Articles

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Kinetics and Mechanisms of the Base Decomposition of Nitrogen Trichloride in Aqueous Solution

Krishan Kumar, Roger W. Shinness, and Dale W. Margerum*

Received June 12, 1987

The rate expression for the base decomposition of nitrogen trichloride is $-d[NCl_3]/dt = 2(k_0 + k_1[OH^-] + k_{HB}[HB][OH^-] + k_2[OH^-]^2)[NCl_3]$, based on the stoichiometry $2NCl_3 + 6OH^- \rightarrow N_2 + 3OCl^- + 3Cl^- + 3H_2O$. Values of the rate constants (25.0 °C, $\mu = 0.5$) are $1.6 \times 10^{-6}\ s^{-1}$ for k_0, 8 $M^{-1}\ s^{-1}$ for k_1, and 890 $M^{-2}\ s^{-1}$ for k_2. The specific-base/general-acid-catalyzed path gives k_{HB} values ($M^{-2}\ s^{-1}$) of 2.1×10^3 for $H_2PO_4^-$, 7.6×10^2 for $B(OH)_3$, 65 for HCO_3^-, and 128 for HPO_4^{2-}. In the proposed mechanism Cl_2NClOH^- is a common reactive intermediate that can react with acids (H_3O^+, HB, and H_2O with a Brønsted α value of 0.48) to form $HNCl_2$ and HOCl or it can react with an additional OH^- to release OCl^-. The $HNCl_2$ so formed reacts rapidly with a second NCl_3 to give products. Kinetics data allow an equilibrium constant of $1.6 \times 10^8\ M^{-1}$ (25.0 °C, $\mu = 0.5$) to be calculated for the reaction $NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$.

Introduction

When excess chlorine is added to potable and waste water, monochloramine, dichloramine, and trichloramine (nitrogen trichloride) are formed.[1] The formation of NH_2Cl and $NHCl_2$ from the reaction of ammonia with chlorine or HOCl is quantitative, while the formation of NCl_3 from the reaction of $NHCl_2$ with HOCl is not.[2,3] There is a loss of active chlorine in the latter reaction due to the formation of N_2 and Cl^-. The overall process, in which ammonia is oxidized and the active chlorine concentration reaches a minimum level, is referred to as breakpoint chlorination.[2] This behavior is very important in water chlorination processes, but the dynamics of the reactions are not well understood. The kinetics of formation[4,5] of NH_2Cl and $NHCl_2$, as well as their disproportionation in acid,[3,4] have been studied previously.

Trichloramine was first prepared by Dulong[6] in 1811 by the action of chlorine with a solution of an ammonium salt. He was seriously injured by its violent explosion.[6] Pure trichloramine is an oily yellow liquid,[7] which is sensitive to heat or shock and will undergo spontaneous explosions[8,9] when it is not in solution. Trichloramine has a powerful irritating odor and limited solubility in water.[10] It is very volatile (its vapor pressure is 150 mmHg at room temperature)[11] and is easily lost from aqueous solution. The ultraviolet spectrum of trichloramine in aqueous solution has absorption peaks at 336 and 220 nm.[12] There is wide disagreement in the values of the molar absorptivities of trichloramine due to a lack of accurate methods for its determination. Although iodometry has been used to determine the concentration of trichloramine, it does not produce quantitative amounts of iodine.[13] The reported ϵ values vary from 180 to 272 $M^{-1}\ cm^{-1}$ at 336 nm.[3,12,14-18] Dilute solutions of NCl_3 in aqueous acid are moderately stable.[9,10] Trichloramine solutions prepared from the reaction of ammonia with a 3-fold excess of hypochlorous acid always have less than the theoretical amount of NCl_3 and low levels of residual hypochlorous acid.

Studies of the formation and decomposition of NCl_3 are very important because these processes occur during breakpoint chlorination. Saguinsin and Morris[19] studied the kinetics of decomposition of NCl_3 at 20 °C and pH 7-9 in a buffered medium. They observed that the reaction was first order in NCl_3, with a hydroxide-independent path ($3.2 \times 10^{-5}\ s^{-1}$) and a path that was first order in OH^- (18.8 $M^{-1}\ s^{-1}$). They proposed that the decomposition of NCl_3 in base produced dichloramine (eq 1), which then decomposed in accord with eq 2. Spectral scans during the

$$NCl_3 + H_2O \xrightarrow{OH^-} NHCl_2 + HOCl \qquad (1)$$

$$2NHCl_2 + H_2O \rightarrow N_2 + HOCl + 3H^+ + 3Cl^- \qquad (2)$$

reaction gave no evidence of $NHCl_2$. Therefore, the reaction in eq 2 was assumed to be fast relative to the reaction in eq 1. Their rate constants were based on a 1:1 stoichiometry, because it was assumed that only one NCl_3 was lost each time it reacted with base. No buffer dependence was reported. These authors also reported a rate constant of 3.4 $M^{-1}\ s^{-1}$ (20 °C) for the formation of NCl_3 (reverse of eq 1). We find significantly different rate constants and different mechanisms.

In a recent study from this laboratory, Hand and Margerum[3] reported kinetics for the reactions of dichloramine. The decomposition of $NHCl_2$ is autocatalytic and speeds up as NCl_3 and HOCl are formed. The reaction between $NHCl_2$ and HOCl (eq 3) is general-base (B) catalyzed and produces NCl_3. The trichloramine formed in eq 3 reacts with $NHCl_2$ to produce N_2, Cl^-, and additional HOCl (eq 4). Thus, NCl_3 is lost in the destruction

$$NHCl_2 + HOCl + B \underset{k_{HB}}{\overset{k_B}{\rightleftharpoons}} NCl_3 + BH^+ + OH^- \qquad (3)$$

$$NHCl_2 + NCl_3 + 3OH^- \rightarrow N_2 + 2HOCl + 3Cl^- + H_2O \qquad (4)$$

---

(1) Palin, A. T. *Water Water Eng.* **1950**, *54*, 151-159, 189-200, 248-256.
(2) Wei, I. W.; Morris, J. C. In *Dynamics of Breakpoint Chlorination*; Rubin, A. J., Ed.; Ann Arbor Science: Ann Arbor, MI, 1975; Chapter 13.
(3) Hand, V. C.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1449-1456.
(4) Margerum, D. W.; Gray, E. T.; Huffman, R. P. In *Organometals and Organometalloids, Occurrence and Fate in the Environment*; ACS Symposium Series 82; Brinkman, F. E., Bellana, J. M., Eds.; American Chemical Society: Washington, DC, 1978; pp 278-291.
(5) Morris, J. C.; Isaac, R. A. In *Water Chlorination: Environmental Impact and Health Effects*; Jolley, R. L., Brungs, W. A., Cotruro, J. A., Cummings, R. B., Matrise, J. S., Jacobs, V. A., Eds.; Ann Arbor Science: Ann Arbor, MI 1983; Vol. 4, p 49.
(6) Work of P. L. Dulong, reported by: Thenard, L. J.; Berthollet C. L. *Ann. Chim. (Paris)* **1813**, *86*, 37-43.
(7) Noyes, W. A.; Haw, A. B. *J. Am. Chem. Soc.* **1920**, *42*, 2167-2173.
(8) Mellor, J. W. *A. Comprehensive Treatise in Inorganic and Theoretical Chemistry*; Longmans Green: New York, 1928; p 598.
(9) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639-665.
(10) Jander, J.; Englehardt, U. In *Developments in Inorganic Nitrogen Chemistry*; Colburn, C. B., Ed.; Elsevier: New York, 1973; Vol. II, pp 70-227.
(11) *The Merck Index*, 9th ed.; Windholz, M., Ed.; Merck: Rahway, NJ, 1976; p 858.
(12) Metcalf, W. S. *J. Chem. Soc.* **1942**, 148-150.
(13) Dowell, C. T.; Bray, W. C. *J. Am. Chem. Soc.* **1917**, *39*, 896-905.
(14) Galal-Gorchev, H.; Morris, J. C. *Inorg. Chem.* **1965**, *4*, 899-905.
(15) Sample, W. R. Ph.D. Dissertation, Harvard University, 1959.
(16) Burden, R. P. Ph.D. Dissertation, Harvard University, 1948.
(17) Huffman, R. P. M.S. Thesis, Purdue University, 1976.
(18) Gray, E. T., Jr. Ph.D. Dissertation, Purdue University, 1977.
(19) Saguinsin, J. L. S.; Morris, J. C. In *Disinfection Water and Waste Water*; Johnson, J. D., Ed.; Ann Arbor Science: Ann Arbor, MI, 1975; pp 277-299.

0020-1669/87/1326-3430$01.50/0

Table I. Absorption Spectral Characteristics of Halogen Species

species	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	ref
OCl^-	292	350	*a*
NCl_3	336	195	*b*
	220	~5000	*b*
$NHCl_2$	294	272	*c*
	203	2120	*d*
I_3^-	353	26400	*e*
Br_2	390	175	*f*

[a] Gray, E. T. Ph.D. Dissertation, Purdue University, 1977. [b] Reference 3. [c] Reference 21. [d] Hand, V. C. Ph.D. Dissertation, Purdue University, 1982. [e] Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1842–1843. [f] Soulard, M.; Block, F.; Hatterer, A. *J. Chem. Soc., Dalton Trans.* **1981**, 2300–2310.

of $NHCl_2$. The proposed mechanism for the formation of trichloramine (eq 3) involves a nucleophilic attack of the dichloramine nitrogen on the chlorine of hypochlorous acid with a simultaneous general-base-assisted removal of a proton from dichloramine.[3]

In the present study, we examine the kinetics of decomposition of NCl_3 in neutral and basic solutions in the presence of several different buffers and in the presence of excess hydroxide ion (up to 0.25 M). All the reactions are first order in NCl_3 concentration, but we find rate terms that are zero order, first order, and second order in OH^- concentration as well as terms with significant rate contributions from buffers. We propose that the reverse reaction in eq 3, coupled to a rapid reaction in eq 4, accounts for the hydroxide- and buffer-catalyzed paths. This means that two NCl_3 molecules are consumed in the reaction rather than the previously assumed stoichiometry.[19] Under high base concentrations a second OH^- can react with Cl_2NClOH^- (a reactive intermediate) to speed the reaction. For the overall reaction, our studies show that the products in dilute base retain 50% of the initial active chlorine.

Experimental Section

Reagents. A 5% (Baker) or 10% (Mallinckrodt) solution of sodium hypochlorite is used as the source of active chlorine. Stock solutions of hypochlorite were standardized by either the absorbance measurement of OCl^- at 292 nm (Table I) or the formation of I_3^- after the addition of excess iodide in acidic medium. Ammonia solutions were prepared by dilution of reagent grade ammonium hydroxide and were titrated with standard acid with the use of bromocresol green indicator. Sodium hydroxide was standardized against potassium hydrogen phthalate. Stock solutions were prepared in carbonate-free water and were protected from atmospheric carbon dioxide. Trichloramine solutions were prepared by mixing ammonia solutions with a 3.0-fold excess of HOCl at pH 3–4 in unbuffered medium 24 h before use. The NCl_3 solutions are relatively stable in dilute acid when protected from light and volatilization. The amount of NCl_3 formed is always less than the initial ammonia concentration due to N_2 formation.[3]

Sodium perchlorate was used to maintain the ionic strength ($\mu = 0.5$) of the solutions. Reagent grade acids, bases, and buffers were used. Distilled deionized water was used for the preparation of solutions.

Methods. Spectrophotometric measurements were made with a Perkin-Elmer Model 320 instrument interfaced to a Perkin-Elmer 3600 data station. The spectral characteristics of various species are given in Table I. Solution pH values were measured with a Corning combination glass electrode and an Orion Model 601 pH meter. All pH values were corrected to the corresponding hydrogen ion concentrations at 25.0 °C and $\mu = 0.5$ M ($NaClO_4$), based on electrode calibration titrations with standard solutions of NaOH and $HClO_4$. Gran plots[20] were used in the calibration of the electrodes.

Although reactions of iodide with HOCl, NH_2Cl, and $NHCl_2$ produce quantitative amounts of I_2, the reaction of NCl_3 with iodide produces only 80% of the theoretical iodine based on the estimated NCl_3 concentration.[21] Early studies[13] of the reaction of NCl_3 (dissolved in CCl_4) with aqueous KI showed that about 18% of the nitrogen was converted to N_2. There is always some loss of N_2 in the preparation of NCl_3 because mixtures of NCl_3 and $NHCl_2$ are not stable (eq 4). Only 60–65% of the active chlorine taken initially to make NCl_3 is recovered as I_2.[21] Other intermediates that may be present in freshly prepared NCl_3 solutions are avoided by aging the solution for 24 h. The resulting solutions have small amounts of HOCl, usually about 5% of the NCl_3 concentration. Stopped-flow studies of the reaction of Br^- with these solutions can be used to distinguish HOCl ($k^{HOCl}{}_{Br} = 1.55 \times 10^3$ M^{-1} s^{-1} at 25.0 °C)[22] from NCl_3 ($k^{NCl_3}{}_{Br} = 8.05$ M^{-1} s^{-1} at 25.0 °C).[23] The initial absorbance jump at 390 nm (due to the formation of $Br_3^- + Br_2$) in the stopped-flow reaction corresponds to the HOCl content, while the rest of the absorbance change corresponds to the NCl_3 reaction with Br^-. On the basis of a 1:1 stoichiometry for the latter reaction (one Br_3^- per NCl_3), the iodine yield with NCl_3 is only 80% of the theoretical amount (i.e. 2.4 I_3^- rather than 3.0 I_3^- per NCl_3). The yield of iodine is determined by measuring the absorbance of I_3^- at 353 nm (Table I). An equilibrium constant of 740 M^{-1} for I_3^- formation ($I_2 + I^- \rightleftarrows I_3^-$) is used to calculate total iodine formed in solution.[24]

Table II. Oxidizing Power Retained by the Products of Trichloramine Decomposition in Base[a]

$[OH^-]$, M	% oxidizing power retained	$[OH^-]$, M	% oxidizing power retained
0.00497	51.7	0.100	47.8
0.00994	50.7	0.150	47.8
0.0249	51.7	0.200	49.4
0.0497	54.5	0.250	47.8
0.050	49.9	0.300	49.9
0.0994	56.4		51 ± 3 (av)

[a] Equal Volumes of $\sim 0.65 \times 10^{-3}$ M NCl_3 and NaOH are mixed. The hydroxide ion concentrations given are after mixing.

In order to determine the stoichiometry of the base decomposition of NCl_3, the initial NCl_3 concentration was calculated from the I_3^- yield, (after reaction with excess I^-) with correction for 5% HOCl and for an 80% reaction efficiency. After the base decomposition, the OCl^- yield was also determined by the formation of I_3^-. Equal volumes of 0.65 mM NCl_3 and NaOH were mixed. An aliquot (1 mL) of this solution was then added to buffered iodide (50 mL) to give $[OAc]_T = 0.16$–0.2 M, pH 4.0–4.4, and $[I^-] = 0.2$ M. Precautions were taken to minimize the loss of trichloramine (due to its volatility) by the use of stoppered containers with minimal head space, and solutions of NCl_3 were stored in a syringe during the experiments.

All reaction rate studies were performed under pseudo-first-order conditions with hydroxide or buffer in large excess. Rates of the reaction were monitored by the disappearance of NCl_3 at 336 nm. In neutral solutions with phosphate buffer the reactions were followed for about 2 half-lives; other reactions were followed for at least 4 half-lives. In all cases 250 data points were collected for a least-squares regression analysis of ln ($A_t - A_\infty$) vs time, where A_∞ and A_t are the final absorbance and absorbance at time t, respectively. The slopes of these plots give a value of $2k_{obsd}$. Under more basic conditions, the rates of disappearance of NCl_3 were monitored with a Durrum stopped-flow spectrophotometer interfaced to a Hewlett-Packard computer (HP 2108 or 2100).[25] Five or more runs were performed under each set of conditions and the first-order rate constants were also evaluated on the basis of eq 5. In

$$-d[NCl_3]/dt = 2k_{obsd}[NCl_3] \qquad (5)$$

buffered medium, the reproducibility of the rate constant depends primarily on the care taken with the measurement of the hydrogen ion concentration.

Results and Discussion

Decomposition Stoichiometry. The reaction of ammonia with excess hypochlorite in base gives dinitrogen almost quantitatively.[26] It has been observed[19] that as NCl_3 decomposes in base, the absorbance of OCl^- at 292 nm increases, but there is no spectral evidence for the formation of NH_2Cl or $NHCl_2$. We determined the ratio of OCl^- produced to NCl_3 decomposed in a series of experiments, where the OH^- concentration was varied from 0.005 to 0.30 M and the trichloramine concentration was held constant at 0.65 mM. The concentrations of initial NCl_3 and of OCl^- produced were determined before and after base decomposition,

---

(20) Rossotti, F. J. C.; Rossotti, H. *J. Chem. Educ.* **1965**, *42*, 375–378.

(21) Kumar, K.; Day, R. A.; Margerum, D. W. *Inorg. Chem.* **1986**, *25*, 4344–4350.

(22) Kumar, K.; Margerum, D. W. *Inorg. Chem.* **1987**, *26*, 2706–2711.

(23) Kumar, K.; Margerum, D. W., to be submitted for publication.

(24) Turner, D. H.; Flynn, G. W.; Sutin, N.; Beitz, J. V. *J. Am. Chem. Soc.* **1972**, *94*, 1554–1559.

(25) Willis, B. G.; Bittikoefer, J. A.; Pardue, H. L.; Margerum, D. W. *Anal. Chem.* **1970**, *42*, 1340–1349.

(26) Bray, W. C.; Dowell, C. T. *J. Am. Chem. Soc.* **1917**, *39*, 905–913.

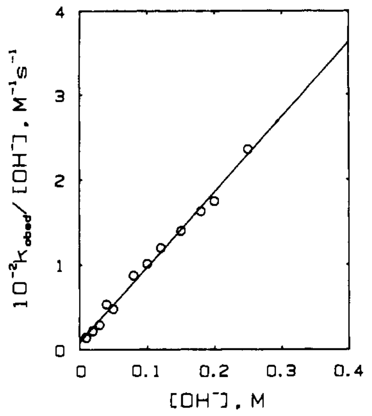


Figure 1. Base decomposition of NCl_3. Plot of eq 10 where the intercept (8 ± 3 M^{-1} s^{-1}) corresponds to k_1 and the slope (890 ± 30 M^{-1} s^{-1}) corresponds to k_2.

and the results in Table II show that there is only 50% of the oxidizing power left after decomposition of NCl_3. This corresponds to the overall reaction in eq 6 where 2 mol of NCl_3 produce 3 mol of hypochlorite. (Any other redox decomposition products of nitrogen are minor species and are neglected.) Equation 6 is a combination of eq 7 and 8, where $NHCl_2$ is an intermediate that reacts rapidly with NCl_3 to produce N_2 and OCl^- (eq 8).

$$2NCl_3 + 6OH^- \rightarrow N_2 + 3OCl^- + 3Cl^- + 3H_2O \qquad (6)$$

$$NCl_3 + OH^- \rightarrow NHCl_2 + OCl^- \qquad (7)$$

$$NCl_3 + NHCl_2 + 5OH^- \rightarrow N_2 + 2OCl^- + 3Cl^- + 3H_2O \qquad (8)$$

The overall stoichiometry is the same as that reported earlier,[19] but we know from studies of the kinetics of dichloramine reactions in neutral solutions and in dilute base that NCl_3 accelerates the decomposition of $NHCl_2$.[3] Hence, reaction 8 rather than reaction 2 reflects the decomposition pathway. As a consequence two NCl_3 molecules are lost every time one reacts with OH^-, and this gives the reaction rate stoichiometry specified in eq 5.

Kinetics. Decomposition of Trichloramine in Sodium Hydroxide Solutions. The rate of decomposition of trichloramine was studied in 0.01–0.25 M NaOH solutions by the use of stopped-flow methods under pseudo-first-order conditions (NCl_3 is the limiting reagent) at constant ionic strength (μ = 0.5) and 25.0 °C. Excellent first-order plots were obtained, and the k_{obsd} values (Table III) have first-order and second-order dependences on the hydroxide ion concentration (eq 9). A plot of eq 10 is shown in Figure 1, and the third-order rate constant (k_2) calculated from the slope is 890 ± 30 M^{-2} s^{-1}, while the intercept (k_1) is 8 ± 3 M^{-1} s^{-1}.

$$k_{obsd} = k_1[OH^-] + k_2[OH^-]^2 \qquad (9)$$

$$k_{obsd}[OH^-]^{-1} = k_1 + k_2[OH^-] \qquad (10)$$

Decomposition of NCl_3 in Buffered Medium. Table III gives the rate constants for the decomposition of NCl_3 in the presence of buffers with OH^- concentrations from $10^{-7.3}$ to $10^{-2.8}$. The k_{obsd} values increase with increase in buffer concentration at constant OH^- concentration. The dependence can be expressed by eq 11,

$$k_{obsd} = k_0 + k_1[OH^-] + k_B[B] + k_2[OH^-]^2 \qquad (11)$$

where B is the basic form of the buffer and k_0 is a hydroxide-independent term. Figure 2 shows the dependence when B is HPO_4^{2-}, where eq 12 is plotted, and the previously determined k_1 and k_2 values are used. The k_0 value from the intercept is (1.6 ± 0.2) × 10^{-6} s^{-1}, which is 20 times smaller than the previously determined value.[19] The main reason for this disagreement is that corrections were not made previously for buffer effects. In addition, a factor of 2 occurs because of the difference in the definition of k_{obsd} in eq 5.

$$k_{obsd} - k_1[OH^-] - k_2[OH^-]^2 = k_0 + k_B[B] \qquad (12)$$

Table III. Pseudo-First-Order Rate Constants for the Base Decomposition of Trichloramine[a]

acid/base	$[HB]_T$, M	$-\log [OH^-]^b$	k_{obsd},[c] s^{-1}
$H_2PO_4^-/HPO_4^{2-}$	0.025	7.26	(0.410 ± 0.004) × 10^{-5}
	0.025	6.64	(0.73 ± 0.02) × 10^{-5}
	0.025	6.51	(1.00 ± 0.005) × 10^{-5}
	0.030	6.75	(0.54 ± 0.02) × 10^{-5}
	0.040	6.78	(0.65 ± 0.02) × 10^{-5}
	0.050	6.73	(0.75 ± 0.02) × 10^{-5}
	0.060	6.88	(0.73 ± 0.02) × 10^{-5}
	0.090	6.83	(1.01 ± 0.02) × 10^{-5}
$B(OH)_3/B(OH)_4^-$	0.025	5.41	(0.770 ± 0.005) × 10^{-4}
	0.025	5.05	(2.23 ± 0.03) × 10^{-4}
	0.025	4.62	(3.77 ± 0.01) × 10^{-4}
	0.025	4.07	(1.32 ± 0.03) × 10^{-3}
	0.0052	4.61	(2.19 ± 0.01) × 10^{-4}
	0.0104	4.61	(2.470 ± 0.005) × 10^{-4}
	0.0156	4.63	(2.81 ± 0.01) × 10^{-4}
	0.0208	4.62	(3.16 ± 0.02) × 10^{-4}
HCO_3^-/CO_3^{2-}	0.020	3.59	(2.58 ± 0.03) × 10^{-3}
	0.050	3.62	(2.65 ± 0.03) × 10^{-3}
	0.100	3.61	(2.87 ± 0.03) × 10^{-3}
	0.120	3.61	(3.09 ± 0.04) × 10^{-3}
	0.150	3.61	(3.16 ± 0.03) × 10^{-3}
HPO_4^{2-}/PO_4^{3-}	0.020	2.79	0.020 ± 0.001
	0.030	2.78	0.022 ± 0.001
	0.040	2.78	0.0235 ± 0.0015
H_2O/OH^-	0.010	2.00	0.140 ± 0.005
	0.020	1.70	0.44 ± 0.01
	0.030	1.52	0.87 ± 0.03
	0.040	1.40	2.1 ± 0.2
	0.050	1.30	2.38 ± 0.06
	0.080	1.10	7.0 ± 1.3
	0.100	1.00	10.1 ± 0.2
	0.120	0.92	14.4 ± 0.5
	0.150	0.82	21.0 ± 0.6
	0.180	0.74	29.3 ± 1.5
	0.200	0.70	35.0 ± 0.9
	0.250	0.60	59 ± 5

[a] Conditions: $[NCl_3]$ = (0.25–0.3) × 10^{-3} M, μ = 0.5 M ($NaClO_4$), 25.0 °C, 336 nm. [b] With buffers, calculated from $-\log [H^+]$ and pK_w = 13.72 at μ = 0.5. [c] Standard deviations of individual runs on the Perkin-Elmer spectrophotometer for rate constants less than 3.2 × 10^{-3} s^{-1}. Standard deviations for five or more runs on the stopped-flow instrument are given for larger rate constants.

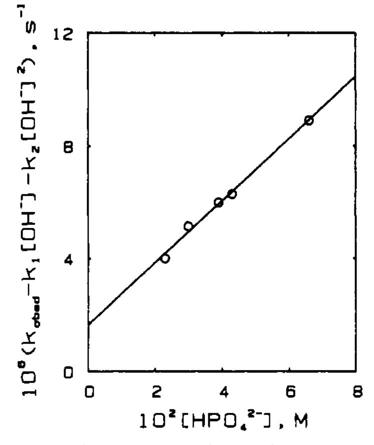


Figure 2. Dependence of the observed first-order rate constant (corrected for contributions from $k_1[OH^-]$ and $k_2[OH^-]^2$) for the decomposition of NCl_3 on the HPO_4^{2-} concentration.

A general-base-catalyzed reaction (the $k_B[B]$ term) usually cannot be distinguished from the product of a specific-base- and general-acid-catalyzed reaction (i.e. a $k_{HB}[HB^+][OH^-]$ term).[27] In the present case there is good reason to consider a rate expression equal to $k_{HB}[HB^+][NCl_3][OH^-]$, because it corresponds

---

(27) Jencks, W. P. *Catalysis in Chemistry and Enzymology* McGraw Hill: New York, 1969; pp 163–242.

Scheme I

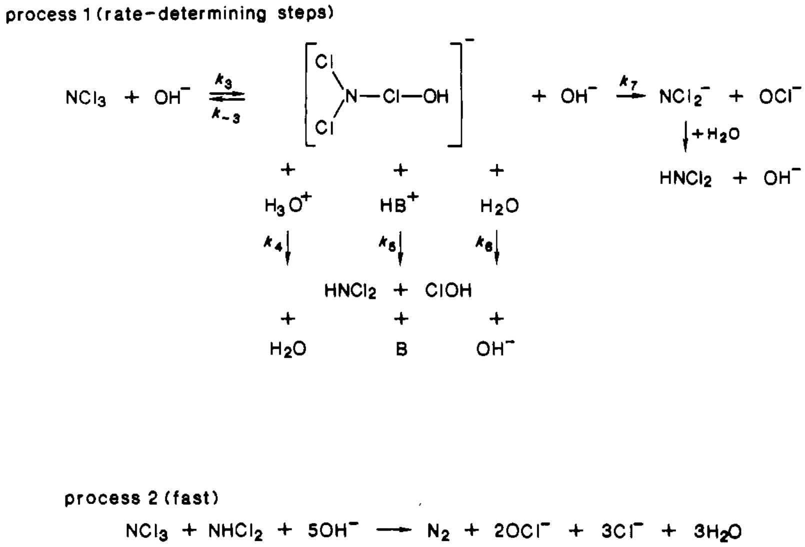
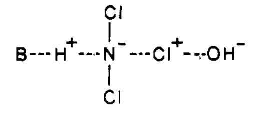


Table IV. General-Acid/Specific-Base-Catalyzed Decomposition Rate Constants for Trichloramine[a]

HB	pK_a	p/q	k_{HB}, M^{-2} s^{-1}
H_2O	15.46[b]	2/3	0.14 ± 0.05
HPO_4^{2-}	11.34[c]	2/3	128 ± 1
HCO_3^-	9.8[d]	1/3	65 ± 6
$B(OH)_3$	8.87[e]	1/4	$(7.6 \pm 0.5) \times 10^2$
$H_2PO_4^-$	6.45[f]	2/3	$(2.1 \pm 0.1) \times 10^3$
H_3O^+	-1.72[g]	3/2	$(8.4 \pm 1.1) \times 10^7$

[a] Conditions: 25.0 °C, $\mu = 0.5$. [b] Sweeton, F. H.; Mesmer, R. E.; Baes, C. F. *J. Solution Chem.* **1974**, *3*, 191–214. The K_a value is calculated by dividing K_w by 55.5 for the water molarity. [c] Nozaki, T.; Mise T.; Torii, K. *Nippon Kagaku Kaishi* **1973**, 2030. [d] Butler, J. N.; Huston, R. *J. Phys. Chem.* **1970**, *74*, 2976–2983. [e] Calculated from: Owen, B. B.; King, E. J. *J. Am. Chem. Soc.* **1943**, *65*, 1612–1620. [f] Mesmer, R. E.; Baes, C. F. *J. Solution Chem.* **1974**, *3*, 307–321. [g] Reference 30, p 200.

to the dependence required for the reverse reaction in eq 3.[3] The combination of general-acid and OH^- reaction with NCl_3 also fits a broader mechanism and a transition state (structure I) consistent



I

with other chloramine reactions where H^+ transfer and Cl^+ transfer occur simultaneously.[21,22] The value of k_{HB} for $H_2PO_4^-$ is $(2.1 \pm 0.1) \times 10^3$ M^{-2} s^{-1}. Other buffers also accelerate the decomposition of NCl_3, and the resulting k_{HB} values are given in Table IV for $B(OH)_3$, HCO_3^-, and HPO_4^{2-}. Since the latter studies are all at higher $[OH^-]$, the k_0 term makes only a small contribution and is best evaluated from the results in $H_2PO_4^-/HPO_4^{2-}$ buffer.

Figure 3 shows the dependence of k_{obsd} on the OH^- concentration (eq 13) when no buffers are present (or the buffer concentration is extrapolated to zero). The values used to generate

$$k_{obsd} = k_0 + k_1[OH^-] + k_2[OH^-]^2 \qquad (13)$$

the curve are 1.6×10^{-6} s^{-1}, 8 M^{-1} s^{-1}, and 890 M^{-2} s^{-1} for k_0, k_1, and k_2, respectively. A simplex program[28,29] also can be used to fit the entire set of data and gives values that are in good agreement with these constants.

Proposed Mechanism. The decomposition of NCl_3 can be divided into two processes as shown in Scheme I, where process 1 is rate determining in base. It is proposed that attack of OH^- on the chlorine of NCl_3 gives a common reactive intermediate, Cl_2NClOH^-, for all the reaction pathways. Process 1 produces $NHCl_2$, which reacts rapidly with another NCl_3 in process 2 to give products. A steady-state approximation in regard to Cl_2NClOH^- gives the expression for k_{obsd} in eq 14. For high hydroxide

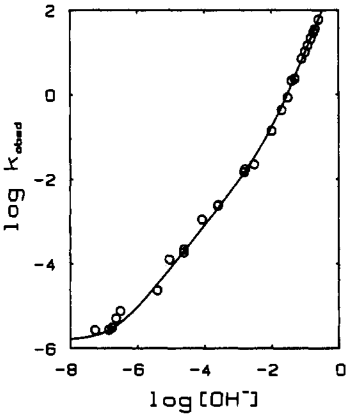


Figure 3. Effect of hydroxide ion concentration on the first-order rate constant for the decomposition of NCl_3 (without buffer catalysis).

$$k_{obsd} = \frac{k_3[OH^-](k_4[H^+] + k_5[HB^+] + k_6 + k_7[OH^-])}{k_{-3} + k_4[H^+] + k_5[HB^+] + k_6 + k_7[OH^-]} \qquad (14)$$

ion concentrations and in the absence of buffers, the H^+ term and HB^+ terms can be eliminated to give eq 15. The observed kinetics

$$k_{obsd} = \frac{k_3[OH^-](k_6 + k_7[OH^-])}{k_{-3} + k_6 + k_7[OH^-]} \qquad (15)$$

has a $[OH^-]^2$ dependence for high base concentrations, so it follows that under all conditions $k_{-3} + k_6 \gg k_7[OH^-]$. Since $k_2 \gg k_1$, it also follows that $k_7 \gg k_6$ and hence $k_{-3} \gg k_6$. The k_1 rate constant with a $[OH^-]$ term corresponds to eq 16 and the k_2 rate constant with a $[OH^-]^2$ term corresponds to eq 17. In the buffered

$$k_1[OH^-] = (k_3k_6/k_{-3})[OH^-] \qquad (16)$$

$$k_2[OH^-]^2 = (k_3k_7/k_{-3})[OH^-]^2 \qquad (17)$$

solutions, there is no evidence that the rate reaches a limit at high buffer concentrations, so it must also follow that $k_{-3} \gg k_4[H^+] + k_5[HB^+]$. Hence, eq 18 and 19 give the composite rate constants

$$k_0 = k_3k_4[OH^-][H^+]/k_{-3} = k_3k_4K_w/k_{-3} \qquad (18)$$

$$k_{HB}[OH^-][HB^+] = k_3k_5[OH^-][HB^+]/k_{-3} \qquad (19)$$

---

(28) Caceci, M. S.; Catheris, W. P. *Byte* **1984**, *9*, 340–362.
(29) Yarboro, L. A.; Deming, S. N. *Anal. Chim. Acta* **1974**, *73*, 391–398.

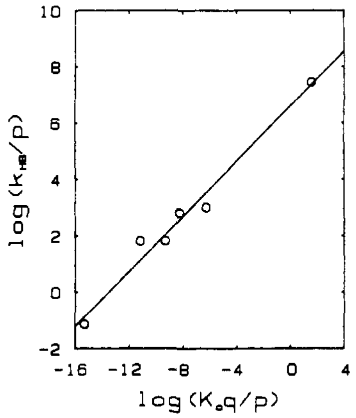


Figure 4. Brønsted plot for the reaction $HB^+ + NCl_3 + OH^-$, where k_{HB} is the third-order rate constant and K_a is the acid dissociation constant of HB^+. Slope = α = 0.48 ± 0.04.

for k_0 and k_{HB}. Thus, Cl_2NClOH^- can be assumed to be a very reactive intermediate that needs to add a proton to the nitrogen as ClOH is eliminated. The intermediate can accept the proton from H_3O^+, H_2O, or HB^+ and gives $HNCl_2$. For high concentrations of base another decay path occurs in which a second proton is removed from the Cl_2NClOH^- intermediate to give an even less stable Cl_2NClO^{2-} species that rapidly dissociates and reacts with water to give OCl^- and $HNCl_2$.

An alternate mechanism was considered where NCl_3 is hydrated to give Cl_2NClOH_2, which then reacts by proton-transfer reactions with H_2O, B, or OH^- as rate-determining steps to give Cl_2NClOH^-. However, this type of mechanism will not fit the observed $[OH^-]^2$ dependence, nor is it consistent with the previously established kinetics for the forward reaction in eq 3.

Brønsted Relationship. The rates for the buffer-catalyzed base decomposition of trichloramine increase with the acid strength of general acids that are present in solution. The rate constants (Table IV) show a Brønsted relationship[30] (eq 20), where p is the

$$\log (k_{HB}/p) = \log G_A + \alpha \log (K_a q/p) \tag{20}$$

number of equivalent acidic protons in HB^+, q is the number of equivalent basic sites in B, K_a is the acid dissociation constant of HB^+, G_A is the proportionality constant and α is the Brønsted coefficient. The plot in Figure 4 includes values for H_2O and H_3O^+ as well as for four buffers and gives a linear relationship with a slope of 0.48 ± 0.04 that corresponds to the α value. Since the reaction is the reverse of eq 3, we would predict an α value equal to $1 - \beta$, where β is the general-base-catalysis coefficient for the forward reaction.[3] The β value (when corrected for p and q) equals 0.56, and the $1 - \beta$ value of 0.44 is within experimental error of the α value determined in the present study. The fact that the combined general-acid and specific-base data follow the Brønsted relationship over a wide range of acid strength supports the proposed mechanism. A close examination of the results suggests that the k_{HB} constant for HPO_4^{2-} is slightly larger than expected from the Brønsted relation in Figure 4. It may be that PO_4^{3-} also contributes to the decomposition rate of Cl_2NClOH^- in a path that is analogous to the $k_7[OH^-]$ path, where PO_4^{3-} helps to remove a proton and gives a $k_7'[PO_4^{3-}]$ term.

Equilibrium Constant for the Formation of Trichloramine from Dichloramine and Hypochlorous Acid. The rate constants for the decomposition of NCl_3 determined in this work are of special interest because the forward rate constants in eq 3 are known[3] for several general bases (OH^-, CO_3^{2-}, and HPO_4^{2-}). Hence, the rate constants determined for the reverse reaction in eq 3 can be used to calculate the equilibrium constant for the reaction in eq 21. It is not possible to determine this constant under equilibrium

$$NHCl_2 + HOCl \rightleftarrows NCl_3 + H_2O \tag{21}$$

conditions, because reaction 3 is coupled with reaction 4. Even in acidic solutions NCl_3 and $NHCl_2$ cannot reach equilibrium because of their reaction to form N_2. Hence, the equilibrium constant must be determined by the ratio of forward and reverse rate constants. The equilibrium stability constant, K_{NCl_3}, is calculated (eq 22) from the k_{HB} values in this work and from k_B

$$K_{NCl_3} = \frac{[NCl_3]}{[NHCl_2][HOCl]} = \frac{k_B}{k_{HB}}\frac{K_a}{K_w} \tag{22}$$

values in earlier work[3] for OH^-, CO_3^{2-}, and HPO_4^{2-}. Table V summarizes the results. The $HPO_4^-/H_2PO_4^{2-}$ data have much greater precision for both the k_B and k_{HB} values. Hence, the statistically weighted[31] value for $K_{NCl_3} = (1.6 \pm 1.1) \times 10^8\ M^{-1}$ is dominated by these data. However, all three pairs of rate constants in Table V give a stability constant greater than 10^8 M^{-1}. Morris and Isaac[5] used the data of Saguinsin and Morris[19] to calculate a value of $4.8 \times 10^4\ M^{-1}$ for this equilibrium constant. Our data gives a value nearly 4 orders of magnitude larger.

Table V. Stability Constants for Trichloramine Calculated from Rate Constants[a,b]

B/HB	k_B, $M^{-2}\ s^{-1}$	k_{HB}, $M^{-2}\ s^{-1}$	$10^{-8}K_{NCl_3}$, M^{-1}
OH^-/H_2O	$(3.3 \pm 0.1) \times 10^9$	0.14 ± 0.05	4.1 ± 1.6
CO_3^{2-}/HCO_3^-	$(6 \pm 2) \times 10^6$	65 ± 6	7.7 ± 2.7
$HPO_4^{2-}/H_2PO_4^-$	$(1.59 \pm 0.09) \times 10^4$	$(2.1 \pm 0.1) \times 10^3$	1.41 ± 0.07
			1.6 ± 1.1 (av)[c]

[a] Conditions: 25.0 °C, μ = 0.50. [b] $K_{NCl_3} = [NCl_3]/([NHCl_2][HOCl]) = (k_B/k_{HB})(K_a/K_w)$. [c] Statistically weighted average. The unweighted average of the equilibrium constants is $(4 \pm 3) \times 10^8\ M^{-1}$. However the $HPO_4^{2-}/H_2PO_4^-$ data have much greater precision in the k_B and k_{HB} values. Relative errors are used to give the statistically weighted average and error.[31]

Conclusions. The thermodynamic stability of NCl_3 in aqueous solution is substantially greater than was previously thought, as indicated by the stability constant of $1.6 \times 10^8\ M^{-1}$ for its formation from $NHCl_2$ and HOCl. Trichloramine appears to be much less thermodynamically stable than is the case, because of its kinetic reactivity with $NHCl_2$ in neutral and basic solutions. We propose that the base decomposition of NCl_3 goes through a common reactive intermediate, Cl_2NClOH^-, which can react with buffer acids to add a proton to the nitrogen and release HOCl or can react with an additional OH^- to release OCl^-. The $NHCl_2$ formed in both cases reacts rapidly with another NCl_3 to give N_2, OCl^-, and Cl^-. The coupled reactions in Scheme I are very important in breakpoint chlorination. Part of these data have been used to give "a unified chlorine–ammonia speciation and fate model" for the breakpoint process.[32] At present, we know little about the detailed mechanism by which N_2 is formed. In view of the importance of buffer and base catalysis in process 1, it is very likely that process 2 (Scheme I) will also be subject to buffer-assisted and base-assisted rates.

Acknowledgment. This work was supported by National Science Foundation Grants CHE-8319935 and CHE-8616666.

Registry No. NCl_3, 10025-85-1; H_2O, 7732-18-5.

---

[30] Bell, R, P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 198.

[31] Bevington, P. R. *Data Reduction and Error Analysis For Physical Science*; McGraw-Hill: New York, 1969; p 73.

[32] Jafvert, C. T., Ph.D. Dissertation, University of Iowa, 1985.