).

Table IV. Influence of the concentrations of amine, NaCl and buffer on the rate of decomposition of N-chlorodiethanolamine.

[NaClO]=0.00197 M pH=10.20 T=298 K

[DEA]/M	$[H_3BO_3]$/M	[NaOH]/M	[NaCl]/M	$k/10^{-3}min^{-1}$
0.002	0.24	0.22		153
0.004	0.24	0.22		157
0.006	0.24	0.22		164
0.010	0.24	0.22		146
0.014	0.24	0.22		140
0.018	0.24	0.22		164
0.022	0.24	0.22		151
0.026	0.24	0.22		153
0.030	0.24	0.22		148
0.010	0.24	0.22	1.00	160
0.80	0.24	0.22	1.00	153
0.60	0.24	0.22	1.00	152
0.40	0.24	0.22	1.00	150
0.20	0.24	0.22	1.00	148
0.010	0.28	0.093		128
0.010	0.24	0.080		143
0.010	0.20	0.067		128
0.010	0.16	0.053		136
0.010	0.12	0.040		129

Table V. Influence of temperature on the rate of decomposition of N-chlorodiethanolamine.

[NaCl]=0.00197 M [DEA]=0.010 M pH=10.20

T/K	304.9	303.0	299.9	298.1	296.7	294.5	292.5	290.6	286.8
$k_{exp}/10^{-4}min^{-1}$	493	383	195	144	96	71.6	47.8	33.6	15.3

E_a= 138.9 kJ mol^{-1} ΔH^{*}= 136.4 kJ mol^{-1} ΔS^{*}= -177.1 J $mol^{-1}K^{-1}$

Table VI. Stability of N-chloramines derived from secondary amines.
[NaClO]=0.0025 M [amine]=0.0027 M T=298 K

	k_{exp} /min^{-1}	
amine	pH=10.9	pH=12.8
diethanolamine	0.062	5.1
ethylethanolamine	0.045	5.4
methylethanolamine	0.036	0.70
ethylmethylamine	$7.9\cdot10^{-5}$	$2.3\cdot10^{-3}$
dimethylamine	$3.2\cdot10^{-5}$	$3.0\cdot10^{-4}$
diethylamine	$7.0\cdot10^{-5}$	$1.8\cdot10^{-3}$
dipropylamine	$8.3\cdot10^{-4}$	$2.4\cdot10^{-3}$
diisopropylamine	$1.9\cdot10^{-4}$	$1.6\cdot10^{-3}$

Table VII. Stability of N-chloramines derived from primary amines.
[NaOH]=2.0 M [NaClO]=0.00215 M [amine]=0.010 M T=298 K

amine	k_{exp} /min^{-1}	$\Sigma\,\sigma^*$
methylamine	0.0028	0.98
ethylamine	0.0185	0.49
n-propylamine	0.020	0.39
n-buthylamine	0.015	0.375
isopropylamine	0.038	0.00
sec-buthylamine	0.044	-0.10
ethanolamine	0.065	1.05
isobuthylamine	0.015	0.30
3-amine-1-propanol	0.029	1.18
2-amine-1-propanol	1.07	0.56
methoxyethylamine	0.040	1.13
2-amine-2-methyl-1-propanol	15.0	0.07

$\Sigma\,\sigma^* = \sigma^*_{R1} + \sigma^*_{R2}$ for $H_2NCHR_1R_2$

Aliphatic amines $\log k_{exp} = -1.40 - 1.06\,\Sigma\,\sigma^*$

Alcoholamines $\log k_{exp} = 1.37 - 2.44\,\Sigma\,\sigma^*$

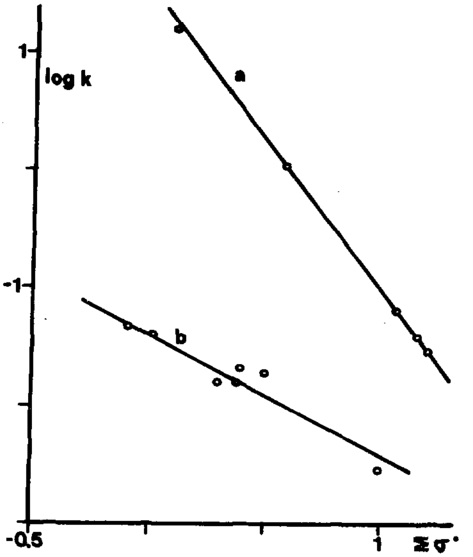

Fig.5. Stability of N-Chloramines derived from primary amines. (a) N-chloroalcoholamines
(b) N-chloramines

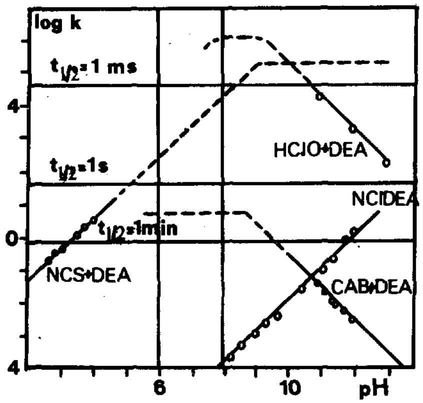

Fig.6. Influence of pH on the rate of the formation of N-chlorodietanolamine by various chlorinating agents.

DISCUSSION

Formation of N-chlorodiethanolamine. N-chlorodiethanolamine can be obtained using various chlorinating agents, including hypochlorite, chloramine T (CAT), chloramine B (CAB) and N-chlorosuccinimide (NCS). The rate of formation of the N-chloramine depends on the chlorinating agent used and the conditions under which the reaction takes place. Table VIII lists the empirical relationships found between reaction rate and pH for the four agents mentioned above. Their comparison is difficult, since only the experiments with CAB and CAT were carried out over the same pH range; Fig. 6 nevertheless shows the experimental data together with possible extrapolations. Note that at pH 6-8 the reaction is fast with CAT, CAB and NCS and very fast with NaClO.

Table VIII

Chlorinating agent	pH	Equation	Reference
NCS	2.7-4.02	log k = 0.94pH - 3.20	19
CAT	11.0-12.1	log k = -0.90pH + 8.50	20
CAB	10.9-12.0	log k = -0.95pH + 8.91	21
NaClO	12.0-13.0	log k = -1.00pH + 15.20	3

The mechanism suggested by the literature [14] for the rapid formation of N-chlorodiethanolamine upon mixing hypochlorite and diethanolamine solutions is shown in Scheme 1. It is assumed that HClO is the only chlorinating agent, and that the substrates are the unprotonated forms of the amine.

scheme 1

$$HClO \overset{K_1}{\rightleftharpoons} ClO^- + H^+$$

$$\begin{tikzcd}
H_2\overset{+}{N}(CH_2CH_2OH)_2 \arrow[r, shift left, "K_2"] & HN(CH_2CH_2OH)_2 \arrow[l, shift left] \arrow[r, shift left, "K_3"] \arrow[d, "k_4"', "HClO"] & HN(CH_2CH_2OH)CH_2CH_2O^- \arrow[l, shift left] \arrow[d, "k_5"', "HClO"] \\
ClH\overset{+}{N}(CH_2CH_2OH)_2 \arrow[r, shift left, "K_6"] & ClN(CH_2CH_2OH)_2 \arrow[l, shift left] \arrow[r, shift left, "K_7"] & ClN(CH_2CH_2OH)CH_2CH_2O^- \arrow[l, shift left]
\end{tikzcd}$$

The dissociation constants featured in the above scheme correspond to the values pK_1= 7.54 [8], pK_2= 8.96 [15], pK_3= 14.7 [16], pK_6=-0.79 (this paper) and pK_7=14.7 [16-18]. For the pH used in this study, at which the N-chloramine is formed[3] within 30 ms, these pK_a's imply that the predominant species must be $ClN(CH_2CH_2OH)_2$; this is in keeping with the invariance of the initial absorbance, which implies that the same species is predominant troughout the pH range considered.

Decomposition of N-chlorodiethanolamine. Table IX lists the empirical relationships found between pH and the rate of decomposition of N-chlorodiethanolamine generated under different conditions by three different chlorinating agents. All four equations (including that obtained in this work) have a slope close to unity, showing that the rate equation of the reaction must feature a term in $[H^+]^{-1}$ (Fig 7). There are two possible mechanisms that account for this, both involving the species $ClN(CH_2CH_2OH)_2$. The first, in which an imine is formed directly in a bimolecular reaction between $ClN(CH_2CH_2OH)_2$ and OH, is shown in Scheme 2;since the hydrolysis of imines is generally very fast, this scheme entails the rate equation

$$v = k_8[ClN(CH_2CH_2OH)_2][OH^-] = k_8K_w[ClNR]/[H^+] = k_{exp}[Cl]_t$$

where

$$\log k_{exp} = pH + \log k_8K_w$$

comparison of which with the empirical equation implies the values

$$\log k_8K_w = -11.2 \ ; k_8 = 631 \text{ min}^{-1} \ ; \quad t_{1/2} = 0.066 \text{ s}$$

Scheme 2

$$OH^- + ClN(C_2H_4OH)_2 \xrightarrow{k_8} CH_2{=}N(C_2H_4OH) + Cl^- + HCHO + H^+$$

$$CH_2{=}N(C_2H_4OH) + H_2O \xrightarrow{k_9} HCHO + H_2N(C_2H_4OH)$$

The other possible reaction mechanism, in which the imine is formed by the decomposition of deprotonated $ClN(CH_2CH_2OH)_2$, is shown in Scheme 3. If the rate controlling step is the formation of the imine, then

$$v = k_{10}[ClN(CH_2CH_2OH)CH_2CH_2O^-] = k_{10}K_7[ClNR]/[H^+] = k_{exp}[Cl]_t$$

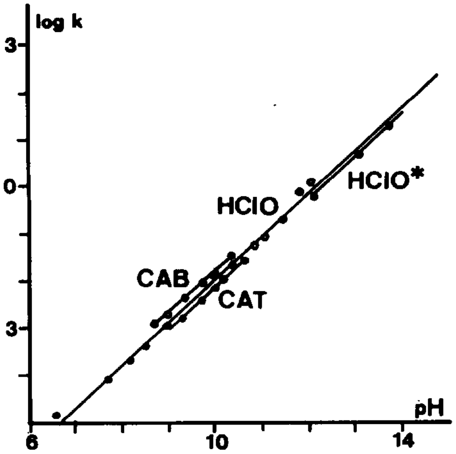

Fig.7. Influence of pH on the rate of the decomposition of N-chlorodiethanolamine formed by various chlorinating agents.

Table IX

Chlorinating agent	pH	Equation	Reference
CAT	9.2-10.6	log k = 0.98pH - 11.9	20
CAB	8.0-10.3	log k = 0.88pH - 10.6	21
HClO	6.5-12.0	log k = 0.93pH - 11.2	this work
HClO	>12	log k = 1.00pH - 12.2	3

where log k_{exp}=pH + log $k_{10}K_7$ = pH - 11.2; and if the N-Cl bond is assumed not to have any significant effect on the acid-base properties of the N-chlorodiethanolamine OH group, the value of pK_7 can be taken as equal to pK_3=14.7 [16-18] whence

$$k_9 = 3.162\ \text{min}^{-1} \text{ and } t_{1/2} = 0.013\ \text{s}$$

scheme 3

$$OH^- + ClN(C_2H_4OH)_2 \xrightleftharpoons{K'_7} ClN(C_2H_4OH)CH_2CH_2O^-$$

$$ClN(C_2H_4OH)C_2H_4O^- \xrightarrow{k_{10}} CH_2{=}N(C_2H_4OH) + Cl^- + HCHO$$

$$CH_2{=}N(C_2H_4OH) + H_2O \xrightarrow{k_9} H_2N(C_2H_4OH) + HCHO$$

Since that N-chloro-tert-butylamine is very stable even in strongly alkaline media, the mechanism of the decomposition of N-chloramines must involve the hydrogen atom on the carbon that is α to the amino group. Since the comparative study of stabilities carried out in this work shows that the OH group of N-chloroalcoholamines makes them less stable than aliphatic N-chloramines, their decomposition must take place primarily via the deprotonated form (Scheme 3).

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Acknowledgement. The authors wish to thank the Spanish Comision Asesora de Investigación Científica y Técnica for subsidizing the research reported in this article (PR84-0630).