Kinetics of the Formation, Decomposition, and Disproportionation Reactions of N-Chlorobutylamines

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Abstract

The formation of N-chlorobutylamines is a reaction of order one with respect to hypochlorite and amine, and order -1 with respect to OH$^-$. Kinetic studies show that N-chlorobutylamines undergo decomposition in basic aqueous media, and disproportionation (with formation of N,N-dichloramines) in acidic media, mechanisms are put forward for both these processes. © 1995 John Wiley & Sons, Inc.

Introduction

In basic aqueous media the reaction of primary amines with hypochlorite to form N-chloramines is such that fast reaction techniques are required for investigation of its kinetics [1–5], and the N-chloramines formed undergo decomposition to amines which are then hydrolyzed to aldehydes [3,6]. In acidic aqueous media, reaction of primary amines with hypochlorite involves consecutive chlorination processes affording N,N-dichloramines [4], which are also formed by disproportionation of N-chloramines in these media [7,8]. In this work we report our results on the kinetics of the processes occurring upon mixing solutions of hypochlorite and butylamines: (a) the formation of N-chlorobutylamine in basic media; (b) the decomposition of N-chlorobutylamines in basic media; and (c) the formation of N,N-dichlorobutylamines. Mechanisms are proposed for these reactions, and the influence of substituents is discussed.

Reagents

Sodium hypochlorite solutions were prepared by saturating a 0.5 M NaOH solution with bubbled chlorine. These stock solutions were stored in opaque flasks at pH 12–13, and their concentrations determined by iodometry [9]. Solutions of n-, iso-, s-, and tert-butylamine were prepared by weight. For experiments at pH $<$ 9, the amines were neutralized with HCl before being added to the other reagents. pH was controlled using solutions of NaOH or HCl, or boric/NaOH, boric/NaOH/HCl, acetic/acetate, or citric/NaOH buffers prepared by standard procedures [10]. N-chloramine solutions were prepared by mixing known volumes of amine and hypochlorite solutions in the presence of such quantities of NaOH, HCl, or buffer as were required to control pH. All reagents were Merck p.a. products.

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Spectrophotometry

Reagents, reaction products, and reaction mixtures were studied spectrophotometrically to determine optimum conditions for monitoring the reaction kinetics (wavelength λ_{max} of the maximum absorbance and the corresponding molar absorption coefficient ϵ_{max} for each relevant species). These experiments were performed in a Kontron Uvikon 820 spectrophotometer equipped with a Uvikon LS48 printer, a Uvikon 21 plotter, and a cell carrier thermostatted to within $\pm 0.1°$ by circulating water from a Haake thermostat.

Kinetic Studies

Formation of N-chloramines. The formation of N-chloramines was studied by following the fall in absorbance by hypochlorite at 292.5 nm, the [amine]/[NaClO] ratio being kept greater than 10 in all cases. Reactions were initiated by mixing hypochlorite and amine, and were followed, in an Applied Photophysics Mod. 15-1705 stopped-flow spectrophotometer that passed absorbance-time data to a Stronger computer, where they were fitted with the first-order equation

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

by an Applied Photophysics program affording A_∞, k_{obs}, and $(A_0 - A_\infty)$. All experiments were performed at least five times; in all cases regression coefficients were better than 0.990, and the estimated error in k_{obs} was less than 5%.

Decomposition of N-chloramines. The decomposition of N-chloramines was studied by monitoring absorbance at the wavelength of maximum absorption, 252 nm. In all the kinetic experiments, the absorbance-time data collected at this wavelength fitted the integrated first-order equation

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_{exp}t.$$

and the values of the initial absorbance A_0 and the experimental rate constant k_{exp} were estimated by least squares. The absorbance at infinite time, A_∞, was determined as zero for all the N-chlorobutylamines studied; the percentages of reaction followed ranged from 70% to 80%. All reactions were performed in triplicate, and the estimated error in the value of k_{exp} was always less than 3%.

Formation of N,N-dichloramines. Reactions were initiated by adding a buffer of acid pH to a solution of N-chlorobutylamine previously prepared in a basic medium. In view of the previous spectrophotometric results, the reactions were followed by monitoring absorbance at 300 nm for n-and iso-butylamine, and at 304 nm for s- and tert-butylamine. Kinetics were followed in the same Kontron Uvikon 820 double beam spectrophotometer as was used for the preliminary spectrophotometric characterization of reagents and products. pH was measured with a Radiometer PHM82 equipped with a Radiometer GK2401C electrode. By means of a method optimizing [11] the values A_∞ and A_0, absorbance-time data were fitted with the second-order equation

$$1/(A_t - A_\infty) = 1/(A_0 - A_\infty) + akt/(A_0 - A_\infty)$$

where a is the initial concentration of N-chlorobutylamine, and A_t, A_0, A_∞ are the absorbances at times t, 0, and infinity, respectively.

Results

Spectrophotometry of Reagents

Figure 1 shows the spectra of sodium hypochlorite solutions of pH 3.97–12.05. In most cases the absorbance maximum lies at 292.5 nm, but its intensity decreases with decreasing pH, this is doubtless due to the leftwards shift of the ionization equilibrium [12]

$$HClO \stackrel{K_a}{\rightleftharpoons} H^+ + ClO^- \qquad pK_a = 7.54$$
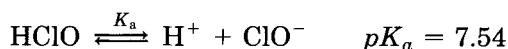
towards hypochlorous acid, since the molar absorption coefficient [9,12] of HClO at 292 nm, 26.9 M^{-1} cm^{-1}, is less than that of ClO^-, 350 M^{-1} cm^{-1}. The spectra of solutions of the various butylamines and of solutions used to control pH had no absorption bands in the range 240–340 nm.

Formation of N-chlorobutylamine

The results (Table I) of series of experiments performed and analyzed as described above showed the reaction to be of order one with respect to both hypochlorite and n-butylamine. Varying NaOH concentration for fixed concentrations of hypochlorite and amine showed the observed rate constant to increase linearly with the reciprocal of $[OH^-]$; at pH < 11, reaction halflives were less than 0.001 s, i.e., too short for the stopped flow technique. Varying NaCl concentration showed that the reaction rate was independent of ionic strength. Reaction rate data obtained at temperatures ranging from 15°C to 40°C fitted Arrhenius' equation and the equation derived from transition state theory; the activation parameters so calculated are listed in Table I. With a view to determining the dependence of the reaction rate on the radical bound to the amino group, all the above experiments were repeated for the other three butylamines, with similar results (Table I).
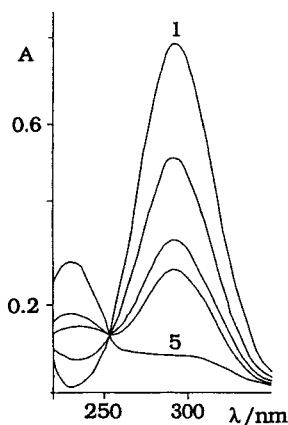

Figure 1. Spectra of NaClO solutions at various pH. [NaClO] = 2.05×10^{-3} M. (1) pH = 12.5, (2) pH = 8.03, (3) pH = 7.44, (4) pH = 7.25, and (5) pH = 3.97.

TABLE I. Rates of formation of N-chloro-butylamines, and the corresponding activation parameters.

[Amine]/M	[NaOCl]/M	NaOH/M	T/°C	N-Cl-n-but		N-Cl-s-but		N-Cl-tert-but		N-Cl-iso-but	
				k_{obs}/s^{-1}	k_r/s^{-1}	k_{obs}/s^{-1}	k_r/s^{-1}	k_{obs}/s^{-1}	k_r/s^{-1}	k_{obs}/s^{-1}	k_r/s^{-1}
0.020	0.0010	0.01	25.0	47.0	23.5	26.20	13.1	15.6	7.8	50.3	25.2
0.020	0.0010	0.02	25.0	29.0	29.0	15.90	15.9	9.59	9.6	28.1	28.1
0.020	0.0010	0.03	25.0	20.1	30.2	10.80	16.2	6.71	10.1	19.6	29.4
0.020	0.0010	0.05	25.0	12.7	31.8	7.01	17.5	4.46	11.2	11.9	29.8
0.020	0.0010	0.10	25.0	6.5	32.3	3.62	18.1	2.16	10.8	5.78	28.9
0.020	0.0010	0.15	25.0	4.1	30.5	2.52	18.9	1.54	11.6	4.16	31.2
0.020	0.0010	0.20	25.0	3.3	32.9	1.48	14.8	1.22	12.2	3.22	32.2
0.020	0.0010	0.40	25.0	1.8	36.0	1.11	22.2	0.71	14.2	1.75	35.0
0.020	0.0010	0.15	25.0	4.1	30.5	2.30	17.2	1.50	11.3	3.99	29.9
0.040	0.0010	0.15	25.0	8.6	32.3	4.96	18.6	3.21	12.0	8.37	31.4
0.060	0.0010	0.15	25.0	11.8	29.5	7.62	19.1	4.79	12.0	12.2	30.5
0.080	0.0010	0.15	25.0	17.0	31.9	10.30	19.3	6.40	12.0	16.5	31.0
0.010	0.0005	0.10	25.0	3.4	34.0	1.81	18.1	1.08	10.8	2.88	28.8
0.010	0.0010	0.10	25.0	3.3	33.0	1.59	15.9	1.03	10.3	2.56	25.6
0.010	0.0015	0.10	25.0	3.1	31.0	1.60	16.0	1.04	10.4	2.40	24.0
0.010	0.0020	0.10	25.0	3.3	33.0	1.70	17.0	1.01	10.1	2.61	26.1
0.010	0.0010	0.10	15.0	1.7	17.3					1.38	13.8
0.010	0.0010	0.10	20.0	2.2	22.0					1.79	17.9
0.010	0.0010	0.10	21.9			1.31	13.1				
0.010	0.0010	0.10	25.0	3.3	33.0	1.59	15.9	1.03	10.3	2.56	25.6
0.010	0.0010	0.10	30.0	5.0	50.0	1.92	19.2	1.47	14.7	3.89	38.9
0.010	0.0010	0.10	35.0	6.7	67.0	2.91	29.1	2.06	20.6	5.70	57.0
0.010	0.0010	0.10	40.0	10.2	102.0	4.40	44.0	2.34	23.4	8.60	86.0
0.010	0.0010	0.10	45.0					4.32	43.2		
			k_r avg.		32.1		17.8		11.0		29.4
			std. dev.		4.5		3.5		1.9		3.0
	E_a/kJ mol^{-1}			54.4		50.5		55.8		55.8	
	$\Delta H^{\ddagger}$/kJ mol^{-1}			52.0		48.0		53.7		53.3	
	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}			−60		−80		−65		−58	

Decomposition of N-chlorobutylamines in Basic Media

Spectrophotometry. When n-, s-, and iso-butylamine were mixed with hypochlorite in a strongly basic medium and successive spectra were recorded, the absorption maximum at 292.5 nm due to the ClO^- disappeared immediately, being replaced by a band at 252 nm due to the *N*-chlorobutylamine (Fig. 2) formed in the reaction

$$HClO + H_2NC_4H_9 \longrightarrow ClHNC_4H_9 + H_2O$$
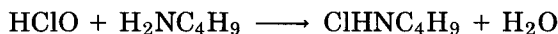
The subsequent decay of the band around 252 nm showed that the *N*-chlorobutylamine formed decomposed slowly by a process that, according to the literature [3] on this kind of reaction, led to an aldehyde as the major product

$$ClHNC_4H_9 + H_2O \longrightarrow HCl + C_3H_7CHO + NH_3$$
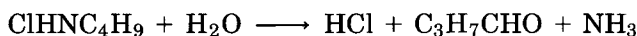
N-Chloro-tert-butylamine, however, proved much more stable, the absorption band at 252 nm remaining unchanged even in very highly basic media.

Molar absorption coefficients. In buffer solutions of pH 4–12, the standard spectrophotometric method was used to verify compliance with Beer's law at the wavelength of the absorption maximum of the *N*-chloro-butylamine and to determine the corresponding molar absorption coefficients (Table II); the *N*-chloro-butylamines were generated in situ, all mixing and measuring operations were carried out in a total time of less than 5 minutes, and the constancy of the absorption during this time was verified. At higher pH, the reaction rate leads to errors in the calculation of the initial absorbance, and at pH < 5 the protonation of the *N*-chloramines and the formation of dichloramines prevents accurate determination of the value of ϵ_{max} for the free *N*-chloramine. At pH > 12, molar absorption coefficients (Table II) were calculated from absorption values A_0 estimated for time zero of the decomposition reaction by fitting the first-order integrated equation ($\ln A_t = \ln A_0 - kt$) to absorbance-time data obtained in kinetic experiments with various different initial concentrations of
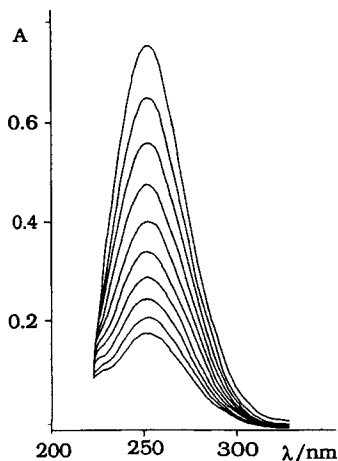

Figure 2. Spectra of *N*-chloro-*n*-butylamine solutions in basic media, at different times. [NaClO] = 2.13×10^{-3} M, [amine] = 1.33×10^{-2} M, [NaOH] = 3.5 M, and Δt = 2 min.

TABLE II. Molar absorption coefficients of N-chloro-n-, N-chloro-s,- and N-chloro-iso-butylamine at various pH.

s-butylamine		n–butylamine		iso-butylamine	
pH	$\epsilon/M^{-1}\ cm^{-1}$	pH	$\epsilon/M^{-1}\ cm^{-1}$	pH	$\epsilon/M^{-1}\ cm^{-1}$
4.00	81	4.06	74	4.10	73
6.70	320	7.50	316	6.30	211
8.66	330	8.90	319	7.90	309
9.33	337	9.20	327	8.40	329
11.65	335	10.50	340	10.20	341
Molar Absorption Coefficient Calculated from Kinetic Measurements [NaOH]:					
3.5 $\longleftrightarrow$ 1.0 M					
	325		349		335

N-chloramine. The slight discrepancies between the kinetic and spectrophotometric measurements of the absorption coefficients are probably the fault of the kinetic method, due to imprecision in the value of t_0 and to the superimposition of the processes of formation and decomposition of the N-chloramines.

Effects of the concentrations of reagents and inert electrolyte, and of temperature. Fitting absorbance-time data obtained at 252 nm to the first-order integrated equation showed the reaction to be of order one with respect to N-chlorobutylamine. Experiments in strongly basic media showed that stability increased as the concentration of NaOH fell (see Table III, which also lists the equation estimated by least squares for the corresponding linear relationship between $\log k_{exp}$ and the acidity function H_-, values of which were obtained from the literature [13] on aqueous solutions of NaOH). Experiments carried out in 3.5 M NaOH showed that the reaction rate was independent of the concentrations of NaClO, NaCl, and amine; see Table III, which also lists activation parameters estimated from the results of experiments carried out at various different temperatures.

The Disproportionation of N-chlorobutylamines and Formation of N,N-dichlorobutylamines in Acid Media

Spectrophotometry and molar absorption coefficients. Acidification of neutral or basic solutions of N-chlorobutylamines gives rise to a disproportionation reaction yielding dichloramines:

$$2ClHNC_4H_9 \longrightarrow Cl_2NC_4H_9 + H_2NC_4C_4H_9$$

In series of successive spectra, the monochloramine band at 250 nm wanes as a new band around 300 nm due to the dichloramine grows (Fig. 3). For all the monochloramines, molar absorption coefficients were calculated from absorption values A_0 estimated for time zero of the disproportionation reaction by fitting the second-order integrated equation to absorbance-time data obtained in the kinetic experiments with various different initial concentrations of N-chloramine (in the case of N-chloro-tert-butylamine the coefficient for absorbance at 250 nm could not be determined because the maximum overlies the isosbestic point and the absorbance is accordingly almost constant); for dichloramines, molar absorption coefficients were calculated from the corresponding values of A_∞. Table IV lists the coefficients calculated for the maximum absorption wavelengths of both mono- and dichloramines and for the corresponding isosbestic points.

TABLE III. Rates of decomposition of *N*-chloro-butylamines, and the corresponding activation parameters.

[NaClO]/M	[Amine]/M	[NaOH]/M	[NaCl]/M	N-Cl-n-but		N-Cl-iso-but		N-Cl-s-but	
				$T/°C$	k_{exp}/min^{-1}	$T/°C$	k_{exp}/min^{-1}	$T/°C$	k_{exp}/min^{-1}
0.00213	0.0132	3.50		25.0	0.0434		0.0428		0.118
0.00213	0.0132	3.16		25.0	0.0339		0.0339		0.099
0.00213	0.0132	2.83		25.0	0.0292		0.0297		0.0770
0.00213	0.0132	2.50		25.0	0.0233		0.0220		0.0676
0.00213	0.0132	2.16		25.0	0.0173		0.0176		0.0489
0.00213	0.0132	1.83		25.0	0.0133		0.0130		0.0398
0.00213	0.0132	1.50		25.0	0.0101		0.0106		0.0306
0.00213	0.0132	1.16		25.0	0.0072		0.0068		0.0219
0.00213	0.0165	3.50		25.0	0.0464		0.0441		0.100
0.00213	0.0132	3.50		25.0	0.0434		0.0428		0.105
0.00213	0.0116	3.50		25.0	0.0420		0.0425		0.121
0.00213	0.0099	3.50		25.0	0.0431		0.0417		0.102
0.00213	0.0083	3.50		25.0	0.0412		0.0447		0.098
0.00213	0.0066	3.50		25.0	0.0426		0.0445		0.099
0.00213	0.0033	3.50		25.0	0.0421		0.0465		0.092
0.00213	0.0132	3.50		25.0	0.0434		0.0428		0.105
0.00187	0.0132	3.50		25.0	0.0444		0.0459		0.099
0.00160	0.0132	3.50		25.0	0.0476		0.0457		0.096
0.00133	0.0132	3.50		25.0	0.0455		0.0437		0.100
0.00106	0.0132	3.50		25.0	0.0509		0.0420		0.094
0.00053	0.0132	3.50		25.0	0.0486		0.0461		0.109
0.00213	0.0033	3.50	0.660	25.0	0.0435				0.082
0.00213	0.0033	3.50	0.500	25.0	0.0377				0.096
0.00213	0.0033	3.50	0.416	25.0	0.0436				0.089
0.00213	0.0033	3.50	0.333	25.0	0.0439				0.087
0.00213	0.0033	3.50	0.250	25.0	0.0456				0.105
0.00213	0.0033	3.50	0.166	25.0	0.0543				0.087

TABLE III. (Continued)

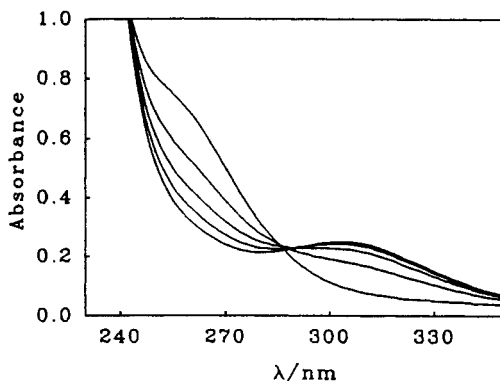| [NaClO]/M	[Amine]/M	[NaOH]/M	[NaCl]/M	N-Cl-n-but		N-Cl-iso-but		N-Cl-s-but	
				$T/°C$	k_{exp}/min^{-1}	$T/°C$	k_{exp}/min^{-1}	$T/°C$	k_{exp}/min^{-1}
0.00213	0.0100	3.50	0.660	25.0			0.0450		
0.00213	0.0100	3.50	0.500	25.0			0.0390		
0.00213	0.0100	3.50	0.416	25.0			0.0400		
0.00213	0.0100	3.50	0.333	25.0			0.0372		
0.00213	0.0100	3.50	0.250	25.0			0.0439		
0.00213	0.0100	3.50	0.166	25.0			0.0438		
0.00213	0.0132	3.50		21.3	0.0280	22.0	0.0309	22.3	0.075
0.00213	0.0132	3.50		23.4	0.0353	23.1	0.0359	25.0	0.105
0.00213	0.0132	3.50		25.0	0.0434	25.0	0.0428	27.3	0.125
0.00213	0.0132	3.50		27.0	0.0536	27.0	0.0566	30.0	0.168
0.00213	0.0132	3.50		29.8	0.0746	29.4	0.0730	32.7	0.227
				$\log k_{exp} = -17.5 + 1.09H_-$		$-17.5 + 1.09H_-$		$-16.0 + 1.02H_-$	
				$r = 0.996$		$r = 0.992$		$r = 0.996$	
			$E_a/kJ\ mol^{-1}$	85.2		86.0		78.1	
			$\Delta H^{\ddagger}/kJ\ mol^{-1}$	82.7		83.6		75.7	
			$\Delta S^{\ddagger}/J\ mol^{-1}\ K^{-1}$	-28		-25		-44	

Figure 3. Disproportionation of *N*-chloro-s-butylamine spectra of the reaction mixtures. pH = 3.00, [NaOCl] = 2.09 × 10^{-3}M, [*N*-chloramine] = 2.8 × 10^{-3}M, [NaCl] = 0.5M, and Δt = 4 min.

Effects of hypochlorite concentration, pH, and temperature. In series of experiments in which hypochlorite concentration was varied while those of all other reagents were kept fixed, absorbance-time data obtained at 300 nm fitted second-order rate equations, and the calculated rate constants were independent of the initial concentration of *N*-chloramine. For similar experiments carried out at 250 nm, the wavelength of the monochloramine absorption maximum, second-order rate equations were fitted by least squares to afford the corresponding experimental rate constants and zero-time absorbance. The rate constants obtained by monitoring the disappearance of the monochloramine band agree totally with those obtained by monitoring the appearance of the dichloramine band. The results obtained in a series of experiments in which pH was varied using HCl (Table V) show that for each amine there was a pH at which the disproportionation rate was a maximum.

The reaction rates determined in series of experiments carried out at different temperatures complied with Arrhenius' equation and the equations derived from activated complex theory, and are listed together with the corresponding activation parameters in Table VI.

TABLE IV.   Molar absorption coefficients (M^{-1} cm^{-1}) of *N*-chloro- and *N,N*-dichlorobutylamines. [NaCl] = 0.5M, pH = 1.84, and T = 25°C.

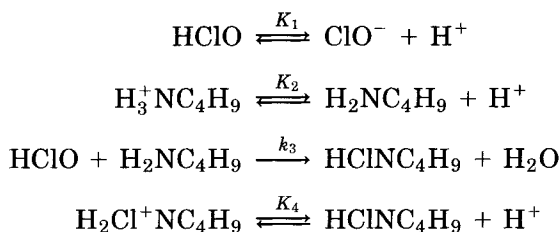| Wavelength/nm	Absorption Maximum			1st Isosbestic Point			2nd Isosbestic Point		
	250	300	304	284	286	279	241	242	247
N-chloro-*n*-butylamine	130			36.2			110.1		
N-chloro-iso-butylamine	115				22.8			69.3	
N-chloro-s-butylamine	133				36			96.6	
N-chloro-tert-butylamine						35.1			
N,N-dichloro-*n*-butylamine		231.2		72.3			220.2		
N,N-dichloro-iso-butylamine		137.4			45.6			138.6	
N,N-dichloro-s-butylamine			231.2	72				193.3	
N,N-dichloro-tert-butylamine			250.6			70.3			167.5

TABLE V. Influence of pH on the formation rate of N,N-dichlorobutylamines in acid media. [NaClO] $= 2.16 \times 10^{-3}$ M, [Amine] $= 2.86 \times 10^{-3}$ M, [NaCl] $= 0.5$M, and $T = 25°$C.

N,N-dichloro-n-but		N,N-dichloro-iso-but		N,N-dichloro-s-but		N,N-dichloro-tert-but	
pH	k_{exp}/M^{-1} min^{-1}	pH	k_{exp}/M^{-1} min^{-1}	pH	k_{exp}/M^{-1} min^{-1}	pH	k_{exp}/M^{-1} min^{-1}
3.01	31.91	2.71	35.87	2.77	15.52	2.83	5.89
2.47	60.63	2.12	92.99	2.30	29.59	2.36	8.76
2.26	81.27	1.98	94.73	2.11	35.81	2.12	10.62
2.11	92.94	1.89	108.38	1.96	39.18	1.97	10.20
1.96	97.33	1.79	122.80	1.73	45.16	1.86	9.60
1.95	108.91	1.38	130.13	1.65	40.95	1.75	9.51
1.86	106.37	1.19	117.67	1.24	34.02	1.27	5.64
1.28	79.65	1.06	100.87				
1.11	73.34						

Discussion

Formation of N-chlorobutylamines

According to the literature [1–5] on this kind of reaction, mixing solutions of hypochlorite and butylamine gives rise to the rapid formation of N-chlorobutylamine in accordance with the mechanism shown in Scheme I, in which it is assumed that HClO is the only chlorinating species and that the only nitrogenated species susceptible to chlorination is the unprotonated amine. Published values for constants appearing in this scheme are listed in Table III.

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

$$H_3^+NC_4H_9 \underset{}{\overset{K_2}{\rightleftharpoons}} H_2NC_4H_9 + H^+$$

$$HClO + H_2NC_4H_9 \xrightarrow{k_3} HClNC_4H_9 + H_2O$$

$$H_2Cl^+NC_4H_9 \underset{}{\overset{K_4}{\rightleftharpoons}} HClNC_4H_9 + H^+$$

Scheme I

TABLE VI. Influence of the temperature on the decomposition rate (k_{exp}/M^{-1} s^{-1}) of N,N-dichlorobutylamines. [NaClO] $= 2.18 \times 10^{-3}$M, [Amine] $= 2.88 \times 10^{-3}$M, and [NaCl] $= 0.5$M.

T/K	N,N-dichloro-n-but	N,N-dichloro-iso-but	N,N-dichloro-s-but	N,N-dichloro-tert-but
293.8	1.024	1.042	0.376	0.082
295.0	1.059	1.064	0.386	0.114
300.5	1.558	1.733	0.662	0.186
302.1	1.746	1.498	0.749	0.218
304.0	2.335	1.838	0.807	0.211
307.0	2.480	2.623	1.073	0.322
309.8	2.515	2.848	1.295	0.427
E_a/kJ mol^{-1}	48.0	49.3	60.2	73.1
$\Delta H^{\ddagger}$/kJ mol^{-1}	45.5	46.8	57.7	70.6
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	-86	-84	-55	-28

TABLE VII.   Influence of Taft substituent polarity parameters on the rates of formation of N-Chlorobutyla-mines. $HClNCR^1R^2R^3$: $\sum \sigma^* = \sigma^*_{RI} + \sigma^*_{R2} + \sigma^*_{R3}$.

	$\sum \sigma^*$	k_r/s^{-1}	pK_2
N–chloro-n–butylamine	0.86	30.9	
N–chloro-iso–butylamine	0.79	29.4	
N–chloro-s–butylamine	0.39	17.6	
N–chloro-tert–butylamine	0.00	11.2	
n-butylamine			10.43[a]
iso-butylamine			10.48[b]
s-butylamine			10.56[a]
tert-butylamine			10.45[a]
$\log k_r = 1.05 + 0.52 \sum \sigma^*$	$r = 0.9988$		

[a] Ref. [14].
[b] Ref. [15].

Assuming that the acid-base equilibria are faster than the k_3 step, the overall reaction implied by the above scheme is

$$v = d[N\text{-chloramine}]/dt = k_3[HClO][H_2NC_4H_9]$$

Bearing in mind the mass balances and the acid-base equilibria in the medium, this equation is equivalent to

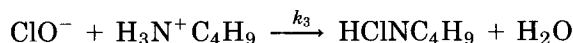$$v = k_3(K_w/K_1)[\text{amine}][Cl_t][OH^-]^{-1}$$

where $[\text{amine}] = [A] + [AH^+]$, $[Cl_t] = [HClO] + [ClO^-]$ and K_w is the ionic product of water.

This rate equation is consistent with the observed reaction orders, and identification with the experimental rate equation $v = k_{obs}[Cl_t]$ implies the expression

$$k_{obs} = k_3(K_w/K_1)[\text{amine}][OH^-]^{-1} = k_r[\text{amine}][OH^-]^{-1}$$

It has been pointed out [5] that the above scheme is kinetically indistinguishable from a mechanism including the ionic step

$$ClO^- + H_3N^+C_4H_9 \xrightarrow{k_3} HClNC_4H_9 + H_2O$$

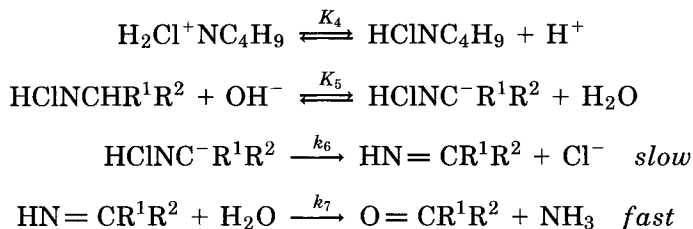which leads successively to

$$v = k_{3'}(K_w/K_2)[\text{amine}][Cl_t][OH^-]^{-1}$$

and

$$k_{obs} = k_{3'}(K_w/K_2)[\text{amine}][OH^-]^{-1} = k_r[\text{amine}][OH^-]^{-1}$$

However, the literature on this kind of reaction suggests that the ionic $k_{3'}$ step can be ruled out [1,5].

Hall [14] reported that the pK_a of amines depend linearly on the Taft parameter σ^* quantifying the polar character of their substituents: $pK_a = 13.23 - 3.14 \sum \sigma^*$. In view of Scheme I, it therefore seems reasonable that the rate constants for the chlorination of amines ought also to be related to σ^*. Table VII lists the values of k_r for the four butylamines studied, together with the corresponding values of σ^*. The excellent correlation between k_r and σ^* ($r = 0.9988$) suggests a relationship between k_r and the pK_a of the amines.

Decomposition of N-chlorobutylamines in Basic Media

In the decomposition of N-chlorobutylamines in strongly basic media, the slow step is the formation of an imine which is subsequently hydrolyzed to an aldehyde (Scheme II).

$$H_2Cl^+NC_4H_9 \xrightleftharpoons{K_4} HClNC_4H_9 + H^+$$

$$HClNCHR^1R^2 + OH^- \xrightleftharpoons{K_5} HClNC^-R^1R^2 + H_2O$$

$$HClNC^-R^1R^2 \xrightarrow{k_6} HN{=}CR^1R^2 + Cl^- \quad slow$$

$$HN{=}CR^1R^2 + H_2O \xrightarrow{k_7} O{=}CR^1R^2 + NH_3 \quad fast$$

Scheme II

Under the working conditions, the K_4 equilibrium must totally favor the right-hand side, since the published pK_a of similar N-chloramines [16] are less than 2. This assumption is confirmed by the values of pK_4 estimated in this work while studying the formation of dichloramines (Table VIII). Accordingly, the proposed reaction mechanism includes no steps for the decomposition of the protonated N-chloramine.

Scheme II implies the rate equation

$$v = -d[\text{products}]/dt = k_6[HClNC^-R^1R^2] = K_5k_6[Cl_t][OH^-] = k_{\text{exp}}[Cl_t]$$

This is in keeping with the experimental results. The k_5 step explains the dependence of the reaction rate on OH^- concentration, and also shows that the carbon binding the amino group must also bear a hydrogen atom. The absence of this hydrogen atom in N-chloro-tert-butylamine explains why the latter is stable under the working conditions employed. More generally, the results for the various chlorobutylamines

TABLE VIII. Influence of Taft substituent polarity parameters on the disproportionation and dissociation of N-chlorobutylamines. $HClNCR^1R^2R^3$: $\sum \sigma^* = \sigma^*_{R1} + \sigma^*_{R2} + \sigma^*_{R3}$.

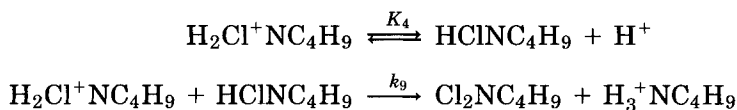| N-chloramine	$\sum \sigma^*$	k_9/M^{-1} min^{-1}	K_H/M^{-1}
N-chloro-n-butylamine	0.86	440	56.9
N-chloro-iso-butylamine	0.79	533	33.2
N-chloro-s-butylamine	0.39	174	53.0
N-chloro-tert-butylamine	0.00	41.9	112.1
N-chloro-3-aminepropanol[a]	1.09	847	6.13
N-chloro-n-propylamine[a]	0.88	490	14.9
N-chloro-iso-propylamine[a]	0.49	152	65.8
N-chloro-4-aminebutanol[a]	1.00	673	30.6
	log $k_9 = 1.67 + 1.18\sum \sigma^*$ $r = 0.959$; $pK_4 = 2.14 - 0.86\sum \sigma^*$		

[a] Ref. [17].

are in keeping with the Taft equation reported [6,14] for *N*-chloramines derived from aliphatic primary amines:

$$\log k_{\text{exp}} = -1.40 - 1.06(\sigma_{\text{R1}}^* + \sigma_{\text{R2}}^*)$$

Formation of N,N-dichlorobutylamines in Acid Media

The pH-dependence of the rate of formation of *N,N*-dichlorobutylamines upon acidification of neutral or basic monochlorobutylamine solutions suggests that there occurs interaction between the neutral and protonated forms of the monochlorinated species (Scheme III)

$$H_2Cl^+NC_4H_9 \xrightleftharpoons{K_4} HClNC_4H_9 + H^+$$

$$H_2Cl^+NC_4H_9 + HClNC_4H_9 \xrightarrow{k_9} Cl_2NC_4H_9 + H_3^+NC_4H_9$$

Scheme III

This mechanism implies the rate equation

$$v = -d[Cl_{t3}]/dt = k_9[H_2Cl^+NC_4H_9][HClNC_4H_9]$$

where $[Cl_{t3}] = [H_2Cl^+NC_4H_9] + [HClNC_4H_9]$ is the total concentration of *N*-chlorobutylamine in the reaction mixture. When the concentrations of protonated and unprotonated monochloroderivative are expressed in terms of the total concentration of *N*-chloramine and the protonation constant $K_H = 1/K_4$, this equation becomes

$$v = k_9K_H[H^+][Cl_{t3}]^2/(1 + K_H[H^+])^2 = k_{\text{exp}}[Cl_{t3}]$$

Hence the [H$^+$]-dependence of the second-order experimental rate constant is given by

$$k_{\text{exp}} = k_9K_H[H^+]/(1 + K_H[H^+])^2$$

Table VIII lists the values of k_9 and K_H obtained using a nonlinear optimization program to fit this equation to the experimental data for k_{exp} at various pH; Figure 4 shows that the corresponding k_{exp}-pH curves fit the experimental data satisfactorily, and the values of K_H are of the same order as potentiometrically measured values for secondary *N*-chloramines [16], which supports the proposed reaction mechanism.

Correlating the values of k_9 and $K_4 = 1/K_H$ with $\sum \sigma^*$ for the *N*-chloramines studied in this work and others [17] yields the Taft equations shown in Table VIII. Correlating the values of pK_4 with the pK_a of the corresponding amines, which also depend on the polarity of the substituents, shows that substituting a chlorine atom for an amino proton greatly increases the acidity of the molecule, the withdrawal of charge by the chlorine atom destabilizing the RNClH$_2^+$ cation:

$$pK_4(\text{N-chloramine}) = 1.72\,pK_a(\text{amine})\text{-}16.5$$
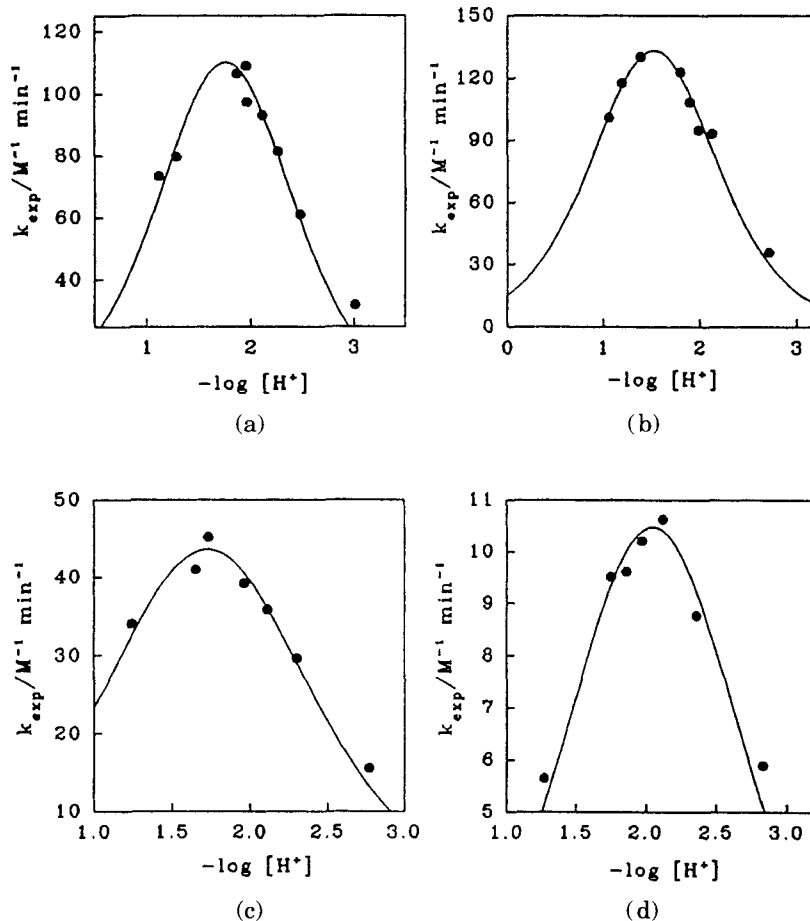
Figure 4. pH-dependence of the rate of disproportionation of N-chlorobutylamines. (A) N-chloro-n-butylamine, (B) N-chloro-iso-butylamine, (C) N-chloro-s-butylamine, and (D) N-chloro-tert-butylamine.

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