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I am submitting herewith a thesis written by Michael Kent Pastorcich entitled "A Kinetic and Thermodynamic Study of the Hydrolysis of Dimethylchloramine." I recommend that it be accepted for eighteen quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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A KINETIC AND THERMODYNAMIC STUDY OF THE HYDROLYSIS OF DIMETHYLCHLORAMINE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Michael Kent Poastorcich

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ABSTRACT

The purpose of this study was to investigate the kinetic and thermodynamic aspects of the hydrolysis of dimethylchloramine under the conditions obtaining in natural waters. The reaction is represented stoichiometrically by the equation:

$$R_2NH + HOCl \underset{k_r}{\overset{k_f}{\rightleftarrows}} R_2NCl + H_2O.$$

In this work, values for the specific rate constant (k_r) and activation energy (ΔE_a) were determined for the hydrolysis of dimethylchloramine.

In principle, the rate constant for the hydrolysis reaction can be determined from the equilibrium expression:

$$K_h = \frac{[R_2NH][HOCl]}{[R_2NCl]} = \frac{k_r}{k_f},$$

where K_h is determined experimentally and k_f is known from the literature. However, Fourier Transform NMR spectrometry and UV-Visible spectrometry were tried without success for determining the equilibrium concentrations of dimethylamine, dimethylchloramine and hypochlorite ion. On the other hand, it was found that the value of the hydrolysis constant could be found by measuring the loss of R_2NCl in an irreversible reaction with phenol. The reaction of dimethylchloramine with excess phenol is pseudo-first order with respect to phenol. Superimposed on this reaction is one that is zero-order with respect to phenol and is characterized as the reaction of dimethylchloramine and water.

The concentration of unreacted dimethylchloramine as a function of time was determined by iodometric titration. Several runs were

made with various phenol concentrations at 25°C and 35°C. Plots of the natural logarithm of concentration vs. time were made and the rate constants found from the slopes of the lines. A plot of rate constant vs. phenol concentration was made and extrapolation to zero phenol concentration gave the value of the rate constant for the hydrolysis reaction. The activation energy of hydrolysis was determined by substitution of the rate constants for two temperatures into the integrated form of the Arrhenius equation.

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CHAPTER I

INTRODUCTION

Natural waters vary widely in composition and, depending on location, the water may be fresh water, seawater or brackish water. The fresh water usually contains traces of organic amines, humic acid, ammonia or ammonium ion, heavy metals, various anions and many forms of living organisms. Seawater, in addition to the organic compounds, contains an abundance of salts of various cations and anions, with the chlorides and bromides of sodium, potassium and magnesium being the most abundant.

The addition of elemental chlorine or hypochlorite solution to the cooling water at a power station to prevent slime formation in the system yields electropositive chlorine in the form of hypochlorous acid and hypochlorite ion. The ratio of the two species is a function of pH and temperature. The active chlorine will react reversibly or irreversibly with many of the organic species and ammonia/ammonium ion. The irreversible loss of chlorine is usually referred to as the "chlorine demand" of the water. The reversible processes usually regenerate the active chlorine as a result of hydrolysis or the chlorinated species act as chlorinating agents themselves. The rates of formation of the chlorinated species are functions of both pH and temperature and are extremely fast.[1] Typical specific rate constants have values of about 10^8 liters/mole-second under the conditions obtaining in natural waters. The compounds of most interest in the reversible systems are the N-chloramines, N-chloramides, and N-chloramino-acids.

The impact of these N-chlorinated compounds on the environment and public health when cooling water is returned to the biosphere is not yet fully known, but would certainly depend on the concentration and length of time these compounds and their degradation products remain in the environment. The major concern is the toxic nature of the chloramines that may persist for hours or even days after blowdown in the waters of a river or estuary. For example, a massive fish-kill in the cooling waters of a large generating station on the shores of Saginaw Bay[2] has been attributed to a lethal concentration of residual chlorine in the water. Halogen residuals in chlorinated waste-water effluents have also been responsible for numerous fish kills in the James River estuary.[3]

M. H. Lietzke[4] has developed a kinetic model for predicting the composition of chlorinated discharge waters from power plants. The model characterizes chlorinated compounds for both reversible and irreversible processes in fresh water. The necessary thermodynamic and kinetic data for most of the chemical reactions are available in the literature. However, the rates of hydrolysis of inorganic dichloramine and organic chloramines have not been thoroughly established by experimentation. Hence this study was undertaken to measure the rates of hydrolysis of the compounds dimethylchloramine and di-n-propylchloramine. In addition the activation energy for the hydrolysis of dimethylchloramine was established.

CHAPTER II

EXPERIMENTAL DETAILS

A. Equipment

Three separate experimental techniques were tried for measuring the change in concentration of the dialkylchloramine as a function of time.

1. Fourier Transform NMR Spectrometry

Each reaction mixture was placed in a standard 5 mm ID NMR tube fitted with a plastic cap. The samples were then placed in a Varian XL-100 NMR spectrometer operated in the pulse mode. Automatic control and numerical analysis of the resulting spectra were provided by a Nicolet Instrument Corporation TT-100 mini-computer interfaced to the spectrometer.

Two scans were taken at five second intervals followed by a ten minute delay period. Forty-eight acquisitions were made over a period of eight hours. The computer performed the transformations and output the data as chemical shift (relative to DSS), peak height and peak area.

The temperature was maintained at $\pm$ 0.5°C by circulating heated air through the sample probe. The sample reached thermal equilibrium within ten minutes.

2. UV-Visible Spectrometry

Samples of the reaction mixture were placed in 1.00 cm quartz cells and stoppered. Three sample cells and one blank cell were

accommodated by the multicell manual selector compartment of a single beam Gilford Instrument Laboratories Inc., 222-A Photometer. The photometer was attached to a Beckman Model DU monochromator.

The photometer operates on the null-balance principle in which the signal generated by the blank cell is stored and later balanced by a summation circuit with the signal generated by the sample. Dark current is eliminated as the bias applied to the dynode of the PM tube is increased until the output from the sample is equal to that of the blank. The increase in bias potential is read directly as absorbance.

Constant temperature was maintained in the sample cells by means of a cooling jacket surrounding the cell compartment through which flowed a 50% methanol solution from a Polyscience Corporation Model 80 Constant temperature circulation and a KR series refrigeration unit. Thermal equilibrium was reached within fifteen minutes and maintained at $\pm$ 0.5°C.

3. Iodometric Titrimetry

A 250 ml volumetric flask containing the reaction mixture diluted to the mark was placed in a constant temperature bath that consisted of an insulated glass vessel filled with water and equipped with a stirrer and an 800-watt heater connected to a micro-set thermoregulator. The temperature was maintained to within $\pm$ 0.1°C and equilibrium was reached within twenty minutes.

Reactant and sample volumes were measured using "Total Delivery" glass pipettes. Volumes having fractional values were delivered from 50 $\pm$ 0.1 ml burettes. All titrations were performed with 10 $\pm$ 0.1 ml burettes.

4. Time Measurements

Except for the NMR study, time measurements were made using a clock with a sweeping second hand. The computer contained a timing circuit which provided the ten-minute delay periods between acquisitions taken on the NMR spectrometer.

5. pH Measurements

All pH values were obtained using a Beckman Model H2 pH meter with a Corning Scientific Instruments Semi-micro Combination pH Electrode.

B. Solutions

1. Fourier Transform NMR Spectrometry

All solutions for the NMR study were prepared using 99.9% D_2O for the purpose of reducing the H_2O and -NH peaks. Dimethylamine was prepared by adding dropwise a concentrated solution of dimethylamine hydrochloride onto solid potassium hydroxide. The dimethylamine gas was condensed over a cold finger at the temperature of dry ice and methanol. The amine was then dissolved in a small amount of D_2O and stored at 0°C in a stoppered flask. Dilutions were made as needed and standardized by titration against 0.100 N HCl to a bromthymol blue end point.

Fresh solutions of sodium hypochlorite were prepared before each run. A 1 g piece of sodium metal cleaned with carbon tetrachloride was dissolved in 100 ml of D_2O. Chlorine gas was then bubbled through the solution until the pH became *ca*. 7. Total available chlorine was determined by iodometric titration.[5] A 10.0 ml aliquot of the sodium

hypochlorite solution was added to acidified potassium iodide solution and titrated with 0.100 N sodium thiosulfate. Concentration was on the order of 0.5 N.

2. UV-Visible Spectrometry and Iodometric Titrimetry

Stock solutions similar to those used in the NMR study were prepared. For these two techniques it was unnecessary to prepare solutions of dimethylamine or di-n-propylamine free of protons that would exchange with the proton of the -NH functional group.

A stock solution of dimethylamine hydrochloride was prepared by adding a weighed amount of the dry salt to triply distilled water and diluting to 1 liter. Di-n-propylamine hydrochloride solutions were prepared by pipetting liquid di-n-propylamine into triply distilled water. One N HCl was added until the pH equalled 7.

Stock sodium hypochlorite solution was prepared by pipetting 5% reagent grade sodium hypochlorite solution into triply distilled water. Standardization was by the method used in the NMR study and performed before each run.

Buffer solutions were prepared by adding sufficient amounts of various salts to 100 ml of solution to yield 0.2 N solutions. One N HCl or 1 N NaOH were added to each salt or combination of salt solution to yield the pH of maximum buffer capacity. The buffers used were sodium phosphate dibasic at pH = 7.6, sodium borate tetrahydrate at pH = 8.8 and sodium phosphate tribasic at pH = 11.7.

A 0.2 N phenol solution was prepared by adding 9.41 g of crystalline phenol to sufficient triply distilled water to make 1 liter. Standardization was by the bromate-bromide method.[6] An

aliquot of the phenol solution was allowed to react for ten minutes with acidified potassium bromate-potassium bromide solution. Solid potassium iodide was then added and the liberated iodine titrated with 0.025 N sodium thiosulfate to a starch endpoint. A blank solution without the phenol was treated in a similar manner. The difference of the titres provided the concentration of the phenol solution.

C. Procedure

All glassware coming in contact with the reactants and mixtures was washed, rinsed in triply distilled water and dried.

1. Fourier Transform NMR Spectrometry

Before each run the pH of the dimethylamine and sodium hypochlorite solutions was adjusted to approximately the same value in the range 7.5 - 8.5. Appropriate volumes of reactants were combined to give an excess of dimethylamine. A one ml aliquot of the solution was placed in an NMR tube along with a small amount of sodium 2,2-dimethyl-2-silapentane-5-sulfonate reference material. The tube was then placed in the sample probe and allowed to reach thermal equilibrium. The magnet homogeneity was adjusted and control given to the computer. Spectral data were stored on magnetic disc and evaluated after each run.

2. UV-Visible Spectrometry

Prior to measuring the absorbances of dimethylchloramine and hypochlorite ion in the reaction mixture, separate absorbance vs.

concentration plots for dimethylchloramine and hypochlorite ion were made to obtain the molar extinction coefficients. Absorbances of dimethylamine and hypochlorite ion were measured at 265 nm and 295 nm, respectively.[7]

The reaction mixtures were prepared to give an excess of dimethylamine and a constant buffer concentration. Aliquots of the mixtures were placed in 1.00 cm quartz cells and stoppered. The cells were placed in the cell compartment and allowed to reach thermal equilibrium. Absorbance values meausred relative to the distilled water blank were taken at regular intervals at both wavelengths. The error introduced by changing the monochromator was checked by placing a neutral density filter in the beam and measuring the absorbance after resetting the monochromator. The error was within $\pm$ 0.003 absorbance units.

3. Iodometric Titrimetry

Appropriate volumes of dimethylamine or di-n-propylamine, sodium hypochlorite and buffer were placed in the reaction flask to yield constant concentrations. Various amounts of phenol were added to each reaction mixture to give different concentrations. The mixtures were diluted to the mark and placed in the constant temperature bath and allowed to reach thermal equilibrium. Aliquots 10.0 $\pm$ 0.1 ml were removed at regular intervals and added to acidified potassium iodide. The liberated iodine was titrated with 0.010 N sodium thiosulfate to yield the concentration of the unreacted dialkylchloramine.

CHAPTER III

APPROACH

In aqueous solutions, electropositive chlorine reacts with ammonia, ammonium ion and various organic amines to give a series of N-chlorinated products. With ammonia the reactions are presumed to be stepwise and are represented by the equations:

$$NH_3 + HOCl \rightleftarrows NH_2Cl + H_2O \quad (1)$$

$$NH_2Cl + HOCl \rightleftarrows NHCl_2 + H_2O \quad (2)$$

$$NHCl_2 + HOCl \rightleftarrows NCl_3 + H_2O \quad (3)$$

Organic amines follow similar paths and are represented by the equations:

$$RNH_2 + HOCl \rightleftarrows RNHCl + H_2O \quad (4)$$

$$RNHCl + HOCl \rightleftarrows RNCl_2 + H_2O \quad (5)$$

$$R_2NH + HOCl \underset{k_r}{\overset{k_f}{\rightleftarrows}} R_2NCl + H_2O \quad (6)$$

where R = methyl, ethyl, etc.

Weil and Morris[1] have characterized the forward reactions and determined the rates to be a function of both pH and temperature. They state that the forward rate in equation (6), where R = methyl, is given by

$$d[(CH_3)_2NCl]/dt = 1.2 \times 10^{11} \exp(-800/RT)[(CH_3)_2NH][HOCl]; \quad (7)$$

or considering the pH,

$$k_f(\text{obs.}) = \frac{k_f \text{ (specific)}}{1 + \frac{K_a K_b}{K_w} + \frac{K_a}{[H^+]} + \frac{K_b}{K_w}[H^+]}, \quad (8)$$

where k_f (specific) = 3.1×10^{10} 1 mole^{-1} min^{-1} at 25°C; K_a is the acid ionization constant of hypochlorous acid,[9] $K_a = 2.95 \times 10^{-8}$; and K_b is the base ionization constant of dimethylamine,[10] $K_b = 5.89 \times 10^{-4}$.

The reverse reaction in equation (6) may be characterized as a pseudo-first order reaction in dilute solution, where water is present in large excess. The equilibrium hydrolysis constant would then be given by the equation:

$$K_h = \frac{[R_2NH][HOCl]}{[R_2NCl]} , \tag{9}$$

while the loss of R_2NCl would be given by:

$$- d[R_2NCl_2]/dt = k_r[R_2NCl] - k_f[R_2NH][HOCl]. \tag{10}$$

In the pH range of natural waters (7.0 - 8.5), R_2NCl exists as the molecular species, where:

$$R_2NHCl^+ \rightleftarrows R_2NCl + H^+, \; K_a \approx 3 \times 10^{-1} \tag{11}$$

does not occur to any appreciable degree. Therefore the specific rate of hydrolysis is equal to the observed rate.

The value of K_h, the hydrolysis constant can be found by determining the equilibrium concentrations of R_2NCl and HOCl. At pH > 8 hypochlorite ion predominates and equation (9) reduces to:

$$K_h = \frac{[OCl^-]^2}{[R_2NCl]} . \tag{12}$$

The value of k_r in equation (6) can be found using the relationship:

$$K_h = \frac{k_r(\text{specific})}{k_f(\text{specific})} . \tag{13}$$

Alternatively, the rate of hydrolysis can be determined by measuring the loss of R_2NCl in an irreversible reaction with another easily chlorinated compound. Brown and Soper[10] measured the reaction rates of various N-chlorinated compounds with phenol. They found that the reaction of dialkylchloramines and excess phenol is pseudo-first order and can be represented by the equation:

$$R_2NCl + PhOH \xrightarrow{k_1} R_2NH + PhClOH. \tag{14}$$

Within the pH range of 4.5-8.5 they found the rate of disappearance of R_2NCl to be independent of pH and proportional to the concentration of phenol. This rate can be expressed as:

$$-\frac{d[R_2NCl]}{dt} = k_1[R_2NCl] = k_2[R_2NCl][phOH], \tag{15}$$

where $k_1 = k_2/[phOH]$. A parallel study by Hurst and Soper[11] following the reaction of N-chloroacetanilide and phenol showed that a plot of k_1 vs [phOH] extrapolated to zero phenol concentration yielded a value of $k_1 > 0$. This implies that another reaction is superimposed on the direct interaction of the N-chlorinated compound and phenol. This imposed reaction would be the reverse reaction in equation (6). Equation (15) will expand to:

$$k_1[R_2NCl] = k_r[R_2NCl][H_2O] + k_2[R_2NCl][phOH] \tag{16}$$

or

$$k_1 = k_r[H_2O] + k_2[phOH]. \tag{17}$$

Since H_2O is in large excess and its concentration essentially constant, equation (17) becomes:

$$k_1 = k_r + k_2[phOH]. \tag{18}$$

The intercept of a plot of k_1 vs. [phOH] will yield k_r, the hydrolysis rate constant for R_2NCl.

CHAPTER IV

RESULTS AND DISCUSSION

A. Treatment of Data and Calculations

1. Fourier Transform NMR Spectrometry

An NMR spectrum of dimethylamine in D_2O will exhibit a singlet corresponding to the two equivalent methyl groups with a chemical shift δ = 2.2 - 2.7 ppm dependent upon the equilibrium:

$$(CH_3)_2ND + D^+ \rightleftarrows (CH_3)_2 ND_2^+ \qquad (19)$$

where $pK_a \overset{\sim}{\sim} 10.8$.[8] The D^+ exchange is slow enough so that at pH values near pK_a, the peaks for both species will be time averaged and the resulting singlet will have a shift value between 2.2 and 2.7 ppm.

Due to the method of solution preparation, it was not possible to have a dimethylamine solution free of amine protons. The exchange of deuterium for hydrogen is virtually complete owing to the excess of D_2O. The protons exchanged with D_2O giving small concentrations of HDO and H_2O. A singlet corresponding to these two species occurred at δ = 4.7 ppm. The substitution of chlorine onto the nitrogen of dimethylamine causes the methyl protons to be deshielded and their resonance to occur downfield near δ = 2.9 ppm. A change in the shift of dimethylchloramine due to the equilibrium in equation (11) would occur at the extreme condition where pH < 1.

Chemical shift data as a function of pH for dimethylamine and dimethylchloramine are shown in Table I, p. 13. The predominant species encountered within the pH range of interest in this study (7.5-8.5) are $(CH_3)_2NH_2^+$ and $(CH_3)_2NCl$.

TABLE I

CHEMICAL SHIFT (PPM) AS A FUNCTION OF pH

pH	$(CH_3)_2NH$	$(CH_3)_2NCl$	H_2O
12.0	2.27	-	4.76
10.7	2.62	-	4.72
8.7	2.72	2.92	4.74
7.6	2.72	2.92	4.74
6.6	2.72	2.92	-
2.2	2.72	2.93	-

Relative concentration data for the two species shown above were extracted from the transformed NMR spectral data. The sum of the area under the peaks for $(CH_3)_2NH_2^+$ and $(CH_3)_2NCl$ is taken to represent the total amount of amine present. The relative concentrations may be expressed using the equations:

$$R_A = \frac{\text{Peak area (dimethylchloramine)}}{\text{Total peak area}} \tag{20}$$

and

$$R_B = \frac{\text{Peak area (dimethylamine)}}{\text{Total peak area}}. \tag{21}$$

Relative abundances expressed as fractions of the total amine present rather than concentrations expressed in molarity have been used to circumvent the necessity of determining activity coefficients for the relatively large concentrations of the dimethylchloramine and dimethylammonium ion. Buffer solutions were not included in the reaction mixtures for the same reason.

Plots of the natural logarithm of R_A and R_B *vs.* time were made and best fitting straight lines were generated using a non-linear least squares computer program devised by M. H. Lietzke.[12] The absolute value of the slope of each line would give the rate constant for the disappearance of dimethylchloramine or the apperance of dimethylammonium ion if the reaction proceeds at a measurable rate before equilibrium is established. Three runs at three temperatures were made and the results are shown in Tables II and III, p. 15.

2. *UV-Visible Spectrometry*

The absorbance bands for dimethylchloramine and hypochlorite ion overlap to a considerable degree and the extraction of concentration data

TABLE II

SLOPES OF PLOTS OF NATURAL LOGARITHM (R_A) VS. TIME FOR $(CH_3)_2NCl$

	35°C	25°C	15°C
Run 1	-2.40×10^{-4}	-2.82×10^{-4}	-4.87×10^{-5}
Run 2	-3.14×10^{-4}	-9.26×10^{-4}	-4.41×10^{-4}
Run 3	-6.76×10^{-4}	-8.33×10^{-4}	-3.91×10^{-4}

TABLE III

SLOPES OF PLOTS OF NATURAL LOGARITHM (R_B) VS. TIME FOR $(CH_3)_2NH$

	35°C	25°C	15°C
Run 1	2.87×10^{-4}	2.27×10^{-4}	3.13×10^{-5}
Run 2	1.95×10^{-4}	1.04×10^{-3}	4.20×10^{-4}
Run 3	4.78×10^{-4}	6.67×10^{-4}	5.18×10^{-4}

from absorbance measurements at 265 nm and 295 nm requires the solution of the two simultaneous equations:

$$A_{\lambda 1} = \varepsilon_{x\lambda 1} C_x + \varepsilon_{y\lambda 1} C_y$$

$$A_{\lambda 2} = \varepsilon_{x\lambda 2} + \varepsilon_{y\lambda 2} C_y \qquad (22)$$

where λ_1 = 265 nm, λ_2 = 295 nm, A = total absorbance, ε = molar extinction coefficient, C_x = concentration of dimethylchloramine, and C_y = concentration of hypochlorite ion.

Molar extinction coefficients were determined by plotting absorbance vs. concentration for each species at both wavelengths and finding the slope of the best fit line. The calculations were performed using the linear regression program of a Texas Instruments SR-51A calculator. Experimental absorbance values and calculated molar extinction coefficients for dimethylchloramine and hypochlorite ion are shown in Table IV, p. 17.

Absorbance measurements at λ_1 = 265 and λ_2 = 295 for reaction mixtures of dimethylamine and sodium hypochlorite buffered at three different pH values indicate no change in concentrations over a period of one hour. Absorbance values as a function of pH and time for the reaction mixture are shown in Table V, p. 18.

Equilibrium concentrations of dimethylchloramine and hypochlorite ion have been calculated by substituting ε values from Table IV, p. 17, and the average absorbance values from Table V, p. 18, into equation (22). Concentrations have been expressed in molarity since the starting concentrations of the reactants were in the 10^{-3} M range and activity coefficients have been taken to be unity. Buffer

TABLE IV

ABSORBANCE AS A FUNCTION OF CONCENTRATION FOR OCl^- (pH = 11.7) AND $(CH_3)_2NCl$ (pH = 6.9) AT 265 nm AND 295 nm

	OCl^- Absorbance		$(CH_3)_2NCl$ Absorbance	
Concentration	265 nm	295 nm	265 nm	295 nm
4.27×10^{-3} M	0.342	0.808	0.792	0.315
2.13×10^{-3} M	0.168	0.395	0.375	0.147
1.07×10^{-3} M	0.085	0.190	0.178	0.070
5.34×10^{-4} M	0.042	0.095	0.091	0.035
Slope = $\varepsilon_{x\lambda 1}$ = 79.9			Slope = $\varepsilon_{y\lambda 1}$ = 18.4	
Slope = $\varepsilon_{x\lambda 2}$ = 18.9			Slope = $\varepsilon_{y\lambda 2}$ = 72.9	

TABLE V

ABSORBANCE MEASUREMENTS FOR THE REACTION MIXTURE AS A FUNCTION OF TIME AND pH. STARTING CONCENTRATIONS OF REACTANTS: $[(CH_3)_2NH]_o$ = 8.0 x 10^{-3} M, $[NaOCl]_o$ = 4.28 x 10^{-3} M; TEMPERATURE = 25°C

	pH = 8.8		pH = 9.8		pH = 11.6	
	Absorbance		Absorbance		Absorbance	
Time (min)	265 nm	295 nm	265 nm	295 nm	265 nm	295 nm
5	0.828	0.322	0.795	0.303	0.807	0.311
10	0.831	0.321	0.795	0.304	0.806	0.311
15	0.831	0.322	0.795	0.301	0.806	0.308
20	0.832	0.319	0.796	0.303	0.807	0.310
25	0.830	0.321	0.794	0.303	0.805	0.310
30	0.831	0.321	0.795	0.305	0.806	0.312
35	0.830	0.323	0.795	0.303	0.805	0.309
40	0.830	0.321	0.793	0.303	0.803	0.310
45	0.832	0.320	0.795	0.302	0.805	0.308
50	0.830	0.320	0.795	0.302	0.804	0.308
55	0.830	0.321	0.794	0.302	0.803	0.308
60	0.830	0.320	0.794	0.302	0.803	0.308
Average	0.830	0.321	0.795	0.303	0.805	0.310

concentrations were held constant at 0.02 M and expressed as the concentration of the salt anion. The calculated values of the equilibrium concentrations are shown in Table VI, p. 20.

3. Iodometric Titrimetry

The overall stoichiometry for the reaction of iodide with dialkylchloramines and thiosulfate with iodine results in a one to one correspondence between the concentration of dialkylchloramine and sodium thiosulfate. The concentration of unreacted dialkylchloramine in each 10.0 ml aliquot will be:

$$[R_2NCl] = (\text{ml of } 0.010 \text{ N } Na_2S_2O_3) \times 10^{-3} \text{ M.} \quad (23)$$

Considerations of the activities of the reactacts in this method are the same as those for the UV-Visible spectrometry method. Constant buffer concentrations of 0.05 M, in phosphate, were used in each reaction mixture. The pH of the reaction mixtures varied over the range of 7.75-8.15 during the course of each run.

Concentrations of unreacted dialkylchloramine as a function of time for each phenol concentration and temperature are summarized in Tables VII-XIV, pp. 21-28. Plots of the natural logarithm of concentration *vs.* time were made in each case. After a brief induction period caused by the approach to thermal equilibrium, the plots of the data points became linear. Straight lines were fitted to the data by the same method used for the UV-Visible spectrometry data. Extrapolation of the lines to zero time gave starting concentrations equal to the calculated value for dialkylchloramine expressed as concentration of hypochlorite ion. The numerical value of the slope of each line is the rate constant k_1(obs.) for the loss of dialkylchloramine. Table XV, p. 29,

TABLE VI

CALCULATED VALUES OF EQUILIBRIUM CONCENTRATION FOR OCl^- AND $(CH_3)_2NCl$ AT 25°C USING EQUATION (22)

	pH = 8.8	pH = 9.8	pH = 11.6
$[OCl^-]_{eq.}$	-3.98×10^{-5} M	-6.70×10^{-5} M	-4.41×10^{-5} M
$[(CH_3)_2NCl]_{eq.}$	4.68×10^{-3} M	4.42×10^{-3} M	4.53×10^{-3} M

TABLE VII

CONCENTRATION OF UNREACTED $(CH_3)_2NCl$ AS A FUNCTION OF TIME FOR [phOH] = 0.020 M, TEMPERATURE = 25°C, AND pH = 7.85-8.15

Time (min)	$[(CH_3)_2NCl] \times 10^3$ M	ln $[(CH_3)_2NCl]$
1	9.95	-4.61
10	9.85	-4.62
20	9.70	-4.64
30	8.25	-4.80
40	7.50	-4.89
50	6.80	-5.00
60	6.15	-5.09
70	5.55	-5.19
80	5.05	-5.29
117	3.55	-5.64

TABLE VIII

CONCENTRATION OF UNREACTED $(CH_3)_2NCl$ AS A FUNCTION OF TIME FOR [phOH] = 0.040 M, TEMPERATURE = 25°C AND pH = 7.95-8.10

Time (min)	$[(CH_3)_2NCl] \times 10^3$ M	ln $[(CH_3)_2NCl]$
3	9.10	-4.70
13	8.75	-4.74
23	7.25	-4.93
33	6.00	-5.12
43	4.90	-5.32
53	4.05	-5.51
63	3.40	-5.68

TABLE IX

CONCENTRATION OF UNREACTED $(CH_3)_2NCl$ AS A FUNCTION OF TIME FOR [phOH] = 0.051 M, TEMPERATURE = 25°C, AND pH = 7.75-7.95

Time (min)	$[(CH_3)_2NCl] \times 10^3$ M	ln $[(CH_3)_2NCl]$
3	10.15	-4.59
12	8.30	-4.79
17	7.30	-4.92
23	6.35	-5.06
29	5.55	-5.19
34	4.80	-5.34
41	4.15	-5.48
46	3.65	-5.61

TABLE X

CONCENTRATION OF UNREACTED $(CH_3)_2NCl$ AS A FUNCTION OF TIME FOR [phOH] = 0.020 M, TEMPERATURE = 35°C, AND pH = 7.85-8.15

Time (min)	$[(CH_3)_2NCl] \times 10^3$ M	ln $[(CH_3)_2NCl]$
3	11.60	-4.46
12	8.85	-4.62
20	8.30	-4.79
28	7.05	-4.95
38	5.70	-5.17
48	4.70	-5.36

TABLE XI

CONCENTRATION OF UNREACTED $(CH_3)_2NCl$ AS A FUNCTION OF TIME FOR [phOH] = 0.030 M, TEMPERATURE = 35°C AND pH = 7.80-8.05

Time (min)	$[(CH_3)_2NCl] \times 10^3$ M	ln $[(CH_3)_2NCl]$
2	11.45	-4.47
13	8.50	-4.77
22	6.55	-5.03
31	5.05	-5.29
39	3.90	-5.55
44	3.35	-5.70

TABLE XII

CONCENTRATION OF UNREACTED $(CH_3CH_2CH_2)_2NCl$ AS A FUNCTION OF TIME FOR [phOH] = 0.020 M, TEMPERATURE = 25°C AND pH = 7.80-7.95

Time (min)	$[(CH_3CH_2CH_2)_2NCl] \times 10^3$ M	ln $[(CH_3CH_2CH_2)_2NCl]$
1	10.85	-4.52
11	9.90	-4.62
21	9.05	-4.70
31	8.10	-4.82
41	7.30	-4.92
57	6.05	-5.11
70	5.00	-5.30

TABLE XIII

CONCENTRATION OF UNREACTED $(CH_3CH_2CH_2)_2NCl$ AS A FUNCTION OF TIME FOR [phOH] = 0.030 M, TEMPERATURE = 25°C AND pH = 7.80-8.00

Time (min)	$[(CH_3CH_2CH_2)_2NCl] \times 10^3$ M	ln $[(CH_3CH_2CH_2)_2NCl]$
2	10.00	-4.61
9	9.10	-4.70
17	8.20	-4.80
26	7.00	-4.96
36	5.80	-5.15
46	4.65	-5.37
56	3.80	-5.57

TABLE XIV

CONCENTRATION OF UNREACTED $(CH_3CH_2CH_2)_2NCl$ AS A FUNCTION OF TIME FOR (phOH] = 0.040 M, Temperature = 25°C, AND pH = 7.80-8.00

Time (min)	$[(CH_3CH_2CH_2)_2NCl] \times 10^3$ M	ln $[(CH_3CH_2CH_2)_2NCl]$
2	10.80	-4.53
12	7.65	-4.87
18	6.75	-5.00
25	5.55	-5.19
30	5.25	-5.25
37	3.85	-5.56
43	3.60	-5.63

TABLE XV

VALUES OF k_1(obs.) FOR $(CH_3)_2NCl$ AND $(CH_3CH_2CH_2)_2NCl$ AS A FUNCTION OF [phOH] AT 25°C

[phOH]	0.020 M	0.030 M	0.040 M	0.051M
$(CH_3)_2NCl$	0.98	-	1.90	2.39
$(CH_3CH_2CH_2)_2NCl$	1.21	1.99	2.64	-

summarizes the k_1(obs.) values as a function of phenol concentration for dimethylchloramine and di-n-propylchloramine at 25°C. The k_1(obs.) values and phenol concentrations for dimethylchloramine at 35°C are shown in Table XVI, p. 31.

The value of k_r in equation (18) was determined by plotting k_1(obs.) vs. [phOH] and extrapolating to zero phenol concentration. Straight lines were fitted and the intercept determined by the lienar regression method. Table XVII, p. 31, summarizes the results for both species at 25°C and dimethylchloramine at 35°C.

B. Discussion of Results and Errors

1. Fourier Transform NMR Spectrometry

The inconsistency of the results shown in Table II, p. 15, is attributable to the method of data normalization and the inherent imprecision of quantitative measurements taken with the NMR spectrometer (ca. 10%). It can be concluded that the plots are horizontal and that the reaction reaches equilibrium much too fast for this method.

2. UV-Visible Spectrometry

The very small value of the concentration calculated for hypochlorite at pH = 8.8 (see Table VI, p. 20) and the negative values calculated at pH = 9.8 and 11.6 indicate that the equilibrium concentrations of dimethylamine and hypochlorite ion are below the detection limit of the photometer. An estimated detection limit of 1×10^{-4} for hypochlorite ion and the calculated value of 4.37×10^{-3} M for dimethylchloramine at pH = 8.8 substituted into equation (12) gives a value of $K_h < 2 \times 10^{-6}$.

TABLE XVI

VALUES OF k_1(obs.) FOR $(CH_3)_2NCl$ AS A FUNCTION OF [phOH] AT 35°C

	k_1(obs.) x 10^2 min^{-1}	
[phOH]	0.020 M	0.030 M
$(CH_3)_2NCl$	2.07	3.01

TABLE XVII

VALUES OF k_r(obs.) FOR $(CH_3)_2NCl$ AND $(CH_3CH_2CH_2)_2NCl$ AT 25°C AND 35°C

	k_r(obs.) x 10^3 min^{-1}	
	25°C	35°C
$(CH_3)_2NCl$	0.73	1.90
$(CH_3CH_2CH_2)_2NCl$	-1.98	-

3. Iodometric Titrimetry

The negative value of k_r extrapolated for di-n-propylchloramine (see Table XVII, p. 31) implies that the hydrolysis is extremely slow and the measurement of the rate would require precision greater than that obtained with this method. The extremely slow rate of hydrolysis is readily explained by the fact that di-n-propylchloramine is only sparingly soluble in water at 25°C and that a necessary step for hydrolysis is solvation of the di-n-propylchloramine molecules. Determination of k_r would require knowledge of the solubility of di-n-propylchloramine which was neither found in the literature nor determined experimentally in this study.

The value of the rate constant for hydrolysis, $k_r = 0.73 \times 10^{-3}$ min^{-1} for dimethylchloramine, is reasonable when compared to $k_r = 2.5 \times 10^{-3}$ min^{-1} determined by Brown and Soper[10] for diethylchloramine and $k_r = 1.77 \times 10^{-3}$ min^{-1} for inorganic chloramine found by Granstram.[13] All values were measured at 25°C.

The activation energy for the hydrolysis reaction of dimethylchloramine can be determined by substitution of the k_r values from Table XVII, p. 31, into the integrated form of the Arrhenius equation,

$$\ln \frac{k_r'}{k_r} = \frac{\Delta E_a (T' - T)}{RT'T} , \qquad (24)$$

where k_r' is the rate constant at $T' = 308°K$ and k_r is the rate constant at $T = 298°K$. The activation energy for the hydrolysis reaction is thus found to be 17 kcal $mole^{-1}$. The overall expression for the rate loss of dimethylchloramine by hydrolysis can be derived by substitution of equation (7) and $k_r = A \exp(-17{,}000/RT)$, where A is the Arrhenius factor and is equal to 4.23×10^9, into equation (10).

The temperature dependent rate expression for the hydrolysis of dimethylchloramine is thus:

$$- d[(CH_3)_2NCl]/dt = 4.23 \times 10^9 \exp(-17{,}000/RT)[(CH_3)_2NCl] - 1.2 \times 10^{11} \exp(-800.RT)[(CH_3)NH][HOCl]. \quad (26)$$

The time of half-reaction for the hydrolysis of dimethylchloramine, calculated using the relationship $t_{1/2} = \ln 2/k_r$, has a value of 15.8 hours at 25°C and of 6.1 hours at 35°C. The corresponding $t_{1/2}$ for the hydrolysis of diethylchloramine is 3.9 hours at 25°C. These values may be compared with a time of half-reaction of 6.5 hours for the hydrolysis of inorganic monochloramine.

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