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Kinetics and Mechanisms of the Decomposition of Dichloramine in Aqueous Solution

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The reaction of hypochlorous acid with dichloramine is general base catalyzed: $NHCl_2 + HOCl + B \xrightarrow{k_B} NCl_3 + OH^- + HB^+$. Base assists proton removal from $NHCl_2$ as the nitrogen attacks the chlorine of HOCl. Values of the third-order rate constants (k_B, $M^{-2}\ s^{-1}$ at 25.0 °C) are 1.6×10^4 for HPO_4^{2-}, 1×10^5 for OCl^-, 6×10^6 for CO_3^{2-}, and 3.3×10^9 for OH^-. The trichloramine formed reacts with dichloramine to generate more hypochlorous acid and hence speeds the decomposition. One postulated reaction is $NHCl_2 + NCl_3 + 3OH^- \rightarrow N_2 + 3Cl^- + 2HOCl + H_2O$, but side reactions produce other oxidized nitrogen products as well. The decomposition of $NHCl_2$ is 5 orders of magnitude slower in neutral solutions that contain ammonium ion, because HOCl reacts rapidly with NH_3 and hence HOCl is not available to form NCl_3. Even traces of NH_3 interrupt these coupled reactions and inhibit the decomposition. In ammoniacal solutions, NH_2Cl is produced from $NHCl_2$ (25% yield) by two pathways. One of these is first order in $NHCl_2$ and first order in NH_4^+ with a second-order rate constant of $3 \times 10^{-5}\ M^{-1}\ s^{-1}$. The other is first order in $NHCl_2$ and first order in OH^- with a second-order rate constant of $150\ M^{-1}\ s^{-1}$.

Introduction

Chloramine (NH_2Cl) was proposed by Raschig[1] as an intermediate in the synthesis of hydrazine from chlorine and excess ammonia. The mechanism of this reaction has been well-characterized.[2,3] Chloramine can be prepared as a pure compound and is useful in a number of synthetic reactions.[4–7] It is readily produced in aqueous solution from the reaction of NH_3 and HOCl.[8,9] When solutions of chloramine are acidified or chlorinated, dichloramine ($NHCl_2$) and trichloramine (NCl_3) are formed.[9–12] Trichloramine can be isolated as a pure liquid,[13] which is explosive.[14] Dichloramine is difficult to isolate because of its instability and has been prepared only in solution. Extraction techniques have been used to separate it from the other chloramines and to identify its spectral characteristics and stoichiometry.[15] It coexists in aqueous solution with NH_2Cl and NH_4^+ or with NCl_3. It is relatively stable in solution at pH 4–5 in the presence of NH_2Cl and NH_4^+ but is less stable when NCl_3 is present.

In the present work we have been able to prepare aqueous solutions of $NHCl_2$ from which NH_4^+ and NH_3Cl^+ have been removed by ion exchange. This method of generating ammonia-free dichloramine solutions is of great importance in understanding the reaction mechanisms of $NHCl_2$ because traces of ammonia inhibit the decomposition of $NHCl_2$.

When excess chlorine is added to remove ammonia from potable and waste waters, chloramines are also formed.[16] This process is referred to as breakpoint chlorination and produces N_2 and Cl^-.[17] In addition to N_2, NO_2^- and NO_3^- may constitute as much as 15% of the nitrogenous products.[18] In base, dichloramine reportedly decomposes by eq 1,[19] although other

$$2NHCl_2 + 4OH^- \rightarrow N_2 + 3Cl^- + ClO^- + 3H_2O \quad (1)$$

reactions must occur to produce oxides of nitrogen in low yield.[19] Morris and Wei[17] showed that dichloramine is produced early in the breakpoint process but that it subsequently decomposes and produces some hypochlorite. Trichloramine also has been identified as a product under the conditions of breakpoint chlorination, especially when the chlorine to ammonia ratio exceeds 1.5.[18]

Mechanisms have been proposed for breakpoint chlorination and the associated dichloramine decomposition, but with limited success because the detailed kinetics of the reactions have not been known. Wei suggested that the mechanism involves NOH,[20] and others have indicated that hydroxylamine is a precursor of this species.[21,22] There is no direct evidence for the presence of NOH. Another suggested intermediate is NCl_2^-,[23] and the pK_a of $NHCl_2$ has even been suggested to be 7,[24] but again evidence is lacking. In the decomposition of tribromamine, NBr_2^- has been suggested as a reaction intermediate,[25] but the protonation constant was not estimated.

Previous studies of the decomposition of dichloramine have been hampered by the speed of the reactions and by the difficulty of observing the reaction without interference from preceding formation reactions. In the present work, stopped-flow techniques are used to monitor the reactions, and solutions of $NHCl_2$ are prepared that are free of monochloramine and ammonia. The decomposition of $NHCl_2$ is autocatalytic and speeds up as NCl_3 and HOCl are formed. The reaction between $NHCl_2$ and HOCl is general base

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catalyzed and produces NCl_3, which in turn reacts with $NHCl_2$ in another base-catalyzed reaction to give N_2, Cl^-, and additional HOCl.

Experimental Section

Reagents. Sodium hypochlorite solution was used as a source of chlorine. Ammonium hydroxide was diluted and assayed by acidimetry using methyl orange indicator. Buffers were prepared from sodium salts of phosphate or carbonate. Ionic strength was maintained at 0.5 M with sodium perchlorate, prepared by the neutralization of sodium carbonate with perchloric acid. All chemicals were reagent grade.

The pH was measured with a glass working electrode and a calomel reference electrode with saturated NaCl-filling solution. The hydrogen ion concentration was determined from the equation $-\log [H^+] = pH + \text{constant}$. The constant was determined by acid–base titration for each pair of electrodes used and varied between 0.15 and 0.17 for 0.5 M $NaClO_4$ and 25 °C.

Procedures. Chloramine solutions were prepared fresh daily by combining solutions of hypochlorite and ammonia through a double twin-jet tangential mixer, such that ammonia was in at least 10% excess in the final solution. Efficient mixing ensured that this excess was maintained throughout the solution and minimized the formation of dichloramine.

Dichloramine was prepared from chloramine by one of two methods, both of which utilized the disproportionation of chloramine (eq 2).[12]

$$2NH_2Cl + H^+ \overset{k_2}{\rightleftharpoons} NHCl_2 + NH_4^+ \tag{2}$$

One method consisted of dropwise addition of perchloric acid to a solution of chloramine with the pH maintained between 3.5 and 4. When the pH changed less than 0.02 unit in 10 min, the solution was placed in a stoppered flask, and the reaction was allowed to reach completion overnight. The final pH increased no more than 0.5 unit. Solutions of dichloramine prepared in this way were relatively stable, decaying by about 10% in 1 day, after which they were discarded. Some chloramine was always present in these solutions. If the pH was allowed to fall below 3 during the preparation, then trichloramine was produced and dichloramine decomposed more rapidly. These solutions were not used.

Preparation of Ammonia-Free Dichloramine. In the second method used to prepare dichloramine, the disproportionation reaction was carried out on a cation-exchange column in the hydrogen ion form. The resin retained the ammonium ion produced in eq 2. Bio-Rad AG50w-X12 50–100 mesh cation-exchange resin (~50 g or 150 mequiv) was placed in a 2 × 25 cm glass column, acidified with 1 L of 3 M HCl, and then equilibrated with 4 L of a solution containing 0.1 M $HClO_4$ and 0.1 M $NaClO_4$. The column was then rinsed with water until the eluate was at neutral pH. To produce dichloramine, 10–25 mL of 0.03–0.05 M NH_2Cl solution was added to the column, which was then eluted with water at ~10 mL/min. The effluent was monitored at 294 nm with a Varian Variscan spectrophotometer equipped with a low-pressure flow cell. After ~60 mL, a small peak due to trichloramine emerged. This was followed by a large peak due to dichloramine, which appeared between 120 and 300 mL of effluent and reached a maximum concentration of ~10^{-3} M at ~180 mL. About 50% of the chloramine was recovered as dichloramine. The remainder was eluted as NCl_3, retained as NH_3Cl^+, or lost through redox reactions.

The dichloramine produced by the cation-exchange method was free of other chloramines and free of ammonia. The UV-absorbance spectrum of the solution indicated no observable NCl_3 or NH_2Cl. Thus, the initial chloramine and trichloramine concentrations are each less than 1% of the dichloramine concentration. The ammonia concentration was shown to be less than 10^{-7} M by extracting dichloramine from solution with diethyl ether and assaying the aqueous layer for ammonia with ninhydrin.[26] These preparations will be referred to as "ammonia-free" dichloramine. When ammonium ion was added to the solutions, the reactivity and other characteristics of the solution were the same as if the dichloramine had been prepared by the direct addition of acid to chloramine. Because of the instability of ammonia-free dichloramine, these solutions were used as soon as possible and discarded if more than 1 h had elapsed after collection.

Table I. Spectral Characteristics of Hypochlorite and Chloramines

compd	λ, nm	ε, M^{-1} cm^{-1}	ref
OCl^-	292[a]	350	27
	294	348	*b*
HOCl	228[a]	120	*b*
	294	31	*b*
NH_2Cl	243[a]	445	27
	278	91	27
	294	27	27
$NHCl_2$	203[a]	2120	29
	243	245	29
	278	182	*b*
	294[a]	276	29
NCl_3	220[a]	~5000	*c*
	336[a]	195	29, 34
	294	~160	*c*

[a] λ_{max}. [b] Calculated from ref 27. [c] Calculated from ref 29 and 34.

The concentrations of OCl^-, NH_2Cl, and $NHCl_2$ were determined spectrophotometrically by using the molar absorptivities in Table I. The values reported for OCl^- and NH_2Cl are based on an earlier iodometric standardization[27] and agree with similar determinations.[28] The value reported for dichloramine was determined by rapidly acquiring a spectrum of ammonia-free dichloramine on a Hewlett-Packard 8450A spectrophotometer as soon as the dichloramine had emerged from the cation-exchange column. Dichloramine was assumed to be the only absorbing species present in solution, but the concentration could not be determined iodometrically before decomposition was apparent. Absorbance data (A) from the spectrum were used to calculate the molar absorptivity of dichloramine at any wavelength (λ) via eq 3.[29] The molar absorptivity at 278 nm (ϵ_{278})

$$\epsilon_\lambda = \epsilon_{278}A_\lambda/A_{278} \tag{3}$$

was known because 278 nm is an isosbestic wavelength during the disproportionation of chloramine to dichloramine (eq 2). Hence, the molar absorptivity of dichloramine at 278 nm is twice the molar absorptivity of chloramine at the same wavelength. (An isosbestic point is observed for reaction 2 only until dichloramine decomposition becomes significant.[30]) Other spectrophotometric data were acquired on a Cary 14 or Perkin-Elmer 320 spectrophotometer.

Mixtures of chloramine and dichloramine were assayed by the DPD–FAS titrimetric method.[31a] This standard method depends upon the different rates at which chloramine and dichloramine oxidize iodide to iodine at neutral pH. The indicator *N*,*N*-diethyl-*p*-phenylenediamine (DPD) is reversibly oxidized by iodine but not by chloramines. When a trace of iodide is added to the sample, the iodine catalyzes oxidation of DPD by chloramine. The indicator is then reduced by titration with standard ferrous ammonium sulfate (FAS) to determine the original chloramine concentration. Excess iodide is added so that dichloramine now oxidizes the indicator. A second titration gives the dichloramine concentration.

Rapid reactions were monitored at a single wavelength by using a Durrum stopped-flow spectrometer interfaced to a Hewlett-Packard computer. Changes of absorbance with time over a 150-nm region were monitored by utilizing a vidicon rapid-scanning stopped-flow spectrometer interfaced to a Hewlett-Packard computer.[32,33] Typically, the decrease in absorbance of dichloramine was observed at 294 nm, and a pseudo-first-order rate constant was calculated from the slopes of plots of ln ($A - A_\infty$) vs. time. If hypochlorite was present in the reaction mixture, then the absorbance background became large

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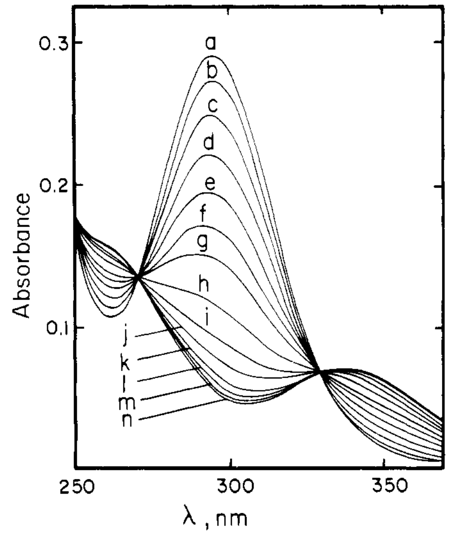

Figure 1. UV-absorbance spectra obtained during the decomposition of ammonia-free dichloramine (path length 1.0 cm; cuvette is stoppered and has no head space; temperature ~25 °C; contains no buffer—initial pH 4, final pH 3.6). Time after collection from cation-exchange column (min): (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60, (h) 80, (i) 100, (j) 120, (k) 150, (l) 180, (m) 210, (n) 330.

at high pH. In the worst case, an absorbance change of 0.03 absorbance unit was observed when the OCl^- absorbance was ~2 absorbance units. Hence, data obtained in basic solutions with hypochlorite present are much less precise than those obtained in neutral solution.

Initial rates of disappearance of dichloramine and appearance of chloramine could be determined by DPD–FAS titration, if the reaction was slow enough. All kinetic data were obtained at 25.0 ± 0.2 °C, and the mean and standard deviations of at least three replicates are reported.

Products were determined by a combination of methods, including spectrophotometric assay, iodometric titration, and high-performance liquid chromatography. The chromatographic system consisted of a Waters 6000 pump, Waters U6K injector, Waters radial compression module (or a conventional stainless-steel column), and a modified Beckman DU set at 231 nm. The stationary phase was octadecylsilica; the mobile phase was a pH 7, 0.1 M sodium phosphate buffer with a flow rate of 1 mL/min. Under these conditions, a baseline separation of chloramine and dichloramine could be achieved in less than 5 min. Dichloramine is more hydrophobic than chloramine; hence, dichloramine is eluted after chloramine. Trichloramine is extremely hydrophobic and was apparently retained by the stationary phase, even when methanol, acetonitrile, or tetrahydrofuran was used as solvent.

Results and Discussion

Stability of "Ammonia-Free" Dichloramine. Dichloramine solutions prepared by the cation-exchange chromatographic method are much less stable than dichloramine solutions with ammonium ion present. The repetitive spectral scans in Figure 1 (for a solution initially 1.05 mM in $NHCl_2$ at pH 4) show the loss of $NHCl_2$ and the formation of NCl_3, which occur after 10–330 min. Despite the isosbestic points seen, only 50% of the theoretical amount of trichloramine is produced on the basis of the expected stoichiometry[11,12] in eq 4. The decomposition reaction generates acid (final pH 3.6) rather than consuming acid as suggested by eq 4. Furthermore, chloride ion and a gas are produced, but no NH_4^+ is detected. After the decomposition reaction, the resulting trichloramine solution (curve n, Figure 1) is stable for months (50% loss in 2 months). Addition of NH_4^+ or NH_2Cl does not give $NHCl_2$ but only destroys NCl_3. The yield of trichloramine is changed little by adding preformed trichloramine to freshly prepared dichloramine at pH 4.

$$3NHCl_2 + H^+ \rightarrow 2NCl_3 + NH_4^+ \qquad (4)$$

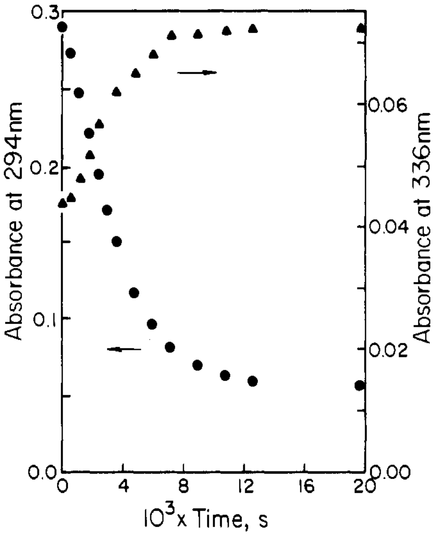

Figure 2. Change in the UV absorbance of dichloramine (λ_{max} = 294 nm) and trichloramine (λ_{max} = 336 nm). Conditions are the same as in Figure 1.

The exact stoichiometry of the decomposition of $NHCl_2$ in acid is not known and indeed may vary with reaction conditions, but eq 5 fits the NCl_3 yield and the other products for the reaction shown in Figure 1. However, neither the Cl^- nor the H^+ concentrations increased as much as eq 5 predicts, and in some reactions 10% more NCl_3 is formed. The isosbestic points in Figure 1 indicate that the stoichiometric ratio of $NHCl_2$ lost to NCl_3 formed remains constant during the reaction. However, the wavelengths of the isosbestic points can be changed by different reaction conditions, and the $NHCl_2$:NCl_3 ratio also can be changed. There may well be other forms of oxidized nitrogen[29,34] such as NH_2OH or NO that can form and give different $NHCl_2$:NCl_3 ratios.

$$3NHCl_2 \rightarrow NCl_3 + N_2 + 3Cl^- + 3H^+ \qquad (5)$$

Although NCl_3 and NH_4^+ can coexist in acid solution,[12] our results indicate that the disproportionation reaction in eq 4 does not occur to an appreciable extent. Mixtures of $NHCl_2$ and NCl_3, which decomposes slowly at pH 0–4, decompose more rapidly at higher pH. For the ammonia-free dichloramine solutions the rates of loss of $NHCl_2$ and formation of NCl_3 are autocatalytic, as seen in Figure 2. It appears that HOCl may be the source of the autocatalysis because it reacts rapidly with $NHCl_2$ to give NCl_3, and the two chloramines can react to generate N_2, Cl^-, and more HOCl. A trace of HOCl may be formed from the hydrolysis of $NHCl_2$. The addition of 0.5 M NaCl speeds the reaction by 1 order of magnitude. High concentrations of chloride ion in acid favor the formation of Cl_2 (eq 6), and Cl_2 has previously been shown to chlorinate dichloramine more rapidly than does HOCl,[35] so that under these conditions chloride increases the rate of NCl_3 formation.

$$HOCl + Cl^- + H^+ \rightleftarrows Cl_2 + H_2O \qquad (6)$$

Decomposition of Ammonia-Free Dichloramine in Neutral and Basic Solutions. When ammonia-free dichloramine is mixed with phosphate buffers at neutral pH, trichloramine is rapidly produced, but the yield is only about 10% of the theoretical. Yields of trichloramine can be increased to as much as 45% by the presence of hypochlorite in the buffer

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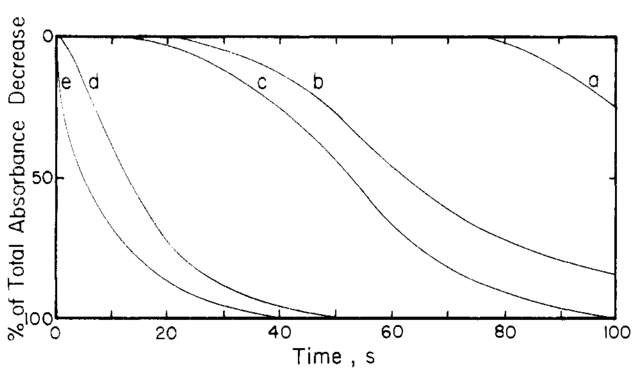

Figure 3. Effect of increasing hypochlorite concentration on the rate of decrease of absorbance due to dichloramine at 294 nm (–log [H^+] = 6.84, [PO_4]$_T$ = 0.05 M): (a) no added hypochlorite, fresh ammonia-free dichloramine solution; (b) no added hypochlorite, ammonia-free dichloramine solution ~30 min after collection; (c) 4.5 × 10^{-6} M added [OCl^-]$_T$ with fresh dichloramine; (d) 2.3 × 10^{-5} M added [OCl^-]$_T$ with fresh dichloramine; (e) 2.3 × 10^{-4} M added [OCl^-]$_T$ with fresh or 30 min old dichloramine.

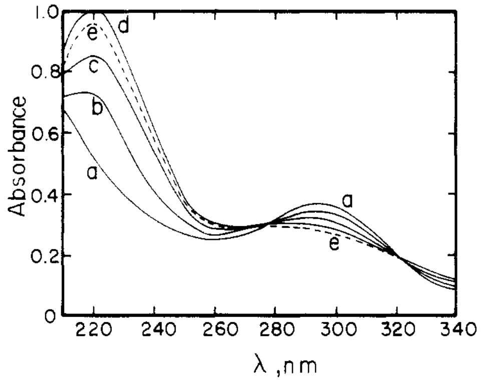

Figure 4. Change in absorbance spectrum with time observed on a vidicon spectrometer when 2 × 10^{-4} M ammonia-free dichloramine reacts with 2.3 × 10^{-3} M [OCl^-]$_T$ at –log [H^+] = 6.84 (buffered with 0.05 M [PO_4]$_T$; path length 1.0 cm). Time after mixing (s): (a) 0.1, (b) 0.5, (c) 1, (d) 2, (e) 5.

solutions. Liquid chromatography proves that dichloramine and chloramine are not among the products. In dilute base or in basic borate or carbonate buffers, OCl^- is the major product of dichloramine decomposition. Some NH_2Cl may also be produced, and small quantities of trichloramine can be observed shortly after mixing. The total oxidizing material in the products is about 25% of that in the initial dichloramine.

The decrease in the absorbance due to dichloramine was observed at the λ_{max} and found to be autocatalytic (Figure 3). The length of the induction period that precedes the major absorbance decrease is somewhat irreproducible but is affected by a number of variables. One of these is the time that the dichloramine is allowed to stand at pH 4 before it is mixed with the buffer solution. This can be seen by comparing curves a and b in Figure 3, which illustrate the decrease in the induction period brought about by increased age of the dichloramine solution. The length of the induction period is also reduced by the presence of hypochlorite in the buffer (curves c and d, Figure 3). At concentrations of hypochlorite comparable to that of the dichloramine, the induction period is almost undetectable (curve e, Figure 3). Sparging the dichloramine solution with N_2, O_2, or Ar for 5–10 min before mixing it with the buffer increases the length of the induction period. The presence of 0.05 M chloride in the buffer under the same conditions as in Figure 3 has little effect on the induction period. The induction period decreases as the pH of the buffer is increased, so that no induction period can be observed in 0.01 M NaOH. In every case, long induction periods are followed by slow reactions and shorter periods are followed by faster reactions.

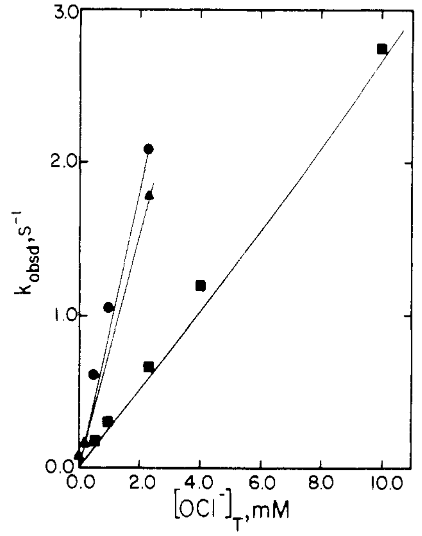

Figure 5. Effect of total hypochlorite concentration on the observed rate constant for the decomposition of dichloramine in phosphate buffer ([PO_4]$_T$ = 0.05 M). –log [H^+] = (●) 7.03, (▲) 6.84, and (■) 6.05. Curves are calculated from the best fit to all data obtained in phosphate buffers.

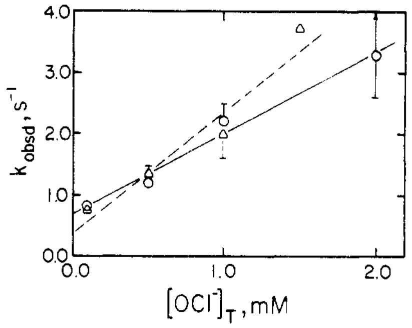

Figure 6. Effect of total hypochlorite concentration on the observed rate constant for the decomposition of dichloramine in carbonate buffer ([CO_3]$_T$ = 0.05 M). –log [H^+] = (○—) 10.63 and (△---) 9.94.

Monitoring these reactions at multiple wavelengths on the vidicon stopped-flow spectrophotometer shows that the concentration of trichloramine first increases and then decreases during the reaction. With increasing hypochlorite concentration in the buffer, the magnitude of the absorbance due to trichloramine increases. The time after mixing, which correponds to the maximum, also increases, so that when [OCl^-]$_T$ > [$NHCl_2$], the decrease in trichloramine absorbance only takes place after most of the dichloramine is already lost. The increased trichloramine yields in the presence of hypochlorite indicate that dichloramine reacts with hypochlorite to produce trichloramine, and a second dichloramine reacts with trichloramine. At low hypochlorite concentrations, most of the dichloramine reacts with trichloramine. At high hypochlorite concentrations, most of the dichloramine reacts with hypochlorite before it can react with the trichloramine that is formed.

The rate of decomposition of dichloramine in the presence of excess hypochlorite is first order in dichloramine concentration. When the concentrations of hypochlorite and dichloramine are approximately equal, there is a slight deviation from first-order behavior early in the reaction, but the decomposition is still pseudo first order for more than 95% of the absorbance change. The deviation results from the induction period discussed earlier. Initial absorbances coincide with values calculated for mixing of the two reactants, so that

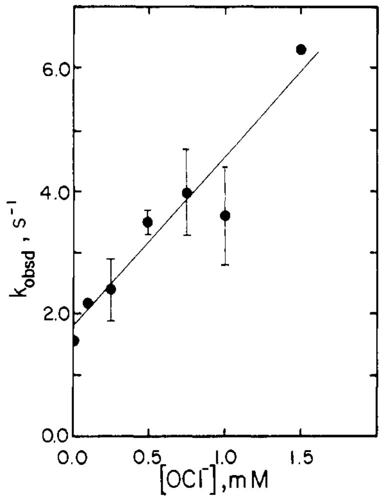

Figure 7. Effect of total hypochlorite concentration on the observed rate constant for the decomposition of dichloramine in NaOH (−log [H$^+$] = 11.63).

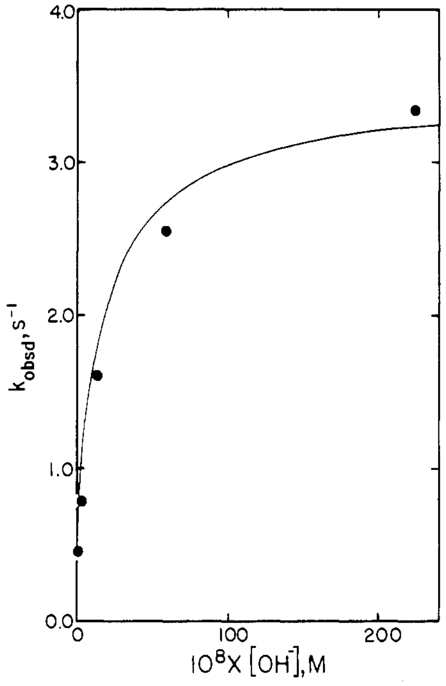

Figure 8. Effect of hydroxide concentration on the observed rate constant for decomposition of dichloramine (buffered with $[PO_4]_T$ = 0.05 M; $[OCl^-]_T$ = 2.3 mM). Curve is calculated from the best fit to all data obtained in phosphate buffers.

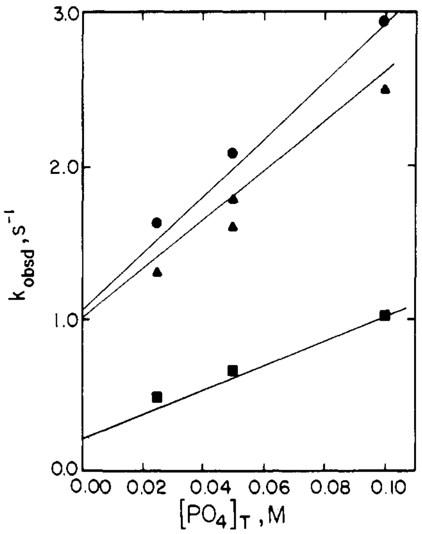

Figure 9. Effect of total phosphate concentration on the observed rate constant for the decomposition of dichloramine ($[OCl^-]_T$ = 2.3 mM). −log [H$^+$] = (●) 7.02, (▲) 6.86, and (■) 6.08. Curves are calculated from the best fit to all data obtained in phosphate buffers.

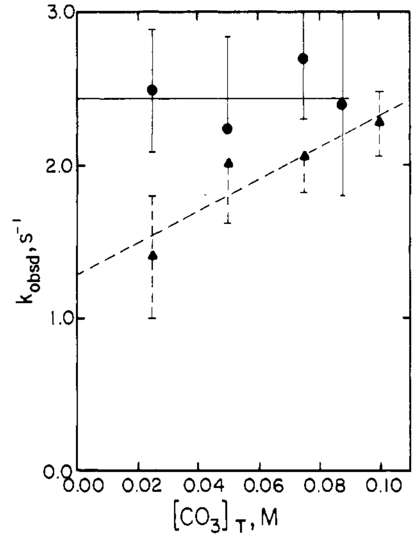

Figure 10. Effect of total carbonate concentration on the observed rate constant for the decomposition of dichloramine ($[OCl^-]_T$ = 1.0 mM). −log [H$^+$] = (●—) 10.66 and (▲- - -) 9.95.

no other reactions are preceding the observed absorbance decrease.

As shown in Figures 5–7, the reaction is also first order in hypochlorite concentration. The slopes of the lines correspond to pseudo-second-order rate constants and increase as the pH increases. The slopes reach a maximum around pH 10 and then decrease. In 0.01 M OH$^-$ the rate constant again increases (Figure 7). Figure 8 illustrates a similar increase to a maximum as [OH$^-$] is increased while hypochlorite and phosphate concentrations are kept constant. Intercepts in Figure 6 and 7 suggest a hypochlorite-independent path, with a rate that increases with increasing [OH$^-$].

The decomposition rate is also first order in total buffer concentration, as illustrated in Figures 9 and 10. When phosphate is the buffer, the slopes of the lines increase with increasing values of −log [H$^+$]. This demonstrates that HPO_4^{2-} is reacting as a general base. In carbonate solutions the slopes of the lines decrease to zero at the higher value of −log [H$^+$], implying that a carbonate-independent pathway predominates under these conditions.

The mechanism of the decomposition of ammonia-free dichloramine can be described by the coupled reactions (7) and (8), where B represents a general base or hydroxide ion. When

$$NHCl_2 + HOCl + B \xrightarrow{k_B} NCl_3 + BH^+ + OH^- \quad (7)$$

$$NHCl_2 + NCl_3 + 3OH^- \rightarrow N_2 + 2HOCl + 3Cl^- + H_2O \quad (8)$$

the initial hypochlorite concentration is low, reaction 7 is slower than reaction 8 and trichloramine concentration remains low throughout the reaction.

Trichloramine or hypochlorite produced from dichloramine that has been allowed to stand at −log [H$^+$] = 4 will accelerate these reactions, so that older dichloramine solutions will decompose more rapidly (Figure 3). Both hypochlorous acid and trichloramine are sufficiently volatile to be removed from solution by sparging, so that the rate of decomposition of sparged solutions will be decreased.

While the mechanism of the reaction in eq 8 is unknown, it is probable that the reaction is base catalyzed. At −log [H$^+$]

Table II. Protonation Constants and Rate Constants for Species Reacting with Dichloramine

species	$\log K_H{}^B$	ref	k_B, $M^{-2}\ s^{-1}$
$HPO_4{}^{2-}$	6.6	*a*	$(1.59 \pm 0.09) \times 10^4$
OCl^-	7.44	9	$(9 \pm 4) \times 10^4$
$CO_3{}^{2-}$	9.8	*b*	$(6 \pm 2) \times 10^6$
OH^-	13.73 (=pK_w)	*c*	$(3.3 \pm 0.1) \times 10^9$
NH_3	9.39	9	$k_{NH_4} = (3 \pm 1) \times 10^{-5}\ M^{-1}\ s^{-1}$

[a] Bates, R. G.; Acree, S. F. *J. Res. Natl. Bur. Stand. (U.S.)* **1943**, *30*, 129. [b] Calculated from: MacInnes, D. A.; Belcher, D. *J. Am. Chem. Soc.* **1935**, *57*, 1683. [c] Lagerström, G. *Acta Chem. Scand.* **1959**, *13*, 722.

= 12, the induction period is entirely absent and the point representing zero [OCl^-] falls on the line in Figure 7. At lower values of $-\log [H^+]$, the induction period decreases with increasing $-\log [H^+]$. The exact nature of this base catalysis is uncertain, but a reaction similar to reaction 8 is responsible for the decomposition of NBr_3.[25] It has been proposed that the decomposition of NBr_3 is base catalyzed because NBr_3 reacts with NBr_2^- formed from $NHBr_2$. Similarly, in reaction 8, NCl_3 may be reacting with NCl_2^- formed from $NHCl_2$.

Reaction 7 can be made faster than reaction 8 by high hypochlorite concentrations. These conditions were used to obtain the data in Figures 5, 6, and 8–10. The rate of reaction 7 is described by eq 9 and 10. Equation 11 accounts for the

$$-d[NHCl_2]/dt = k_{obsd}[NHCl_2] \qquad (9)$$

$$k_{obsd} = k_B[HOCl][B] \qquad (10)$$

$$[HOCl] = [OCl^-]_T K_H{}^{OCl} K_w / ([OH^-] + K_H{}^{OCl} K_w) \qquad (11)$$

fraction of total hypochlorite, $[OCl^-]_T$, that is present in solution as HOCl at a given [OH^-] on the basis of the protonation constant for OCl^-, $K_H{}^{OCl}$ (Table II). Equation 12

$$[B] = [B]_T[OH^-]/([OH^-] + K_H{}^B K_w) \qquad (12)$$

accounts for the fraction of the total buffer that is in the basic form. (Equation 12 is not necessary when B = OH^-.) Substituting eq 11 and 12 into eq 10 gives eq 13. When there

$$k_{obsd} = k_B K_H{}^{OCl} K_w [OCl^-]_T [B]_T [OH^-] / [([OH^-] + K_H{}^{OCl} K_w)([OH^-] + K_H{}^B K_w)] \qquad (13)$$

is more than one base in solution (e.g., OH^- and $HPO_4{}^{2-}$), k_{obsd} is a sum of terms, all of which have the same form as eq 13.

The values of k_{OH}, k_{HPO_4}, and k_{OCl} were evaluated simultaneously by a multiple linear-regression computer program[36] using the data in Figures 5, 8, and 9. The values are reported in Table II. The curves shown in these figures are the best fit to all of the data in these figures and not just the best fit to a single set of conditions. The value of k_{CO_3} (Table II) was calculated from the slope of the carbonate dependence plot at $-\log [H^+] = 9.94$ (Figure 10). The values of k_{OH} and k_{CO_3} can be used to predict the slopes of the lines in Figure 6. Agreement is excellent, indicating that the same mechanism applies in phosphate and carbonate buffers.

The slope of the line in Figure 7 is approximately twice the value predicted from k_{OH} for the following reason. The rate of reaction 7 reaches a plateau at high pH because the concentration of HOCl decreases. However, the rate of reaction 8 seems to increase with pH, so that in 0.01 M OH^-, the rate of reaction 8 exceeds the rate of reaction 7. Hence, every time reaction 7 occurs, a second molecule of dichloramine is immediately lost through reaction 8, effectively doubling k_{obsd}.

The reactivity of the general bases, $HPO_4{}^{2-}$, OCl^-, $CO_3{}^{2-}$, and OH^-, toward $NHCl_2$ can be correlated with their protonation constants (Table II). This linear free energy relationship is plotted in Figure 11 and has a slope of 0.6. Such a relationship confirms that the same proton-removal mechanism operates over the pH range 6–12. The reaction in eq 7 is a nucleophilic attack of dichloramine nitrogen on the chlorine of hypochlorous acid with a simultaneous removal of the dichloramine proton by the base (Figure 12).

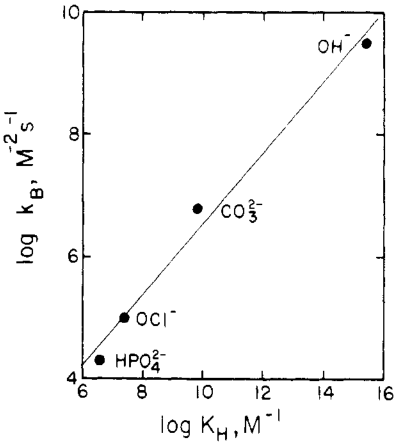

Figure 11. Linear free energy relationship between general-base-catalyzed rate constants and base protonation constants. Rate constants are for the termolecular reaction among $NHCl_2$, HOCl, and base (B).

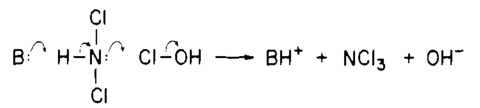

Figure 12. Base-assisted proton removal from $NHCl_2$ as the nitrogen attacks the chlorine of HOCl.

The intercepts in the plots of k_{obsd} vs. OCl^- (Figures 6 and 7) are a consequence of the autocatalytic nature of the coupled reactions (7) and (8). Because traces of hypochlorite are produced by the hydrolysis of dichloramine at pH 4, it is not possible to measure the rate of decomposition with hypochlorite totally absent. This small amount of hypochlorite will produce more hypochlorite when the pH is increased, due to the autocatalysis implied by eq 7 and 8. The rate constants in Figures 6 and 7 are measured after the induction period, and hence after the hypochlorite has built up. (High hypochlorite concentrations effectively reduce the length of this induction period to zero.) In the presence of base and buffer, the hypochlorite builds faster and it builds to a higher level, so that the intercepts depend upon the base and buffer concentration. Hence, the intercept is a measure of the effect of buffers on the buildup and not an estimate of the rate constant with hypochlorite absent.

Decomposition of Trichloramine. Since trichloramine is formed by the chlorination of dichloramine and is subsequently decomposed by reaction with dichloramine, the decomposition of trichloramine was investigated separately. At neutral pH in phosphate buffers, trichloramine decomposes by an autocatalytic pathway. As with dichloramine, the induction period decreases and the rate of the subsequent reaction increases as the pH is increased. Results are sometimes erratic, but the reaction slows markedly after ~20% of the trichloramine has been lost. The initial reaction is over in less than 10 min, and a subsequent reaction is about 100 times slower. At pH 10.5 in carbonate buffer and excess hypochlorite, trichloramine decomposes with a pseudo-first-order rate constant of 0.02 s^{-1}. This rate constant is independent of hypochlorite concentration. The final absorbance is zero.

All of these reactions are too slow to interfere with observation of the decomposition of ammonia-free dichloramine.

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[36] Nie, N.; Bent, D. H.; Hull, C. H. "Statistical Package for the Social Sciences"; McGraw-Hill: New York, 1970.

Table III. Effect of $[H^+]$ and $[NH_4^+]$ on the Rate Constants for the Decomposition of Dichloramine and the Simultaneous Formation of Chloramine

$-\log [H^+]^a$	$[NH_4^+]$, M	$10^6 \times k_{obsd}^{NHCl_2}$, s^{-1}	$10^6 \times k_{obsd}^{NH_2Cl}$, s^{-1}
6.16	0.115	11 ± 2	6.6 ± 0.4
6.17	0.228	12 ± 3	9.6 ± 2.2
6.19	0.341	13 ± 4	8.6 ± 1.4
6.25	0.454	12 ± 2	14 ± 2
6.19 ± 0.04^b			
6.42	0.014	17 ± 5	6.2 ± 1.2
6.45	0.115	18 ± 1	10 ± 1
6.45	0.172	19 ± 3	13 ± 2
6.43 ± 0.02^b			
6.97	0.013	42 ± 10	25 ± 2
6.99	0.024	54 ± 3	27 ± 1
7.03	0.115	57 ± 7	32 ± 4
7.00	0.171	45 ± 1	31 ± 1
7.00 ± 0.03^b			

^{a} Buffered with $[PO_4]_T = 0.01$ M. ^{b} Mean.

Table IV. Effect of Ammonia Concentration on the Rate Constant for the Decomposition of Dichloramine at $-\log [H^+] = 10.14$

$[NH_3]_T$, M	$k_{obsd}^{NHCl_2}$, s^{-1}	$[NH_3]_T$, M	$k_{obsd}^{NHCl_2}$, s^{-1}
0.0113	0.029 ± 0.001	0.0506	0.0262 ± 0.0003
0.0162	0.0266 ± 0.0002	0.0604	0.0250 ± 0.0003
0.0260	0.0269 ± 0.0002		0.0266 ± 0.0013^a
0.0407	0.0259 ± 0.0004		

^{a} Mean.

Decomposition of Dichloramine in the Presence of Ammonia. Chloramine can be produced from dichloramine decomposition at neutral pH in the presence of excess ammonia. As expected from earlier work on the equilibrium between these two compounds, the ratio of chloramine to dichloramine in product solutions increases with increasing hydroxide concentration.[9-11] However, equilibrium is never attained at pH values greater than 6 due to a side reaction. The actual yield of chloramine is only ~25% of the initial oxidizing chlorine, consistent with an earlier report.[19] Nitrogen is probably the other major product,[19] but another compound, not present in the starting material, is separated by liquid chromatography. On the basis of retention time, this compound is more polar than chloramine yet is probably not ionized at neutral pH. The compound absorbs UV radiation of wavelengths less than 300 nm, with a maximum absorbance around 245 nm. It does not oxidize I^- but is oxidized by cold, dilute MnO_4^-. Hydrazine and hydroxylamine can be excluded by chemical tests and chromatography of standards. A compound with similar properties is also produced during the decomposition of concentrated (>0.1 M) NH_2Cl, giving credence to the suggestion[23] that dichloramine is an intermediate in this decomposition.

The rate of decomposition of dichloramine in the presence of ammonia is much slower than the reactions observed when ammonia is absent. This sluggishness allows simultaneous determination of the initial rate of disappearance of dichloramine and the rate of appearance of chloramine at neutral pH (Table III). In higher pH solutions, stopped-flow techniques are needed to observe the decomposition of dichloramine (Tables IV and V).

Table V. Effect of Ammonia Concentration on the Rate Constant for the Decomposition of Dichloramine at $-\log [H^+] = 12$

$[NH_3]_T$, M	$k_{obsd}^{NHCl_2}$, s^{-1}	$[NH_3]_T$, M	$k_{obsd}^{NHCl_2}$, s^{-1}
0.00663	1.00 ± 0.02	0.100	2.21 ± 0.01
0.0104	1.08 ± 0.01	0.106	2.16 ± 0.05
0.0115	1.22 ± 0.04	0.201	2.15 ± 0.05
0.0214	1.58 ± 0.02	0.211	2.21 ± 0.08
0.0254	1.56 ± 0.04	0.421	2.06 ± 0.03
0.0312	1.78 ± 0.04	0.630	2.14 ± 0.02
0.0508	2.02 ± 0.05	1.05	2.23 ± 0.03
0.0555	2.01 ± 0.02		

The value of $k_{obsd}^{NH_2Cl}$ increases linearly with $[NH_4^+]_T$ (Table III) but also depends on the acidity. At constant $[NH_4^+]_T$, $k_{obsd}^{NH_2Cl}$ increases as $-\log [H^+]$ is increased. These data are consistent with the rate law in eq 14 and 15. Because k_{NH_4} does not increase with $-\log [H^+]$, the first term in eq 15 does not reflect direct nucleophilic attack by NH_3 on the dichloramine chlorine. Nucleophilic attack by NH_4^+ is implausible, but reactions 16 and 17 can account for the observations.

$$d[NH_2Cl]/dt = k_{obsd}^{NH_2Cl}[NHCl_2] \qquad (14)$$

$$k_{obsd}^{NH_2Cl} = k_{NH_4}[NH_4^+] + k_0[OH^-] \qquad (15)$$

$$NHCl_2 + H^+ \xrightleftharpoons{K_H^{NHCl_2}} NH_2Cl_2^+ \qquad (16)$$

$$NH_3 + NH_2Cl_2^+ \rightleftarrows 2NH_2Cl + H^+ \qquad (17)$$

The value of $K_H^{NHCl_2}$ is expected to be very small so that $NH_2Cl_2^+$ is not present in appreciable concentrations, and the observed rate law is best expressed in terms of NH_4^+. The value of k_{NH_4} is 3×10^{-5} M^{-1} s^{-1}.

The rate constant for the reaction of ammonium ion with dichloramine to produce chloramine is of special interest because the forward rate constant in eq 2 is known ($k_2 = 3.2 \times 10^4$ M^{-2} s^{-1}), and evaluation of the reverse rate constant permits the equilibrium constant to be calculated. Far larger concentrations of NH_4^+ (and higher pH) are required to reverse the reaction in eq 2 than previous estimates of the equilibrium constant suggested. The equilibrium concentrations cannot be measured accurately because decomposition of $NHCl_2$ occurs before equilibrium is reached. Hence, the stability constant must be determined by the ratio of the rate constants. This gives an equilibrium constant of 1×10^9 M^{-1} for the reaction in eq 2.[29,30]

Hydroxide ion attacks $NHCl_2$, causing decomposition. The products include NH_2Cl and chloride. This gives the second term in eq 15, where k_0 has a value of 150 ± 10 M^{-1} s^{-1}. The mechanism is unknown, but it cannot be the direct attack of OH^- on $NHCl_2$ to give NH_2Cl and OCl^- because this would predict much too large a rate constant for the reverse reaction. The rate constant for the disappearance of dichloramine, $k_{obsd}^{NHCl_2}$, always exceeds $k_{obsd}^{NH_2Cl}$ (Table III). This cannot be accounted for by eq 15 alone. Hence, $NHCl_2$ is decomposed in a third reaction, which does not produce NH_2Cl. This reaction may produce the unidentified compound observed by HPLC, but the rate constant cannot be calculated.

Even though the reaction of dichloramine with HOCl is some 5 orders of magnitude faster than the reaction of dichloramine with ammonia, the hypochlorite pathway makes little contribution to the loss of dichloramine when ammonia is present. The reaction of HOCl with NH_3 has a rate constant of 2.9×10^6 M^{-1} s^{-1}.[9] At neutral pH the rate of this reaction is at least 10 times faster than the reaction of HOCl and HPO_4^{2-} or OH^- with dichloramine. Hence, any hypochlorite present will be rapidly consumed by ammonia, allowing slower reactions to be observed without interference.

Deprotonated Dichloramine, NCl_2^-. Throughout this investigation, attempts were made to observe NCl_2^-, or at least to prove its existence. The protonation constant of NCl_2^- has been estimated to be 10^7.[24] Although the formation of NCl_2^- may be the reason that reaction 8 is base catalyzed, alternative reactions are possible, so that this observation alone is insufficient to verify the existence of NCl_2^-. It is probable that NCl_2^- would have a UV-absorbance spectrum different from that of dichloramine, yet the absorbance of dichloramine does not change from pH 4 up to at least pH 12, when observed by conventional or stopped-flow spectrophotometry. At pH 13 and higher the rate of basic decomposition of $NHCl_2$ is fast, and this interferes with the spectral measurements of the initial absorbance. If it is assumed that a 10% change in the concentration of $NHCl_2$ could be detected by a change in the initial absorbance, then the protonation constant for NCl_2^- must exceed 10^{13} M^{-1}. The protonation constant for NCl_2^- will not exceed that of $NHCl^-$, which is estimated[3,37] to be greater than 10^{18}.

Conclusion

It is not uncommon for traces of a species to catalyze a reaction, but it is less common for such traces to inhibit a reaction. This work shows that traces of ammonia inhibit the decomposition of dichloramine. This is because ammonia reacts with hypochlorous acid, which is responsible for the instability of dichloramine.

Solutions of dichloramine free of other nitrogen compounds can be prepared by cation-exchange chromatography. With use of these solutions, it has been shown that dichloramine is unstable in the presence of even trace concentrations of hypochlorous acid, a compound which is produced in the decomposition of dichloramine. Consequently, the decomposition is an autocatalytic process. Dichloramine produces trichloramine in a termolecular mechanism involving the simultaneous removal of the proton by a general base and chlorination by HOCl. Dichloramine also reacts with trichloramine to produce nitrogen gas and more hypochlorous acid. This latter reaction may cause trichloramine concentrations to increase when more hypochlorite is added to a system than is necessary to reach breakpoint stoichiometry. All of the dichloramine could be rapidly converted to trichloramine and be unavailable to participate in the subsequent production of N_2. The general-base catalysis observed suggests that the breakpoint chlorination reactions will be speeded by the presence of phosphate or other buffers in the solution.

Hypochlorite reacts more rapidly with ammonia than with dichloramine, so that dichloramine solutions are stabilized by the presence of ammonia. The slow decomposition of dichloramine in the presence of ammonia produces chloramine and other compounds.

The instability of dichloramine has implications for the analysis of chlorinated water for free and combined chlorine. Several of the standard methods for these analyses, namely the amperometric[31b] and syringaldazine[31c] protocols, require that the sample first be buffered at neutral pH. If the sample is initially at a lower pH and does not contain ammonia, then this step will cause some or all of the dichloramine to decompose before analysis. As a result, the values determined for total and combined chlorine will be low and the value for free chlorine may be high.

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Registry No. $NHCl_2$, 3400-09-7; HOCl, 7790-92-3; NH_3, 7664-41-7; NCl_3, 10025-85-1; HPO_4^{2-}, 14066-19-4; OCl^-, 14380-61-1; CO_3^{2-}, 3812-32-6; OH^-, 14280-30-9.

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Kinetics of the Reduction of the Linkage Isomers of the Pentaamminecobalt(III) Complexes of 4-Cyanobenzoic Acid by Chromium(II)

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The chromium(II) reduction of the nitrile-bonded pentaamminecobalt(III) complexes with 3- and 4-cyanobenzoic acids has been studied. For the 4-cyanobenzoic acid complex, the rate law at 25 °C and $I = 1.0$ mol L^{-1} was $k_{obsd} = (k_H[H^+] + kK_a)/(K_a + [H^+])$. A nonlinear least-squares fit of the data to this equation gave $k_H = 0.290 \pm 0.005$ L mol^{-1} s^{-1}, $k = 0.99 \pm 0.12$ L mol^{-1} s^{-1}, and $K_a = 0.0031 \pm 0.0007$ mol L^{-1}. The reduction was shown to occur via remote attack of Cr(II) to produce a (carboxylato)chromium(III) product. At higher temperatures the inverse hydrogen ion term disappears, and the activation parameters for the k_H term were $\Delta H^* = 7.1 \pm 0.5$ kcal mol^{-1} and $\Delta S^* = -37 \pm 3$ eu. The V(II) reduction of this complex followed the rate law $k_{obsd} = k_1 + k_2[H^+]^{-1}$ with $k_1 = 11.1 \pm 0.2$ L mol^{-1} s^{-1} and $k_2 = 0.21 \pm 0.04$ s^{-1} at 25 °C and $I = 1.0$ mol L^{-1}. The nitrile-bonded 3-cyanobenzoic acid complex is reduced by chromium(II) without ligand transfer and follows the simple rate law $-d \ln [Co(III)]/dt = k_2[Cr(II)]$. At 25 °C and $I = 1.0$ mol L^{-1}, $k_2 = (4.89 \pm 0.23) \times 10^{-2}$ L mol^{-1} s^{-1}, $\Delta H^* = 8.3 \pm 0.4$ kcal mol^{-1}, and $\Delta S^* = -37 \pm 2$ eu. The reductions are discussed in terms of the reducibilities of the ligands and the stabilities of possible precursor complexes.

Introduction

It is generally thought that the necessary criteria for remote attack in redox reactions between transition-metal complexes in solution are (1) a reducible ligand system and (2) a remote polar donor group capable of forming a precursor complex.[1-3] The relative importance of these requirements and the mechanism of electron transfer through the ligand are not fully understood. Complications in interpretation have arisen because the majority of studies have involved the reduction of (carboxylato)pentaamminecobalt(III) complexes by chromium(II) which can also proceed by adjacent attack of the reductant at the carbonyl oxygen of the coordinated carboxylate.[4,5] For example,[4] reduction of (terephthalato)penta-

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