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Reaction Pathways Involved in the Reduction of Monochloramine by Ferrous Iron

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The maintenance of disinfectants in distribution systems is critical to ensure the safety of drinking water. Reduced iron is one type of reactive constituent believed to play a central role in disinfectant loss as the water travels through the pipe. Specifically, reactions involving Fe(II), both in solution and at the pipe–water interface, are felt to be important processes that account for this loss. This work shows that the rate-limiting reactions responsible for the disappearance of monochloramine involve a direct reaction between molecular monochloramine and Fe(II), leading to the formation of the amidogen radical ($\cdot\text{NH}_2$) as a reactive intermediate. In addition, the mechanism was found to be autocatalytic with the ferric oxide precipitate acting to accelerate the overall reduction of monochloramine. A variable stoichiometry was observed for this system, and this was rationalized by accounting for radical scavenging in the reaction scheme.

Introduction

Maintaining the biological and chemical integrity of drinking water while minimizing treatment costs is a primary concern of the drinking water industry. To ensure the safety of drinking water, a disinfectant residual is maintained within water distribution systems. Unfortunately, the oxidants commonly used as disinfectants react with dissolved and solid materials in the distribution system. These reactions not only lead to the loss of the disinfectant residual but may also lead to a variety of water quality problems and customer complaints.

Utilities that have difficulty maintaining free chlorine residuals in their distribution systems often switch to chloramines as secondary disinfectants (1). Strictly speaking, the chloramines include monochloramine (NH_2Cl), dichloramine (NHCl_2), and trichloramine (NCl_3). However, monochloramine is the predominant species under typical water treatment conditions. Monochloramine has the same oxidizing capacity as free chlorine on a chlorine atom basis, but it is a weaker disinfectant (2). As such, it is often possible to maintain chloramine residuals at acceptable levels in distribution systems where it is impossible to sustain a free chlorine residual.

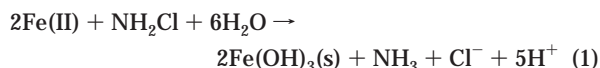
Chloramines do however disappear. Chloramines are unstable at neutral pH values, even without the presence of reactive inorganic or organic substances, and decompose by a complex set of reactions. These reactions ultimately result in the oxidation of ammonia and the reduction of active

chlorine (auto-decomposition). This reactive system has been characterized, and the rate of monochloramine auto-decomposition can be reasonably predicted (3). When oxidizable substances are present, monochloramine loss may occur via reactions with these substances as well as via auto-decomposition. These processes occur concurrently and may involve complex and interrelated pathways.

Reduced iron, produced either by the corrosion of cast iron pipes or initially present in raw waters, is potentially one of the most important reactive constituents in distribution systems. This reduced iron exists within distribution systems in the water phase, adsorbed to deposits present at the pipe wall, or it may be a constituent of one of the reduced oxide species (e.g., Fe_3O_4 or FeCO_3) found in the deposits at the pipe wall (4). Monochloramine therefore has the potential to interact not only with soluble reduced iron but also with reduced iron present either on the surface of the deposits or within the deposits themselves.

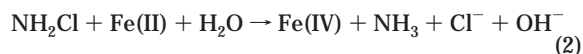
In water treatment, both free chlorine and oxygen are often used to oxidize soluble ferrous iron. It is well-known that the reactions between these oxidants and ferrous iron are sufficiently fast to be economically exploitable. The oxidation of ferrous iron by monochloramine, however, has apparently never been investigated quantitatively. This may be because of the belief that the reactions are too slow to be of economic relevance. Residence times in distribution systems are, however, long enough that reactions between Fe(II) and monochloramine could be an important disinfectant loss pathway.

Previous research has established that when ferrous iron is oxidized by free chlorine that a 2:1 net stoichiometry [Fe(II) oxidized:HOCl reduced] exists (5). In principle, a 2:1 net stoichiometry [Fe(II) oxidized: NH_2Cl reduced] would also exist for the NH_2Cl –Fe(II) system if all of the oxidizing potential of monochloramine oxidizes Fe(II):



This 2:1 stoichiometry could potentially be a result of two different mechanisms. The first is that monochloramine concertedly accepts two electrons in a two-electron transfer reaction, and the second is that two sequential one-electron transfers occur.

Were monochloramine to accept two electrons, it would imply that ferryl ion [Fe(IV)] forms:

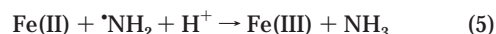
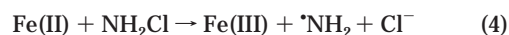


Once formed, Fe(IV) will rapidly oxidize additional Fe(II) (6):



A concerted two-electron transfer pathway involving Fe(IV) in the oxidation of Fe(II) by HOCl and O_3 has previously been established (6), and it is possible that one exists here.

Alternatively, monochloramine could oxidize Fe(II) via two sequential one-electron transfer steps:



In this second mechanism, one atom of monochloramine

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oxidizes one atom of Fe(II) leading to the production of Fe(III), chloride (Cl⁻), and the ammonia radical amidogen (*NH₂).

Not only can the oxidation of Fe(II) occur by more than one reactive pathway, but also the presence of oxidizable nitrogen in monochloramine may potentially lead to the existence of a number of additional reactions. At one extreme, the intermediates formed when Fe(II) is oxidized could react with monochloramine or species involved in monochloramine auto-decomposition. At the other extreme, Fe(II) could simply catalyze monochloramine auto-decomposition and thereby lead to monochloramine loss without Fe(II) oxidation. The role of metal ions as catalysts has been widely reported in the literature (7), and it has been previously shown that monochloramine disproportionation



is a general acid-catalyzed process (3). Additionally, reaction products other than ferric oxide, ammonia, and chloride are possible. Changes in the product speciation would lead to a variety of "apparent" relationships between the amount of Fe(II) oxidized and the amount of monochloramine reduced.

The reactions between ferrous iron and monochloramine may govern the presence of reduced iron and "red-water" in distribution systems when monochloramine is the disinfectant. They may also affect the ammonia loading to the distribution system, which in turn could lead to enhanced nitrification. Lastly, the kinetics could be sufficiently fast enough that monochloramine may be a practical replacement for free chlorine in the oxidation of ferrous iron for waters where disinfection byproduct (DBP) formation is a concern.

This paper reports on experiments conducted to characterize the nature of the rate-limiting reactions between monochloramine and Fe(II). In particular, we wanted to assess the importance of a direct reaction of ferrous iron with molecular monochloramine versus one involving hypochlorous acid produced by monochloramine hydrolysis. Second, we wanted to elucidate the effect of the ferrous oxide product on the kinetics of monochloramine reduction. This work is an important step toward fully understanding the complicated reactions between monochloramine and Fe(II), and it accounts for monochloramine loss, iron oxidation, and perhaps the formation of a number of important products.

Materials and Methods

All experiments were conducted with deionized water produced by a Barnstead Ultro pure water system. A Fisher Scientific model 50 pH meter coupled with an Orion Scientific low ionic strength combination reference/analytical electrode was used for all pH measurements.

Preparation of Monochloramine Solutions. All monochloramine solutions used in these experiments were prepared by diluting a concentrated stock to the desired concentration. This stock was made by adding a predetermined amount of potassium hypochlorite solution to an ammonium sulfate stock (8). The final concentration of monochloramine in the stock was measured using either the DPD-FAS method (9) or via potentiometric titration with phenylarsine oxide (PAO) (8).

Once prepared, the stock was used to produce dilute monochloramine solutions of the same ionic strength and bicarbonate concentration. All experiments were conducted using de-aerated conditions (DO < 1 mg/L). In control experiments, it was found that monochloramine reduction was observed when the solution was saturated with dissolved oxygen. However, to minimize the potential complicating effects of dissolved oxygen on these reactions, the experiments were conducted under de-aerated conditions. At concentrations less than 1 mg/L, dissolved oxygen did not

lead to significant levels of iron oxygenation within the time scale of the Fe(II)–monochloramine reactions.

Experimental Procedure. The experiments were initiated by adding concentrated ferrous sulfate (10 µg/µL) to a sealed 120-mL vial containing 100 mL of monochloramine solution. For the experimental conditions employed in these experiments, volatilization and partitioning of ammonia into the headspace and microbial growth were all assumed to be negligible. The dissolved and total Fe(II) concentration was determined using a modified Ferrozine method (10). Monochloramine was quantified via potentiometric titration with phenylarsine oxide (PAO). This method was used because of the interference of Fe(II)/Fe(III) in the standard DPD/FAS method.

Sequential Spike Experiments. These experiments were conducted using a sealed reactor with an overhead stirrer and a constant CO₂ feed into the headspace. This experimental setup ensured that the oxide particles produced by the sequential spikes were well mixed, and it kept the reaction pH stable. An aliquot of Fe(II) was added to a solution containing a great excess of monochloramine such that an Fe(II) concentration of 0.0895 mM was obtained, and the reaction kinetics were followed by measuring the loss of Fe(II) from solution. Once the Fe(II) from the initial spike was oxidized, the solution was respiked with Fe(II), and its oxidation kinetics were observed. This process was then repeated.

Stoichiometry Experiments. Experiments to determine the stoichiometry of the NH₂Cl–Fe(II) system were conducted with either Fe(II) in excess or with monochloramine in excess. The reactions were allowed to proceed to completion (e.g., either all of the ferrous iron was oxidized or all of the monochloramine was reduced), and then the final monochloramine or final ferrous iron concentration was measured. The apparent stoichiometry (= Δ[Fe(II)]/Δ[NH₂Cl]) was then calculated.

Product Measurement. Experiments were conducted in which chloride, nitrate, ammonia, and labeled nitrogen gas production were measured. In these experiments, (15NH₄)₂SO₄ was used as the ammonia source. Labeled nitrogen gas (15N₂) was measured using the procedure of Vikesland et al. (11). Anion and cation analyses were conducted according to published procedures (12).

Electron Spin Resonance. Electron spin resonance experiments were conducted using a Bruker ESP-300 electron spin resonance spectrometer. This spectrometer was operated at 9.77 GHz with a 100 kHz modulation frequency. Other spectrometer settings were as follows: gain, 2.5 × 10⁵; modulation amplitude, 0.144 G; microwave power, 39.9 mW; time constant, 40.96 ms; sweep rate, 80 G/84 s; sweep width, 80 G. Radical production was measured using spin trapping techniques (13).

All spin trap experiments used 50 mM 5,5-dimethylpyrrolidine-*N*-oxide (DMPO) as the spin trap. All reactions were carried out at room temperature in a flat quartz cell. The ESR experiments were conducted by mixing DMPO with a phosphate-buffered or unbuffered monochloramine solution and then adding Fe(II) to initiate the experiment. The time between experiment initiation and the onset of ESR scanning was kept to a minimum (<2 min).

The effect of dissolved oxygen on the radical formation process was studied by conducting experiments in both aerated and de-aerated solutions. The de-aerated samples were produced by sparging the solution with an argon gas stream for at least 10 min prior to adding ferrous iron. These experiments showed that the presence of dissolved oxygen did not effect radical formation or measurement.

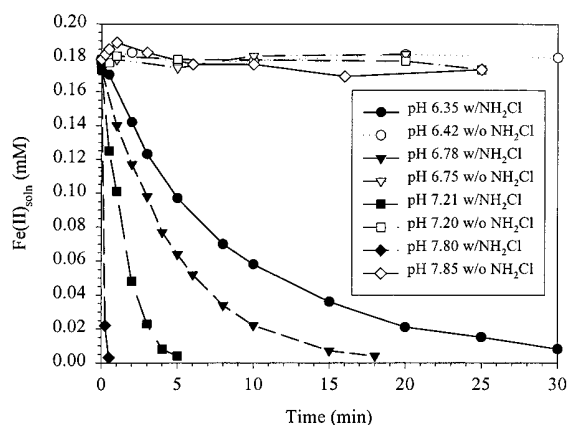


FIGURE 1. Comparison of iron oxidation rates in the presence and absence of monochloramine for four different pH values. $[\text{NH}_2\text{Cl}]_0 = 0.704 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.179 \text{ mM}$, $\mu = 0.1 \text{ M}$, $C_{\text{T,CO}_3} = 0.006 \text{ M}$, $\text{DO} < 1 \text{ mg/L}$, 25°C .

Reaction Characterization

In a de-aerated solution without monochloramine present, it was observed that Fe(II) is stable (Figure 1). When monochloramine is present, however, the Fe(II) concentration decreases rapidly, and a ferric oxide precipitate is produced. As Fe(II) is oxidized, a simultaneous decrease in the monochloramine concentration is observed. This decrease indicates that monochloramine is reduced by Fe(II).

In addition, it was observed that increases in pH accelerate the apparent rate of the monochloramine–ferrous iron reactions (Figure 1). This rate acceleration implies that the hydroxide ion concentration may affect the reaction kinetics. Previous work has shown that increases in pH greatly accelerate the rate at which ferrous iron is oxidized by oxygen (14–16). The interpretation of and the implications of this rate acceleration on the reaction kinetics will be addressed in a future paper.

Effect of Ammonia on Reaction Rates. The measured loss of Fe(II) in monochloramine solutions indicates that ferrous iron is oxidized when monochloramine is present. This oxidation could be attributable both to a direct reaction with monochloramine and to a simultaneous reaction with hypochlorous acid produced by monochloramine hydrolysis (17):



If hypochlorous acid is assumed to be in equilibrium with monochloramine, its concentration should be inversely proportional to the ammonia concentration. Therefore, increasing the ammonia concentration by 10-fold will decrease the hypochlorous acid concentration by 10-fold. The concentration of hypochlorous acid is fixed by the concentrations of monochloramine and ammonia [e.g., the molar ratio of chlorine to nitrogen (Cl/N)]:

$$[\text{HOCl}] = K_{\text{eq}} \frac{[\text{NH}_2\text{Cl}]}{[\text{NH}_3]} \quad (8)$$

This relationship facilitates the evaluation of the role of hypochlorous acid in ferrous iron oxidation. In principle, if hypochlorous acid plays an important role, the maximum effect would be expected at the highest Cl/N molar ratios.

The relative contribution of each pathway was investigated using a fixed monochloramine concentration but variable ammonia levels. A monochloramine solution with a Cl/N molar ratio of 0.5:1 was produced and allowed to mix

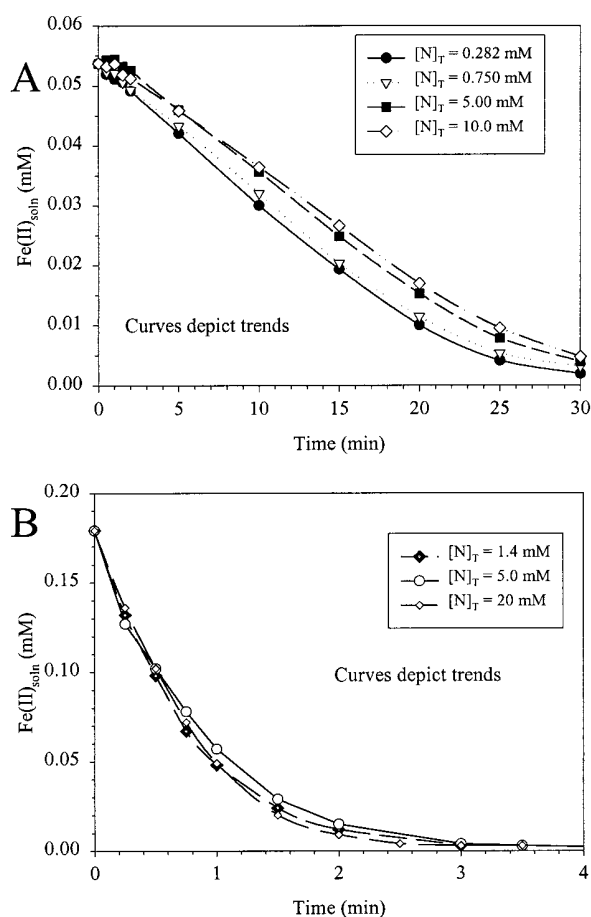


FIGURE 2. Effect of ammonia concentration on Fe(II) oxidation at (A) pH 7.00, $[\text{NH}_2\text{Cl}]_0 = 0.141 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.0537 \text{ mM}$ and (B) pH 7.35, $[\text{NH}_2\text{Cl}]_0 = 0.704 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.180 \text{ mM}$, $\mu = 0.1 \text{ M}$ (NaClO_4), $C_{\text{T,CO}_3} = 0.0104 \text{ M}$, 25°C , $\text{DO} < 1 \text{ mg/L}$. $[\text{N}]_{\text{T}}$ (total nitrogen) = $[\text{NH}_3] + [\text{NH}_4^+] + [\text{NH}_2\text{Cl}]$.

completely. Additional ammonia was then added after the monochloramine had formed, thereby varying the Cl/N ratio.

Increasing the ammonia concentration by both 35-fold (Figure 2A) and 14-fold (Figure 2B) did not significantly affect the rate of iron oxidation. It can therefore be asserted that a direct reaction between monochloramine and ferrous iron governs under these conditions. Were hypochlorous acid involved, one would expect the reaction to be significantly faster at low ammonia concentrations, where more hypochlorous acid is present, than at higher ammonia concentrations. Since this was not observed, it is clear that a direct reaction between monochloramine and ferrous iron is the dominant reactive pathway under these conditions.

Effect of Iron Oxide Product. When Fe(II) is oxidized by monochloramine, an iron oxide precipitate is produced. Previous work examining the oxidation of Fe(II) by oxygen has shown that the oxide precipitate acts to accelerate the overall Fe(II) oxidation rate through the formation of Fe(II) surface complexes (18). A similar mechanism could describe the oxidation of Fe(II) by monochloramine. If this were to occur, the overall reaction would be considered autocatalytic if the rate of the surface reaction exceeds that of the aqueous-phase reaction.

A sequential spike experiment was conducted to determine if the ferric oxide precipitate accelerates the NH_2Cl –Fe(II) reactions. By sequentially spiking Fe(II) to a concentrated monochloramine solution, it is possible to qualitatively observe the effect of stepwise increases in the ferric oxide concentration on the reaction rate. The observed reaction

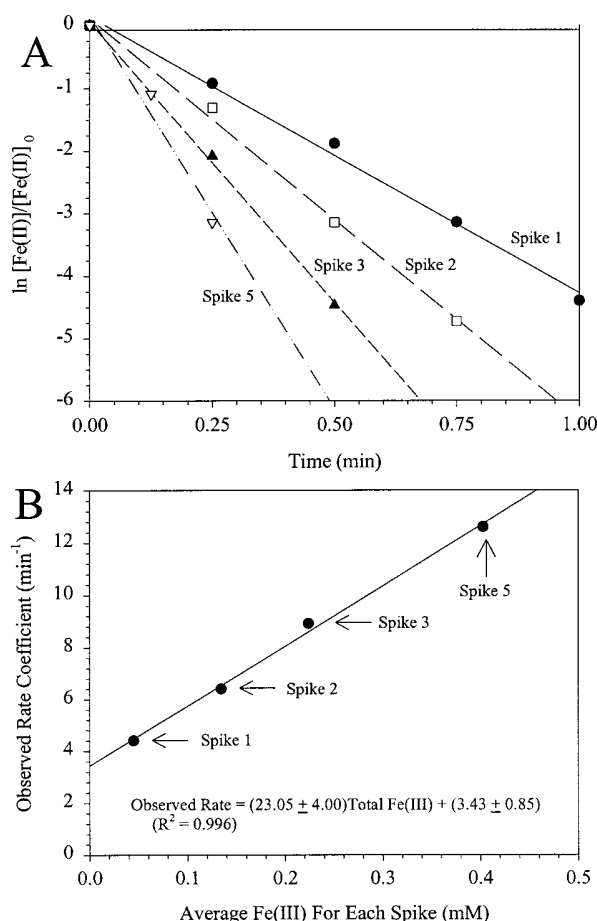


FIGURE 3. Effect of sequential spikes on the Fe(II) oxidation rate. (A) First-order approximation. (B) Observed rate coefficients versus Fe(III) concentration. $[NH_2Cl]_0 = 0.980$ mM, $[Fe(II)]_0 = 0.0895$ mM added with each spike, $pH_0 = 7.354$, $C_{T,CO_2} = 0.006$ M, $DO < 1.0$ mg/L. Average Fe(III) concentration for each spike = the amount of Fe(III) present when the sample was spiked plus one-half the amount of Fe(II) added with each spike. Errors in slope and intercept are based on 95% confidence level. Data from spike 4 is omitted due to an experimental error in the measurement of Fe(II).

rate increases with each spike (Figure 3A), thereby implying that the reaction is catalyzed by the iron oxide precipitate.

Apparent rate coefficients were determined for each spike using a pseudo-first-order approximation. These rate coefficients reflect both the aqueous-phase as well as the solid-phase reactions. The observed rate increases from 4.41 min^{-1} for the first spike to 12.6 min^{-1} for the fifth spike. Because the ferric iron concentration is not constant for all of the spikes, the use of a first-order relationship cannot be rigorously justified, and these rate coefficients only provide a rough approximation of the true rates. Nevertheless, when these rate coefficients are plotted versus the average Fe(III) concentration present for each spike, a linear relationship results (Figure 3B). This semiquantitative linear relationship implies that the overall reaction rate is proportional to the ferric iron concentration.

The rate acceleration observed for each spike is most likely due to a combination of factors. Primarily this acceleration is a result of surface-mediated reactions, as evidenced by enhanced precipitate formation; however, some of the observed acceleration may be due to mass transfer limitations associated with transporting Fe(II) to the oxide surface. Were surface Fe(II) to not react with monochloramine, there would not have been an observed decrease in the monochloramine

concentration nor enhanced precipitate formation for the latter spikes. These observations indicate that reactions involving adsorbed Fe(II) need to be considered when examining the fate of monochloramine in this system.

Reaction Intermediates. In the Introduction, it was hypothesized that two different mechanisms for Fe(II) oxidation by monochloramine could exist. One mechanism, involving two sequential one-electron transfers, results in the formation of the radical amidogen ($\cdot NH_2$). To see if this radical does form, a series of electron spin resonance (ESR) experiments were conducted.

When ferrous iron is added to a buffered monochloramine solution in the presence of the spin trap DMPO, a strong ESR signal is observed (Figure 4A). Upon comparing this ESR signal to a theoretical spectrum for amidogen ($\cdot NH_2$) (Figure 4B), it can be concluded that the $NH_2Cl-Fe(II)$ reactions do lead to the formation of amidogen. The identity of this radical was further shown by using unbuffered solutions, adjusting the solvent (switching from H_2O to D_2O), and using ^{15}N -labeled monochloramine (8).

The formation of amidogen suggests that the two sequential one-electron transfer mechanism (eqs 4 and 5) occurs in this system. Once produced, amidogen may however react with species other than ferrous iron. If so, this would lead to apparent stoichiometries other than 2:1.

Reaction Stoichiometry. The apparent stoichiometry ($= \Delta[Fe(II)]/\Delta[NH_2Cl]$) for the $NH_2Cl-Fe(II)$ reactions at pH 7.08 is not 2:1, but is in fact much closer to 1:1 (Figure 5). The approximate 1:1 stoichiometry was obtained regardless of whether iron or monochloramine was present in excess. This observation has several implications on the mechanistic interpretation of the reactions occurring in this system. A constant stoichiometry for various Fe(II)/ NH_2Cl ratios suggests a redox reaction that is not dependent on the presence of either excess iron or monochloramine. Conversely, if both approaches yielded different apparent stoichiometries, it might indicate that a catalytic process involving Fe(II) was occurring when monochloramine was present in excess.

Control studies conducted to compare the measured apparent stoichiometry of the $HOCl-Fe(II)$ system (known to be 2:1) to the measured apparent stoichiometry of the $NH_2Cl-Fe(II)$ system showed that the apparent 1:1 stoichiometry is not an analytical artifact (8). Therefore, the observation that the apparent stoichiometry of the $NH_2Cl-Fe(II)$ system is less than 2:1 implies that part of the oxidizing potential of monochloramine does not go toward Fe(II) oxidation.

The effect of pH on the apparent stoichiometry was examined, and it was observed that the apparent stoichiometry decreases with a decrease in pH (Figure 6). The stoichiometry varies from approximately 1:1 at pH 6.8 to approximately 2:1 for pH values greater than 9.21. Presumably the observed stoichiometry is a function of pH because reactions that lead to the loss of oxidizing potential, but not to Fe(II) oxidation, are occurring simultaneous to those that lead to Fe(II) oxidation. At high pH values, these competitive reactions are slow enough that the theoretical stoichiometry of 2:1 is observed. As the pH is decreased, however, the relative rate of the competitive reactions increases such that, for a given amount of Fe(II) oxidized, the amount of monochloramine reduced increases.

A series of experiments were conducted in an effort to assess which processes could be responsible for the observed pH dependence of the apparent stoichiometry. These experiments examined the effects of changes in the solids concentration, the ammonia concentration, and the bicarbonate concentration on the apparent stoichiometry. The relative importance of each of these species is affected by the solution pH, and they could therefore be responsible for the observed pH effect. Neither changes in the solids

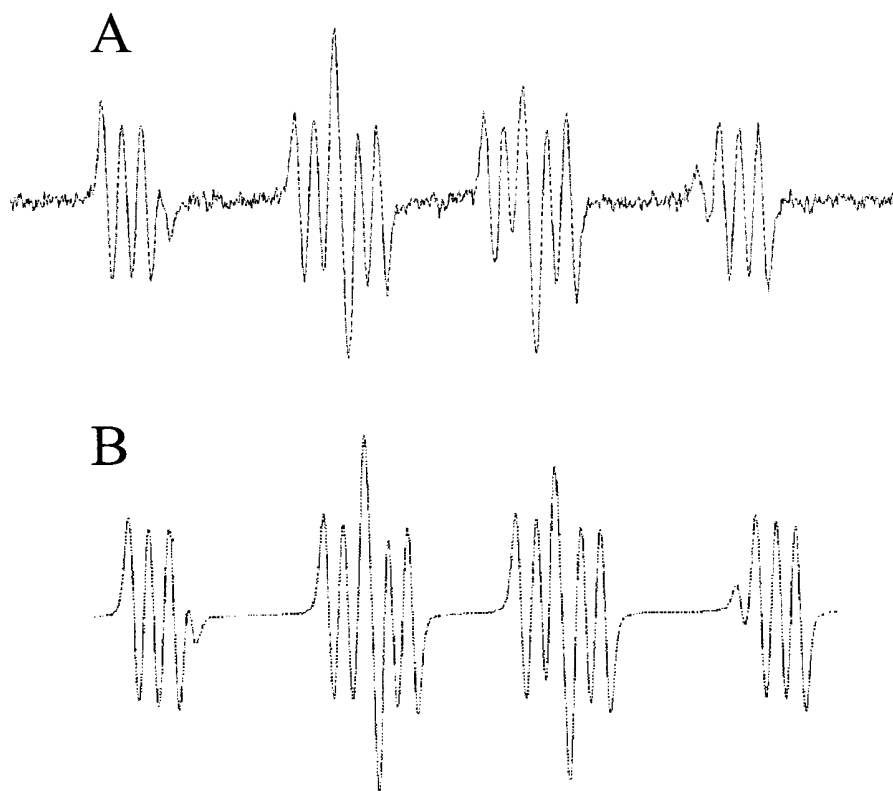


FIGURE 4. (A) Experimental ESR spectrum. (B) Simulated ESR spectrum. $[\text{NH}_2\text{Cl}]_0 = 0.89 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.5 \text{ mM}$, $\text{DMPO} = 50 \text{ mM}$, $\text{pH}_0 = 8$, $\text{pH}_t = 7.7$.

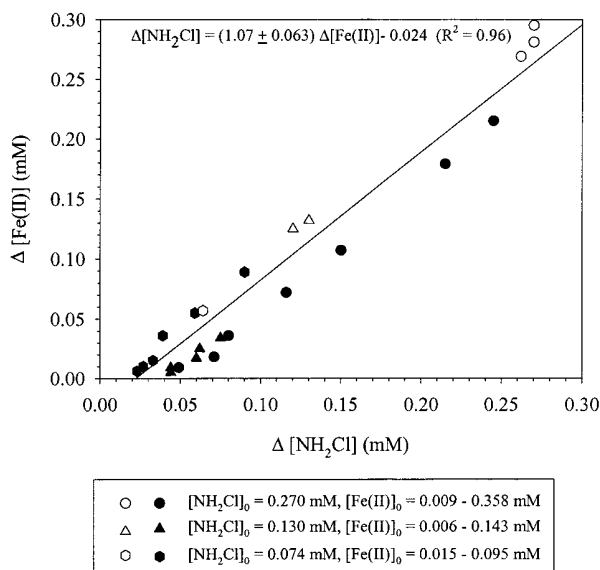


FIGURE 5. Apparent stoichiometry of the monochloramine–ferrous iron reactions. Filled symbols indicate experiments with an initial excess of monochloramine, and open symbols indicate an initial excess of ferrous iron. $\text{DO} < 1 \text{ mg/L}$, $\text{Cl/N} = 0.2$, $C_{\text{T,CO}_3} = 0.006 \text{ M}$, $\text{pH} = 7.24$, $T = 25^\circ\text{C}$. Line is linear regression based on least-squares fit. Error in slope corresponds to 95% confidence interval.

concentration nor changes in the ammonia concentration had any discernible effect on the apparent stoichiometry (8). Because changes in the solids concentration did not affect the apparent stoichiometry, it can be asserted that the solution and surface-mediated reactions have the same stoichiometry. There was, however, a noticeable decrease in the apparent stoichiometry as the bicarbonate concentration was increased for a given pH (Figure 7). This decrease implies

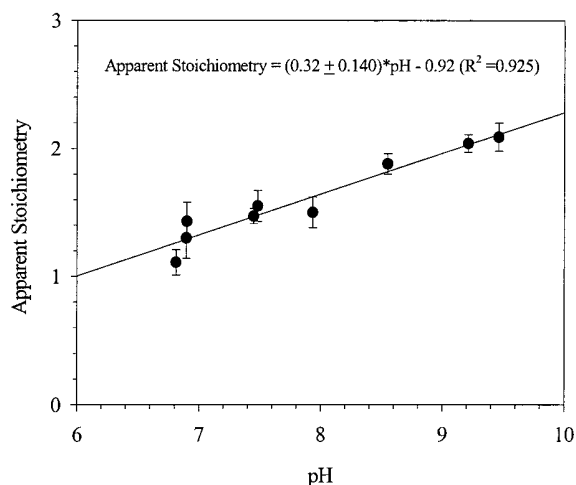


FIGURE 6. Effect of pH on apparent stoichiometry of NH_2Cl – Fe(II) reactions. $[\text{NH}_2\text{Cl}]_0 \approx 0.4 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.0\text{--}0.4 \text{ mM}$, $C_{\text{T,CO}_3} = 0.006 \text{ M}$, $\text{DO} < 1 \text{ mg/L}$. Apparent stoichiometry = $\Delta[\text{Fe(II)}]/\Delta[\text{NH}_2\text{Cl}]$. Error bars represent 95% confidence level of stoichiometric determination.

that bicarbonate may play a role in the changing apparent stoichiometry with pH. This role will be fully addressed at the end of this paper.

Monochloramine Decomposition Product Measurement. Mass balance experiments were conducted in which nitrogen gas, nitrate, nitrite, chloride, and ammonia production were accounted for. These reaction products were measured at different initial pH values to investigate the nature of the competitive reactions that occur in this system. On the basis of a reaction stoichiometry of 2:1, corresponding to all of the oxidizing capacity of monochloramine going toward Fe(II) oxidation, 1 mole of ammonia will be produced for each mole of monochloramine reduced (eq 1). When the

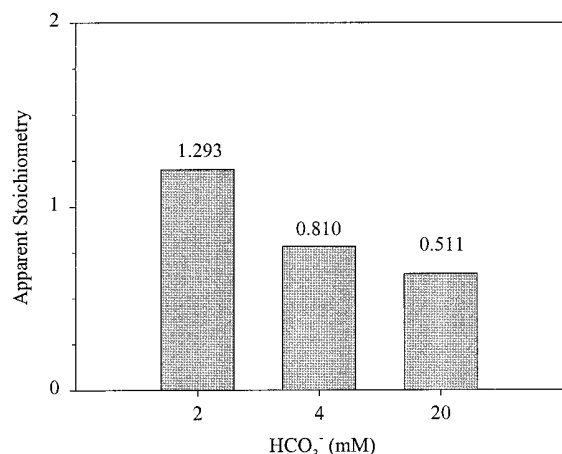


FIGURE 7. Effect of changes in the bicarbonate concentration on the apparent reaction stoichiometry. $[\text{NH}_2\text{Cl}]_0 = 0.142 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.0398 \text{ mM}$, $\text{pH} = 7.05$, $\text{DO} < 1 \text{ mg/L}$. Apparent stoichiometry = $\Delta[\text{Fe(II)}]/\Delta[\text{NH}_2\text{Cl}]$.

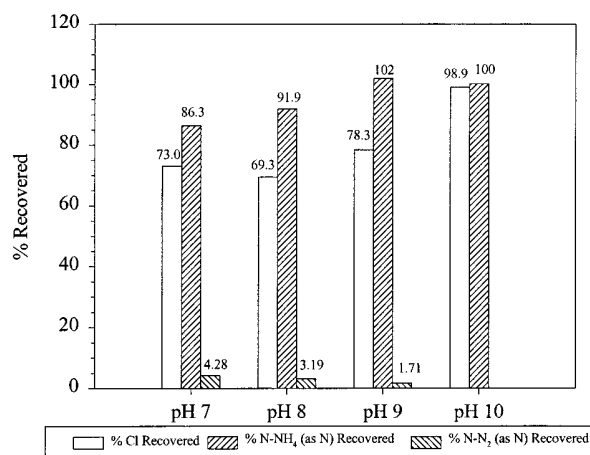
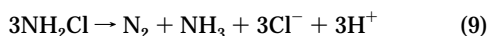


FIGURE 8. Mass balance as a function of solution pH. $[\text{NH}_2\text{Cl}]_0 = 0.5 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.376 \text{ mM}$, $\text{Cl/N} = 0.5$, $C_{\text{T,CO}_3} = 0.006 \text{ M}$, $\text{DO} < 1.0 \text{ mg/L}$. Recovery % = $(\Delta\text{species}/\Delta[\text{NH}_2\text{Cl}] \times 100)$ where $\Delta\text{species}$ refers to change in species of interest.

reaction stoichiometry is less than 2:1, the nature of the reaction products may differ. For example, nitrogen gas is the dominant oxidized nitrogen product when monochloramine undergoes auto-decomposition (3):



Examining the nitrogenous product distribution for a given set of conditions may provide insight into the types of processes responsible for the observed variable stoichiometry.

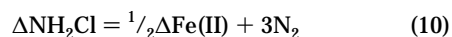
Over the pH range of 7–10, it was found that ammonia is the dominant nitrogenous product (Figure 8). For all tested conditions, monochloramine nitrogen recovery as ammonia is greater than 86%. No nitrate or nitrite formation was observed at any pH. However, it was found that as the pH is decreased from 10 to 7 small amounts of nitrogen gas are produced. At pH 9 and 10, there is little nitrogen gas formed (<1.71% of monochloramine nitrogen), but as the pH approaches 7, more nitrogen gas is produced (3.19% of monochloramine nitrogen at pH 8 and 4.28% of monochloramine nitrogen at pH 7). In control reactors, which did not contain ferrous iron, there was no detectable nitrogen gas production at any pH. This indicates that, over the time frame of the measurements, no nitrogen gas forms via the normally occurring (e.g., noncatalyzed) auto-decomposition pathway.

TABLE 1. Redox Balance for $[\text{NH}_2\text{Cl}]_0 = 0.5 \text{ mM}$; $[\text{Fe(II)}]_0 = 0.376 \text{ mM}$, $\text{Cl/N} = 0.5$, $C_{\text{T,CO}_3} = 0.006 \text{ M}$, $\text{DO} < 1.0 \text{ mg/L}$ ^a

pH	$\Delta\text{NH}_2\text{Cl}$ (mM)	$\Delta\text{Fe(II)}$ (mM)	N_2 (mM)	Σ oxidized species (mequiv)	oxidized species recovery (%)
7	0.365 (± 0.009)	0.376	0.0078 (± 0.0003)	0.211	58
8	0.196 (± 0.010)	0.376	0.0047 (± 0.0005)	0.202	68
9	0.243 (± 0.017)	0.376	0.0021 (± 0.0000)	0.194	80
10	0.215 (± 0.007)	0.376	0.0000 (± 0.0000)	0.188	87

^a Errors are the standard deviation of replicate measurements. Σ oxidized species = $1/2\Delta\text{Fe(II)} + 3\text{N}_2$ (in mequiv).

The formation of nitrogen gas is of potential mechanistic importance since it suggests that Fe(II) could be catalyzing monochloramine auto-decomposition, and this would increase the apparent monochloramine demand in the presence of reduced iron. As discussed earlier, the potential catalytic role of dissolved metal ions has been well established. A redox balance (eq 10) that equates the loss of monochloramine to the number of electrons involved in the oxidation of Fe(II) and in the formation of nitrogen gas was used to compare the extent of electron flow going toward nitrogen gas formation versus that going toward iron oxidation:



By equating the observed production of oxidized products (normalized to equivalences) to monochloramine decay, it is possible to gain insight into the reaction pathways. In this manner, it is possible to quantitatively assess whether the observed changes in the apparent stoichiometry with pH can be accounted for by the formation of nitrogen gas.

On the basis of this redox balance, the measured production of nitrogen gas is generally much smaller than can account for the loss of monochloramine in excess of that involved in the oxidation of Fe(II) (Table 1). For pH 9 and 10, the oxidized product recovery is greater than 80%, while for pH 7 and 8 the recovery is only 58–68%.

The low oxidized product recovery at the lower pH values indicates that unidentified oxidized species form at low pH values. The comparatively high recovery of ammonia indicates that these unidentified products may not contain nitrogen, although this conclusion is not certain as a high oxidation state product could be produced at extremely low concentrations. The formation of unknown oxidized products at low pH values may explain why the apparent stoichiometry changes as a function of the solution pH. In addition, the low oxidized product recovery indicates that if Fe(II) does catalyze monochloramine decomposition that it is only a minor reactive pathway.

Reaction Scheme

On the basis of the data presented in this paper, it is clear that the NH_2Cl –Fe(II) system is quite complex. The reaction characteristics elucidated thus far were synthesized into a mechanistic description that is consistent with the known chemistry of the reactive species involved. This simple mechanism is depicted in Figure 9 and the steps involved in its development are described in the following paragraphs.

The oxidation of Fe(II) by monochloramine occurs both in solution and at the surface of the ferric oxide precipitate produced by the solution-phase reaction. A 2:1 [Fe(II) oxidized: NH_2Cl reduced] stoichiometry was initially predicted. It was found, however, that the apparent stoichiometry is not necessarily 2:1 but changes as a function of the solution

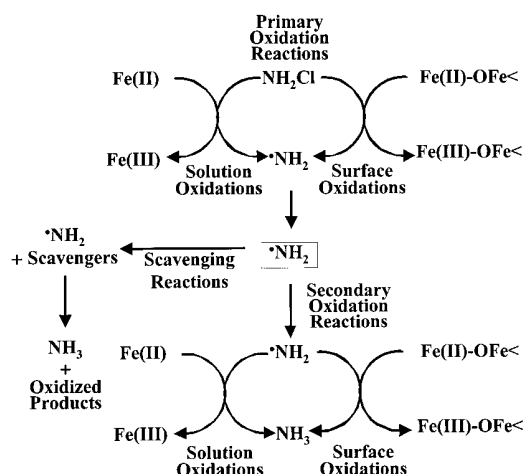
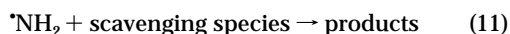


FIGURE 9. Hypothetical reaction scheme for monochloramine reduction in the presence of ferrous iron.

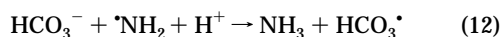
pH. In addition, it was found that the radical species amidogen ($\cdot\text{NH}_2$) is produced as an intermediate in these reactions. It is hypothesized that the ultimate disposition of the amidogen radical affects the apparent stoichiometry of the NH_2Cl – $\text{Fe}(\text{II})$ reactions.

As discussed earlier, a 2:1 stoichiometry will be observed if amidogen reacts with $\text{Fe}(\text{II})$ (eq 5). Conversely, were amidogen to react with other species (eq 11) and the reaction products do not oxidize $\text{Fe}(\text{II})$, an apparent



stoichiometry less than 2:1 will be observed. These “scavenging” reactions would lead to an apparent observed decrease in the oxidizing potential of monochloramine since only half of its oxidizing capability goes toward $\text{Fe}(\text{II})$ oxidation.

One possibly important group of radical scavengers present in this system are the carbonate species. It was experimentally observed that increases in the bicarbonate concentration lead to a decrease in the apparent stoichiometry. This decrease could be a result of the action of bicarbonate as either a general acid catalyst or as a radical scavenger. In addition to its ability to form complexes with $\text{Fe}(\text{II})$ (15), bicarbonate can not only act as a general acid catalyst that will increase the rate of monochloramine auto-decomposition (3) but can also take part in radical reactions. Bicarbonate readily reacts with amidogen (19):



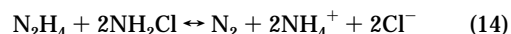
If this reaction occurs and HCO_3^* preferentially reacts with solution components other than $\text{Fe}(\text{II})$, the apparent stoichiometry would differ from 2:1. The existence of this reaction is consistent with the oxidized product deficit at the lower pH values. If HCO_3^* reacts to form oxidized products other than those tested for in the mass balance studies, a deficit in the oxidized product balance would occur. In addition, the formation of ammonia via reaction 12 is consistent with the observed recovery of most of monochloramine nitrogen as ammonia.

Another potential radical scavenging mechanism would be a radical–radical reaction leading to the production of hydrazine (19):



Were hydrazine to form, it would rapidly react with

monochloramine (eq 14), leading to additional disinfectant loss (20):



If this were to occur, it would be consistent with the observed production of N_2 . The amount of N_2 measured in the mass balance experiments was quite small and could not be explained via $\text{Fe}(\text{II})$ -catalyzed monochloramine decomposition. However, considering the concentrations of the other reactive species present in this system [e.g., $\text{Fe}(\text{II})$ and HCO_3^-], one would expect the yield from a radical–radical recombination reaction to be very small.

In summary, a mechanism that describes the rate-limiting reactions that occur between $\text{Fe}(\text{II})$ and monochloramine was developed. The rate-limiting aqueous-phase reaction was identified to be a direct reaction between $\text{Fe}(\text{II})$ and monochloramine that produces a ferric iron precipitate and an amidogen radical ($\cdot\text{NH}_2$). Presumably, the ferric oxide precipitate then acts to accelerate the overall reaction rate by allowing highly reactive $\text{Fe}(\text{II})$ surface complexes to form.

The production of the amidogen radical is of interest as it may be involved in reactions with other constituents in distribution systems, possibly giving rise to products of some health concern. As will be shown in our forthcoming work, by accounting for the disposition of amidogen, the mechanism shown in Figure 9 is able to quantitatively account for the experimental observations discussed in this paper.

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