Reaction Scheme for the Chlorination of Ammoniacal Water

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A kinetic model of the reacting aqueous chlorine-ammonia system is proposed which describes equally well the rapid "breakpoint" oxidation of ammonia, where the applied chlorine dose (Cl₂) to ammonia-nitrogen molar ratio (Cl/N) is greater than approximately 1.6; the slow oxidation of ammonia in aqueous chloramine solutions (Cl/N < 1); and the transition region of 1 < Cl/N < 1.6, where rapid initial decay results in chloramine species residuals. Calculated time-dependent concentrations of the chlorine species, determined by numerical solution of the rate expressions, compare favorably to measured values, determined during experiments performed over ranges of initial pH (6–8) and Cl/N (0.25–2.0) conditions. The experimentally measured species include free chlorine (HOCl + OCl⁻), monochloramine (NH₂Cl), and dichloramine (NHCl₂). In addition, the model appropriately considers the catalysis of certain key reactions by several commonly encountered inorganics, such as bicarbonate and phosphate species.

Introduction

Chlorination remains the predominant method of drinking water and wastewater disinfection and cooling water biofouling control in the United States. In the process of chlorination, either sufficient chlorine is added to oxidize all existing ammonia to stable products and to retain a residual of free chlorine [hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻)] or chlorine is added with ammonia to produce a residue of chloramine species. Operationally, the former method is commonly referred to as "breakpoint chlorination", where the applied chlorine (HOCl + OCl⁻) dose to ammonia ratio on a molar basis (Cl/N) is greater than ≈1.6, while the latter is referred to as "chloramination" or "combined residual chlorination", where Cl/N < 1. The exact ratio of ammonia oxidized to chlorine reduced at the breakpoint is a function of solution pH and ionic composition with both N₂ and NO₃⁻ formed as stable products. (For discussion purposes, therefore, we arbitrarily refer to the breakpoint as ≈1.6 when it is not known or may vary around this value.)

The resulting oxidant species upon chlorination, their concentration, and their stability are the result of a series of reactions involving aqueous chlorine (HOCl and OCl⁻), aqueous ammonia (NH₃ and NH₂⁻), and the chlorinated derivatives of ammonia [monochloramine (NH₂Cl), dichloramine (NHCl₂), and nitrogen trichloride (NCl₃)]. Hence, an understanding of these reactions is critical to maximizing the efficacy of disinfection, including minimizing the formation of undesirable byproduct, whose
The purpose of this paper is to present a reaction model of the aqueous chlorine-ammonia system that is applicable to molar chlorine dose to ammonia ratios within both the combined and breakpoint dose regions and applicable also to the transition region \((1 < \text{Cl}/\text{N} < 1.6)\), where the rapid oxidation of some ammonia occurs, resulting in a combined residual. The value of the model as a suitable algorithm to describe chlorine-ammonia speciation and fate, under conditions applicable to the disinfection of potable, waste, and cooling waters, has been examined by comparing experimental kinetic data of all three regions to numerical solutions of the rate expressions.

Comprehensive reaction schemes have been proposed previously. Their utility, however, is limited to either breakpoint \((4, 5)\) or combined chlorine \((6-8)\) conditions. In addition, major discrepancies exist among current model formulations, precluding their simple compilation to obtain a model capable of predicting speciation and fate over a continuum of dose ratios. In particular, no existing model is capable of predicting the speciation and fate of chlorine-containing oxidants over the transition region \((1 < \text{Cl}/\text{N} < 1.6)\), a range over which the rate of ammonia oxidation increases by several orders of magnitudes. To overcome this, we have included within the model a reaction scheme proposed by Hand and Margerum \((9)\) that describes the decay of dichloramine in the presence of free chlorine. Previous “breakpoint” models \((4, 5)\) have included reactions for dichloramine decay which are much more empirical and incompatible with reaction mechanisms in the combined region. The distinction between “breakpoint reactions” and those occurring in the presence of excess ammonia is artificial anyway and stems from the fact that the oxidation of ammonia by chlorine occurs at considerably different rates depending on the Cl/N dose ratio. Unlike the rapid redox reactions that occur under breakpoint conditions, the oxidation of ammonia under combined chlorine conditions is very slow, with oxidant half-lives typically on the order of days.

We report, therefore, on two sets of chlorine-ammonia speciation and fate experiments, performed under vastly different time scales (minutes and days), both of whose results were compared to calculated species concentrations of model simulations of the same rate expressions.

**Model Formulation**

The proposed model includes reactions which are easily grouped by their attributes. The four logical subdivisions are as follows: (1) the substitution reactions involving HOCl and ammonia or the chlorinated derivatives of ammonia, and the corresponding hydrolysis reactions; (2) the disproportionation reactions of chloramine species, and the corresponding back-reactions; (3) the redox reactions that occur in the absence of measurable free chlorine; and (4) the facile redox reactions that occur when free chlorine is in solution. The model also includes several acid dissociation equilibria of the reacting species.

Historically, in determining stoichiometry and rate, reactions of the chlorine-ammonia system have been either isolated and studied by traditional kinetic methods or studied through construction and evaluation of plausible reaction schemes. The reason for the latter is because the complexity and integral nature of all the reactions has made it difficult, if not impossible, to experimentally isolate several important redox reactions, and even some substitution reactions. Hence, the substitution reactions, which sometimes can be isolated sufficiently from redox reactions, generally have been characterized more thoroughly with respect to their order and magnitude than the redox reactions. Equilibrium reactions (those involving the solvent, water) are even more thoroughly characterized.

**Equilibrium Reactions.** Equilibrium reactions include the hydrolysis of chlorine \((\text{Cl}_2)\), the dissociation of HOCl, and the dissociation of \(\text{NH}_3^+\). The forward \((10)\) and equilibrium constants \((11)\) for the hydrolysis of chlorine

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons K_{\text{HOC}} \text{HOC}_{\text{H}} + \text{H}^+ + \text{Cl}^- \quad (e1)
\]

imply that, in freshwater above pH 4, equilibrium is reached within seconds and dissociation is essentially complete. While \(\text{Cl}_2\) is a potent oxidant, it does not exist in significant concentrations in natural freshwaters. It may be important, however, in saline systems.

The equilibrium constant for the acid dissociation of HOCl

\[
\text{HOCl} \rightleftharpoons K_{\text{HOCl}} \text{OC}^- + \text{H}^+ \quad (e2)
\]

has been measured and extrapolated to zero ionic strength as \(K_{\text{HOCl}} = 2.9 \times 10^{-2} \text{ M at 25 °C} \) \((12)\). The species HOCl and OC\(^-\) together are commonly referred to as “free chlorine”. Ammonium ion \((\text{NH}_4^+)\) ionizes according to eq \(3\) at 25 °C and zero ionic strength, where \(K_{\text{NH}_3} = 5.0 \times 10^{-10} \) \((13)\).

\[
\text{NH}_4^+ \rightleftharpoons K_{\text{NH}_3} \text{NH}_3 + \text{H}^+ \quad (e3)
\]

Another potentially important equilibrium reaction involves protonation of \(\text{NH}_2\text{Cl}\)

\[
\text{NH}_2\text{Cl} + \text{H}^+ \rightleftharpoons K_{\text{NH}_2\text{Cl}} \text{NH}_2\text{Cl}^+ \quad (e4)
\]

where \(K_{\text{NH}_2\text{Cl}} = 28 \text{ M}^1 \text{ at 25 °C and ionic strength 0.5 M} \) \((14)\). Because of its low \(pK_a\) value \((pK_a = 1.5)\), any reaction involving \(\text{NH}_2\text{Cl}^+\) in natural waters can be expressed as an acid-catalyzed reaction of \(\text{NH}_2\text{Cl}\).

**Substitution Reactions Involving HOCl.** The stoichiometry and rate expressions of the proposed model are given in Table I. The first four equations describe the nucelophilic substitution reactions of HOCl with \(\text{NH}_3\) and the chlorinated derivatives of \(\text{NH}_3\), and the corresponding hydrolysis reactions. The first reactions (eqs 1 and 2) describe the formation and hydrolysis of \(\text{NH}_2\text{Cl}\) \((1, 15-18)\). Morris and Isaac \((18)\) have evaluated the data of numerous investigators to propose \(k_{\text{NH}_3} = 4.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \) at 25 °C. The value given for the first-order rate constant for the hydrolysis of \(\text{NH}_2\text{Cl} (k_{\text{HOC}} \text{ at 25 °C})\) has been calculated by Isaac \((2)\) based on Granstrom’s data \((19)\).

The second substitution reaction (eq 3) results in \(\text{NHCl}_2\) formation. There exists a considerable range in the calculated values for \(k_{\text{NH}_3} \) \((4, 5, 17, 18)\). These differences may be attributable to the difficulty in isolating the reaction. Margerum et al. \((17)\) measured \(k_{\text{NH}_3}\) to be \(150 \text{ M}^{-1} \text{ s}^{-1} \) at 25 °C at an ionic strength of 0.5 M with stop-flow techniques. Wei \((4)\), however, has used a value of \(425 \text{ m}^{-1} \text{ s}^{-1}\) in a breakpoint chlorination model at low ionic strength. A good estimate may lie within this range \((150-425 \text{ M}^{-1} \text{ s}^{-1})\). Margerum et al. \((17)\) have given a value of \(6.5 \times 10^{-2} \text{ s}^{-1}\) at 25 °C, ionic strength 0.5 M, for the hydrolysis rate constant of \(\text{NH}_2\text{Cl} (k_{\text{HOC}})\). This value compares favorably to that calculated by Morris and Isaac \((18)\) of \(7.6 \times 10^{-2} \text{ s}^{-1}\).

The third substitution reaction involves formation of \(\text{NCl}_3\) (eq 11). This reaction has been most difficult to isolate because of the instability of \(\text{NCl}_3\) in the presence of \(\text{NCl}_3\) at near-neutral pH and, therefore, is discussed
Table I. Reactions and Associated Constants

<table>
<thead>
<tr>
<th>reaction stoichiometry</th>
<th>rate expression</th>
<th>rate constant (25 °C)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) HOCl + NH₂ → NHCl₂ + H₂O</td>
<td>k_{abs}[HOC][NH₂]</td>
<td>k_{abs} = 1.5 × 10^{10} M⁻² s⁻¹</td>
<td>18</td>
</tr>
<tr>
<td>(2) NHCl₂ + H₂O → HOCl + NH₂</td>
<td>k_{abs}[HOC][NH₂]</td>
<td>k_{abs} = 7.6 × 10⁻³ M⁻² s⁻¹</td>
<td>18</td>
</tr>
<tr>
<td>(3) HOCl + NHCl₂ → NHCl₃ + H₂O</td>
<td>k_{abs}[HOC][NHCl₂]</td>
<td>k_{abs} = 1.0 × 10⁻⁵ M⁻¹ s⁻¹</td>
<td>4, 17</td>
</tr>
<tr>
<td>(4) NHCl₃ + H₂O → HOCl + NH₂Cl</td>
<td>k_{abs}[NHCl₃]</td>
<td>k_{abs} = 2.5 × 10⁻³ M⁻¹ s⁻¹</td>
<td>17</td>
</tr>
<tr>
<td>(5) NH₂Cl + HOCl → NHCl₂ + NH₂</td>
<td>k_{abs}[NHCl₂][NH₂][H⁺]</td>
<td>k_{abs} = 2.16 × 10⁻⁶ M⁻² s⁻¹</td>
<td>9</td>
</tr>
<tr>
<td>(6) NHCl₃ + H₂O → NHCl₂ + NH₃</td>
<td>k_{abs}[NHCl₂][OH⁻]</td>
<td>k_{abs} = 4.0 × 10⁻⁴ M⁻¹ s⁻¹</td>
<td>20, 28</td>
</tr>
<tr>
<td>(7) NHCl₃ + H₂O → I⁻</td>
<td>k_{abs}[I][NHCl₃]</td>
<td>k_{abs} = 1.0 × 10⁻⁴ M⁻¹ s⁻¹</td>
<td>6</td>
</tr>
<tr>
<td>(8) I⁻ + NHCl₂ → HOCl + products</td>
<td>k_{abs}[I][NHCl₂]</td>
<td>k_{abs} = 3.0 × 10⁻⁴ M⁻¹ s⁻¹</td>
<td>6</td>
</tr>
<tr>
<td>(9) I⁻ + NHCl₃ → products</td>
<td>k_{abs}[I][NHCl₃]</td>
<td>k_{abs} = 5.5 × 10⁻⁴ M⁻¹ s⁻¹</td>
<td>6</td>
</tr>
<tr>
<td>(10) NHCl₂ + NHCl₃ → products</td>
<td>k_{abs}[NHCl₂][NHCl₃]</td>
<td>k_{abs} = 2.0 × 10⁻³ M⁻¹ s⁻¹</td>
<td>9</td>
</tr>
<tr>
<td>(11) NHCl₃ + NCl₃ + H₂O → NCl₄ + H₂O</td>
<td>k_{abs}[NHCl₃][NCl₃][OH⁻]</td>
<td>k_{abs} = 5.0 × 10⁻² M⁻¹ s⁻¹</td>
<td>9</td>
</tr>
<tr>
<td>(12) NCl₄ + 2H₂O → HOCl + products</td>
<td>k_{abs}[NCl₄][H₂O]</td>
<td>k_{abs} = 8.3 × 10⁻³ M⁻¹ s⁻¹</td>
<td>9</td>
</tr>
</tbody>
</table>

For purposes of calculating products, we assumed to contain H⁺ for each reaction, consistent with NH₃ formation.

In the breakpoint region, both N₂ and NO₃⁻ are formed (23, 24). Pressley et al. (24) observed at Cl/N = 2 that, at pH 5, only about 1.0% of the initial NH₃ was converted to NO₃⁻, while at pH 8, 15% was converted, after 2 h. Although not a final product, NCl₃ is stabilized in the presence of free chlorine (5, 18, 26). It is produced in significant amounts only at high values of Cl/N, generally at lower pH values, upon initial chlorination (at short time periods). When the concentration of free chlorine is very low or when other combined species are present, NCl₃ is unstable (26, 27).

NHC₃ Decomposition in the Presence of Excess Ammonia. Leao (6) proposed the first kinetic model describing the speciation and fate of chlorine under conditions of Cl/N < 1, employing reactions identical to eqs 7–10 of Table I to describe nitrogen oxidation. No single specific reactive intermediate (1) was proposed. Indeed, the values of k_{dp} and k_{abs} (eqs 8 and 9) were set very high to maintain I at a low pseudo-steady-state level; it is only the ratio of k_{dp}/k_{abs} that is significant. Equation 10 was incorporated into his overall model because doing so resulted in a better fit between predicted and measured chloramine residuals. Because of the magnitude of k_{dp}, it is impossible to isolate this reaction from competing reactions. More recently, we have studied decay of NHCl₂ under conditions where it quickly decomposes, by rapidly raising the pH of essentially pure aqueous NHCl₂ solutions in 25 mM ammonia–ammonium-buffered solutions (20, 28). We determined whether one set of rate constants for eqs 7–9 was sufficient to model the system over a range of reaction conditions. Generally, less than 25% of the initial dichloramine (as Cl₂) was recovered as monochloramine, consistent with the need for inclusion of the reaction involving monochloramine (eq 9) or some other decomposition reaction, possibly involving formation of the unknown compound previously mentioned. While results of the numerical curve fitting were quite favorable for individual experiments, some discrepancies existed among rate constants of experiments with different initial monochloramine concentrations.

Hand and Margerum (9) also acknowledged the existence of a hypochlorite-independent decomposition reaction involving dichloramine from studies of chlorine decay.
in the presence and absence of measurable free chlorine. Their spectrophotometric data also alluded to the formation of an unidentified product. Until this product is characterized, eqs 7–10 represent a reasonable pH-dependent mechanism for NHCl₂ decay in the absence of free chlorine.

**NHCl Decomposition in the Presence of HOCl + OCl⁻**

We (4) first proposed a reaction scheme similar to eqs 7–9 and 14 to model decay of oxidant when excess free chlorine is in solution. We’s reaction scheme varied somewhat from that given in Table I in that, although no intermediate was identified, NOH was invoked as this species. Additionally, the formation of NO₃⁻ (eq 14) was modeled through reaction of NOH with HOCl, resulting in the same stoichiometry described in Table I (eqs 7 and 14). The value of the rate constant for eq 7, determined by Wei at Cl⁻/N₂ > 1.6, is approximately 1000 times greater than that determined by Leao (6) under an initial Cl⁻/N₂ < 1.

Hand and Margerum (9) have proposed, however, that decay of NHCl₂ can occur through formation of NCl₃, which acts as the reactive intermediate, as described by eqs 11 and 12. Equation 11 results from a second-order, general-base-catalyzed nucleophilic attack of the dichloramine nitrogen on the hypochlorous acid chlorine, forming NCl₃, which then acts as a reactive intermediate in the presence of NHCl₂ at high pH (eq 12). The value of k_{diss} was indeterminate because of its very transient nature in these experiments.

There is much evidence to support this mechanism over simple catalysis by OCl⁻. Spectrophotometric evidence shows that, upon mixing ammonia-free NHCl₂ with HOCl at pH 6.84, a very sharp increase in absorbance at 220 nm occurs, where NCl₃ has a peak, followed by decay of this peak after only 5 (9).

Very early stoichiometric information also supports this mechanism. Chapin (29) showed that NCl₃ formed at low pH in the presence of excess ammonia, decays almost completely after only 30 min at pH 4–5, the pH range where NHCl₂ is most stable if formed from a solution of NH₄Cl (see Figure 1). If, however, the pH of a NCl₃ solution is raised to pH 9, over 30% of the oxidant can be recovered as NHCl₂. If the first step of NCl₃ decay involves hydrolysis to form NHCl₂ and HOCl, the HOCl formed would rapidly react with any excess ammonia to give NH₄Cl. At pH 9, NH₄Cl is stable. At pH 4, NH₄Cl disproportionateates to form more NHCl₂, which in turn reacts with NCl₃, once again forming HOCl, repeating the cycle. Hence, the instability of NHCl₂ formed from the decay of NCl₃ at pH 4, where nitrogen trichloride free NHCl₂ is stable, can be explained if reaction with NCl₃ is assumed.

Indeed, recent studies by Kumar et al. (30), who use stopped-flow techniques, show that the products at higher pH actually retain 50% of the initial total oxidant, suggesting the correct stoichiometry, and indicating Chapin’s lower recovery (about 35%) at pH 9 is caused only by inadequate mixing.

Another evidence is that inorganic bases such as phosphate (HPO₄²⁻) do not enhance NHCl₂ decay in the absence of HOCl (28), suggesting OCl⁻ would not directly catalyze NHCl₂ decay. OCl⁻, however, is a well-known α nucleophile (31–33), indicating that it may be near impossible to calculate ab initio the reactivity of OCl⁻ to the proton on NHCl₂.

More recently, Yu and Margerum (34) have investigated the reaction of NCl₃ with NHCl₂ (reaction 12 of Table I) in excess ammonia, in 50 mM phosphate buffer, from pH 6.13 to 6.88, ionic strength 0.5 M, at 25 °C. Under these conditions, the reaction rate was found to be proportional to HPO₄²⁻ concentration, giving a third-order rate coefficient k_{HPO₄²⁻} = 1.05 × 10⁶ M⁻² h⁻¹. From these data, and an experiment they performed at high pH, limits on the rate constant for OCl⁻ catalysis can be calculated to be 1.4 × 10¹¹ M⁻² h⁻¹ < k_{OCl⁻} < 2 × 10¹³ M⁻² h⁻¹ for their experimental conditions. The catalysis by phosphate suggests that, under breakdown conditions, OCl⁻ will catalyze this reaction also. Because the rate coefficients for OH⁻ and OCl⁻ are unknown, and because all reacting species have similar (but not identical) pH dependency, the rate-determining step of this reaction is given in Table I for only OH⁻ catalysis, where k_{diss} is an empirical constant to be determined and compared to these other values, corrected for our experimental conditions.

Kumar and Margerum (ref 34, with data to be submitted for publication) have determined the OH⁻-catalyzed reaction rate constant between NH₃Cl and NCl₃ (reaction 13 of Table I) to be 5.65 × 10⁴ M⁻² h⁻¹, at 25 °C, ionic strength 0.5 M. Similar to reaction 12, it is most likely catalyzed by OCl⁻ and phosphate species. Therefore, similar to reaction 12, an empirical constant, and simply pH dependence (OH⁻ catalysis) is assumed. In previous breakdown models (4, 5) in which NHCl₂ was assumed as the reactive species (instead of NCl₃), a stoichiometrically comparable reaction to eq 13 was included identical to eq 9, with NOH as the intermediate. In these breakdown models (4, 5), the relative rates of the intermediate reacting with NH₄Cl is generally set at 1/10, that of reaction with NHCl₂. NCl₃ and NHCl₂, however, are usually not present together in significant concentrations during breakdown conditions.

Kumar et al. (30) found the reverse reaction of eq 11

$$NCl_3 + B + H_2O \xrightarrow{k_{id}} NHCl_2 + B + HOCl$$  (r1)

to be general base catalyzed, with a rate expression of $r = k_{id}[HB][NCl_3][OH^-]$, where HB denotes a general acid, consistent with the principle of reaction mechanism reversibility. Under our experimental conditions, the shortest half-life of NCl₃ due to r1 occurs at pH 8 and is ~9 h. Because eq 12 proceeds much faster than the hydrolysis of NCl₃, eqs 11 and 12 are the primary determinants of the pseudo-steady-state concentration of NCl₃ under typical chlorination conditions.

Very little appears in the literature regarding the mechanism of NO₃⁻ formation. It generally has been assumed that its formation involves the same initial rate-limiting step as that proposed for N₃⁻ formation, presumably resulting from the fact that all redox reactions are of the same general magnitude past the breakpoint. Pressley et al. (24) showed that, for given Cl⁻/N₃ dose ratios past the
breakpoint, the formation of nitrate increases dramatically from pH 6 to 7, while the increase from pH 7 to 8 is only about half as significant. Given this pH dependence, eq 14 of Table I is proposed. Considerably more evidence is required to either prove or disprove the associated rate expression as the rate-limiting term for NO₃⁻ formation.

The rapid oxidation rate of nitrite ion (NO₂⁻) according to the elementary reaction (35, 36)

\[ \text{HOCI + HNO}_2 \rightarrow \text{Cl}^- + 2\text{H}^+ + \text{NO}_3^- \]  

(r2)

indicates that, under breakpoint conditions, NO₃⁻ can be viewed as a reactive intermediate.

**Model Summary and Solution.** The 14 equations of Table I, the equilibrium reactions e1–e3, and the associated constants constitute the proposed reaction scheme for the chlorination of ammoniacal water under conditions of near-neutral pH (approximately 5–9). This scheme is shown in Figure 2 in a more descriptive manner. All reaction rates are expressed in terms of reactant molar concentrations, including those for hydrogen ion. Note, many of these constants have been determined under similar conditions of ionic strength. The set of six simultaneous differential equations, of NH₃, NH₄⁺, HOCI + OCl⁻, NH₂Cl, NHCl₂, NCl₃, and pH, as functions of time (contained in a subroutine of a FORTRAN program) was solved by the Adams predictor-corrector method of the DGEAR subroutine of IMSL (International Mathematical and Statistical Library). Prior to each call by DGEAR to the subroutine of differential equations, several material balance constraints were updated. These included reevaluation of all equilibrium expressions, including those of the buffer, and calculation of the pseudo-steady-state concentration of the intermediate, I. The change in pH is calculated from the buffer intensity (β), which resulted from both phosphate, ammonia and/or carbonate species and the change in hydrogen ion concentration (13)

\[ \text{d(pH)} = \text{d[H}^+] / \beta \]  

(r3)

During actual experiments, mono- and dibasic sodium phosphate was used to buffer solutions, resulting in pH changes (formation of H⁺) of less than 0.1 unit. The calculated pH drop was always within 0.03 unit of measured values.

Of the 18 individual rate expressions proposed (for phosphate-buffered systems), suitable rate constants for only eqs 12–14 (of Table I) are not known. Recall, eqs 12 and 13 represent empirical pH-dependent reactions, whose rates we may compare to estimated values based on Margerum’s data (ref 34, with data to be submitted for publication). The rate coefficient for eq 14 is determined largely by overall reaction stoichiometry. Our values for these coefficients, reported in Table I, have been determined by comparing model predictions to experimental data under breakpoint conditions as discussed under Results. The program code is available from the authors.

**Experimental Methods.**

**Reagents.** All chemicals were reagent grade. All water was deionized, run through a Millipore Milli-Q system, chlorinated to a free residual of 3–6 mg/L before aging in the dark for 24 h, and dechlorinated by either sunlight or a sunlamp. Stock solutions of mono- or dibasic sodium phosphate were filtered through 0.45-μm filters, followed by chlorinating and dechlorinating as above. Stock aqueous chlorine (Mallinckrodt, sodium hypochlorite) was kept refrigerated and had a consistent titer of 60000 mg/L as Cl₂.

The pH was measured with a Ag/AgCl general purpose pH electrode and a calomel reference electrode calibrated with standard buffer solutions at pH 4, 7, and 10. In all experiments, ionic strength was controlled at 50 mM by addition of NaClO₄. For each experiment, the required amount of NaClO₄ necessary for this was calculated by simultaneously solving the equations for initial conditions of activity coefficients (Davies equation, ref 37), ionic strength (mono- and dibasic sodium phosphate and sodium perchlorate), the acid dissociation of H₂PO₄⁻, the proton condition, and the necessary mass balance equations.

**Procedures.** The speciation and decay of chlorine in ammoniacal aqueous solutions was examined under various initial conditions of pH and Cl/N in batch experiments. Temperature of all reaction solutions was maintained at 25 °C by incubation in either water baths or constant-temperature chambers. Depending upon the initial value of Cl/N, the reaction was followed for either 25 min (breakpoint and transition regions) or 170 h (combined chlorine region).

Each combined chlorine dose reaction experiment was initiated by the slow addition of 10 mL of a 5000 mg/L NaOCl (as Cl₂) solution, dropwise, to a 1 L (total volume each experiment) ammonia solution (containing the phosphate buffer) with rapid mixing on a stirring plate. This solution was then proportioned into smaller flasks, which were then stoppered and incubated in the dark until a portion was sacrificed for analysis.
To investigate the transition and breakpoint dose regions, two calibrated Monostat repeatable pipeters were utilized to quantitatively deliver through a restricted mixing chamber equal volumes of ammonia (containing the phosphate buffer) and chlorine solutions to a reaction vessel. Each experiment consisted of three replicate runs (of combining chlorine–ammonia solutions) in which subsamples were periodically taken for analysis. Chlorine species (HOCl + OCI, NH₂Cl, and NHCl₂), measured by the \( N,N \)-diethyl-p-phenylenediamine (DPD) titrimetric method (38), were determined in this series procedure as follows: In one run, thioacetamide was added to each subsample, allowing for free chlorine determination. In another, free chlorine and monochloramine were titrated together upon addition of 100 µL of a 0.5% solution of KI, and in the third, total oxidant was titrated. Logistically, this procedure allowed for acquisition of several data points over the first few minutes of each experiment and proved to be very reproducible. In the DPD method, samples are buffered to slightly acidic conditions (6.3 < pH < 6.5) with 25 mM phosphate. Small sample volumes were analyzed, such that only 2% of the total buffer during each analysis.
was from the kinetic experiment.

Results

Cl/N < 1. Experimental results are shown in Figure 3 for the slow decay of chloramine solutions under initial conditions of pH = 7.5, 7, or 6.5; Cl/N = 0.25, 0.5, or 0.75; and total phosphate, P= 10 or 20 mM. Also shown in Figure 3 for each experiment are the calculated concentrations of NH₃Cl and NHCl₂ from model simulations, and the initial conditions. Though the model includes several more reactions than our formerly proposed combined chlorine model (9), the calculated results are nearly iden-
tical. This results from the imperceptible contribution of eqs 11 and 14 (those involving HOCl or OCl⁻) to dichloramine loss under conditions where essentially all free chlorine is reacted with ammonia. Calculated concentrations of free chlorine are generally less than 10⁻³ M. Indeed, variation in Cl/N at the same pH (down a column of Figure 3), which results in changes in the pseudo-steady-state free chlorine concentration, results in little change in decay rates.

An increase in P₁ from 10 to 20 mM (rows 2 and 3, respectively) affects the overall rate of NH₂Cl disproportionation. At higher pH, this reaction by and large determines the rate of oxidant loss, as dichloramine is relatively unstable. In experiments with Cl/N = 0.5 at pH ≈ 7.5, 63% of NH₂Cl is lost after 170 h with 10 mM P₁, compared to 70% with 20 mM P₁. This effect of buffer is more fully described in previous papers (8, 27).

Under these conditions, the two reactions limiting or controlling the loss of oxidant species are eqs 5 and 7. At low pH, eq 7 (NHCl₂ decay) is relatively rapid compared to eq 5, and disproportionation controls loss. At high pH, both reactions are significant, as disproportionation (eq 5) limits monochloramine loss, and eq 7 limits dichloramine loss.

Cl/N > 1. Experimental results are shown in Figure 4 for the rapid decay of chlorine species at initial conditions of pH = 8, 7, or 6; Cl/N = 1.25, 1.5, 1.75, or 2.0; P₁ = 10 mM; and total ammonia, N₃ = 0.107 or 0.214 mM. Also shown in Figure 4 for each experiment are the calculated concentrations of HOCl + OCl⁻, NH₂Cl, and NHCl₂ from model simulations, and the initial conditions.

Equations 12–14 of Table I determine not only the relative rates of NO₃⁻ and NCl₄ formation, but also the location of the breakpoint. Because neither of these products was measured, the values of k₅, k₆, k₇, and k₈ were established to adequately predict the location of the breakpoint, hence, the final ratio of chlorine reduced to ammonia oxidized. Also, qualitative consideration was given to Pressley's (24) experiments, in which NO₃⁻/NO₂⁻ and NCl₄ were measured after 2-h contact times under similar conditions but with much higher initial ammonia concentrations (20 mM) and presumably much higher buffer concentrations. Both Pressley's data and calculated results by the explicit inclusion of differential equation on NO₃⁻ and NCl₄ formation within the model show decrease of NCl₄ and increase of NO₃⁻ with increase in pH (20).

The rate of the empirical pH-dependent reaction between NCl₄ and NHCl₂ can be compared to Yin and Margerum's experimental data, in which this reaction was investigated in isolation in solutions containing ammonium. Our empirical constant, k₈, is ≈1 order of magnitude greater than the upper limit placed on this reaction by their data for specific OH⁻ catalysis, and over 1 order of magnitude greater than their measured rate if one assumes catalysis by HPO₄²⁻ only. This implies strong catalysis by another species, presumably OCl⁻, and/or strong ionic strength dependency. Similarly, the value of k₉ is much greater than that determined by Kumar and Margerum (ref 34; to be submitted for publication) for OH⁻-specific catalysis of this reaction. Even at this value, however, this reaction is fairly insignificant because of its relative magnitude to k₈.

An interesting assumption inherent within the model is that NO₃⁻ formation is not general base catalyzed while NCl₄ formation is (eq 11). Although this assumption is mechanistically important, for natural waters, where related carbonate concentrations are low, this assumption may make little difference. Both reactions involve OCl⁻.

Figure 5. Calculated breakpoint surfaces of total chlorine residual at pH 6, 7, and 8. To generate these surfaces, initial values of N₃ = 0.1 mM and P₁ = 10 mM were chosen.

pH and Cl/N dependency is clearly shown in these experiments. At 1.25 < Cl/N < 1.75, residuals of NH₂Cl and NHCl₂ remain after 25 min with no or little free chlorine; further decay will eventually occur over a matter of days

as described previously, or conceivably through the autocatalytic decay of high NHCl2 concentrations at low pH and relatively high Cl/N (9). At Cl/N ≈ 2, the residual oxidant is free chlorine at all pH values, with small amounts of NCl3.

At pH = 8, NHCl2 decays rapidly (through eq 11) at all Cl/N ratios; hence, its formation (eq 3, which is implicitly pH dependent) limits oxidant loss. At pH = 6, NHCl2 formation is rapid (free chlorine is not dissociated), hence, its base-catalyzed decay (eq 11) limits oxidant loss. At the high Cl/N (~2), a stable free chlorine residual is reached most rapidly between these conditions at pH 7.

The stoichiometry of eqs 12 and 13 denotes the formation of free chlorine through decay of combined chlorine species. This is evident in both experiments (N1 = 0.107 and 0.214 mM) at low pH (~6) beyond the breakpoint (Cl/N ~ 2), where NHCl3 accumulates considerably before decaying. At these conditions, both the data and model predictions show this stoichiometry by the occurrence of a minima in the free chlorine concentration at 4–5 min.

Conclusions

The reactions given in Table I, constrained by the associated dissociation equilibria, are shown to be a reasonable model of the reactions resulting from the chlorination of ammoniacal water at conditions of pH and Cl/N applicable to the disinfection of most natural waters. Unlike previous proposed reaction schemes, the model is not constrained by Cl/N. Conceptually, this can be shown through model calculation of “breakpoint surfaces” at various pH values (Figure 5). These graphs are three-dimensional analogues of traditional two-dimensional breakpoint curves that show total oxidant concentration as a function of both time and Cl/N ratio for particular reaction conditions. Although all species concentrations are known, only total oxidant is shown in Figure 5 to avoid confusion. The general shapes of the breakpoint curves at 24 min (total chlorine versus Cl/N) agree favorably with measured curves (from the data, herein, and ref 24). The pH dependence on the general shape of these graphs is determined largely by the pH-dependent rates of NHCl2 formation and decay within the transition region (1 < Cl/N < 1.6).

Finally, despite what is known about this reaction scheme, there is a considerable amount of critical information lacking, particularly information regarding reaction products. In most cases, little quantitative information exists regarding even the amount of N2 recovered, despite the fact it is assumed to be a major product under all conditions. Additional research is necessary to identify all products over wide ranges of reaction conditions. Consideration of temperature dependencies is lacking for most reactions, and finally, more detailed analysis of all redox reactions, which herein have been modeled fairly empirically, is possible.

Registry No. Cl, 7782-50-5; NH4+, 7664-41-7; NH3, 14798-03-9; HOCl, 7790-92-3; NH4Cl, 10599-90-3; NHCl2, 3400-09-7; NCl3, 10025-85-1.

Literature Cited


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