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THE CHEMISTRY OF COMBINED RESIDUAL CHLORINATION

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The Chemistry of Combined

Residual Chlorination

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INTRODUCTION

The decay of the combined chlorine residual was investigated in this work. Recent concerns about the formation of undesirable compounds such as chloroform with free residual chlorination have focused attention on the alternative use of combined residual chlorination. This work investigates the applicability of reactions proposed to describe the transformations and decay of the combined residual with time. The reactions presently accepted proved in some instances to be inadequate to explain the results observed, with modifications being proposed.

PROCEDURES

Sodium hypochlorite was added to buffered solutions of ammonia with the chlorine residual being monitored over periods extending up to 10 days. The reaction was studied at four initial concentrations of hypochlorite of 100, 50, 25 and 10 mg/L as Cl₂ with molar application ratios of chlorine to ammonia, defined herein as M ratios, of 0.90, 0.50, 0.25 and 0.05 at each hypochlorite dose. Sixty-eight experiments were conducted at the pH of 6.6 and 7.2.

The NaOCl solution was prepared by sparging research grade chlorine gas into a dilute NaOH solution. Phosphate salts were used for buffering and KClO₄ for maintenance of the ionic strength at µ = 0.05. After the addition in batch with vigorous mixing of hypochlorite to the solution containing all other components, the test volumes were decanted into 200 mL glass stoppered flasks and stored in the dark at 25 ± 1°C. Factors accounting for changes in pH with time were used in the kinetic constants described later.

The combined chlorine residuals were monitored with the DPD Titrimetric procedure, with some of the results checked with UV scans for reaction times up to 72
hours. The molar absorptivities used for the wavelengths of 231 and 295 nm were in agreement with published data\(^1-2-3\). Free chlorine and nitrogen trichloride were never detected at any time with either method of analysis, and the total oxidant contained in the first sample collected always equaled \((\pm 3\%)\) the total oxidant added to the experiments.

The presence of contaminants, specially bromine, were considered because the reactions studied are very slow. Such bromine effects were believed to be minor because approximate calculations based on available information\(^4-5\) indicate that a rather severe bromine contamination is necessary to affect the results significantly.

The DPD and the UV scan results for monochloramine and dichloramine were nearly identical at a pH of 6.6. The UV scans did give higher concentrations of monochloramine after several hours at the pH of 7.2 with the disagreement increasing with reaction time. The nature of this difference has not yet been ascertained but it could be caused by the oxidation of a small fraction of the \(\text{NH}_3-N\) to either \(\text{NO}_2^-\) or \(\text{NO}_3^-\).

RESULTS AND DISCUSSION

The continuous decay of monochloramine together with the establishment of a rather flat peak followed by a decay in dichloramine were observed in all of the experiments at the pH of 6.6. See Fig.1.

The occurrence of several important simultaneous reactions precluded the use of conventional methods of analysis such as the initial rate method. However, at low M ratios monochloramine disappearance could be described well with a second-order reaction. This overall second-order rate decreased with larger ammonia concentrations, especially at the pH of 7.2. Finally, it was commonly observed that the concentration of dichloramine beyond the peak was more or less independent of the ammonia
concentration as shown in Fig. 2.

**Reaction Modeling**

The general approach used was first to propose a logical reaction scheme and then to integrate numerically the resulting simultaneous differential equations. The rate constants were subsequently adjusted and the reaction scheme modified. The concentration of NH$_3$—N was obtained by computation based on the assumption that N$_2$ was the only end product of the ammonia nitrogen oxidation. This is supported by results of separate experiments not discussed herein$^6$ which indicate that the N$_2$ end product fits the observed stoichiometry of the Cl$_2$/NH$_3$ redox system.

The well studied rate constants for reactions 1 through 4 listed below could not be checked using batch procedures. The rate expressions proposed by Gray *et al.*$^3$ at 25°C were used first in the numerical integration, with the equilibrium acid dissociation constants for HOCl, NH$_4^+$ and NH$_3$Cl$^+$ at 25°C being

\[ K_A = 10^{-7.44}, \quad K_B = 10^{-9.39}, \quad \text{and} \quad K_C = 28, \quad \text{respectively}. \]

\[ \begin{align*}
\text{NH}_3 + \text{HOCl} &\rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad k_1 = 10^{10} \frac{L}{\text{mole hr}} \\
\text{NH}_2\text{Cl} + \text{H}_2\text{O} &\rightarrow \text{NH}_3 + \text{HOCl} \quad k_2 = 0.070 \quad \text{hr}^{-1} \\
\text{NH}_2\text{Cl} + \text{HOCl} &\rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \quad k_3 = 5.5 \times 10^5 \frac{L}{\text{mole hr}} \\
\text{NHCl}_2 + \text{H}_2\text{O} &\rightarrow \text{NH}_2\text{Cl} + \text{HOCl} \quad k_4 = 0.002 \quad \text{hr}^{-1}
\end{align*} \]

It appears that all of these reactions can become significant in combined residual chlorination at neutral pH values.
Reaction 5 shown below was first proposed by Granstrom\(^1\) in a slightly different form. An assumed equilibrium expression \([\text{[NH}_2\text{Cl]}^2/\text{[NHCl]}_2\text{[NH}_3\text{]}]\) was the basis of the proposed existence of reaction 6, with the rate constants shown being those reported by Gray and co—workers\(^3\)

\[
\text{NH}_3\text{Cl}^+ + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_4^+ \quad k_5 = 3.5 \times 10^6 \quad \frac{L}{\text{mole hr}} \quad (5)
\]

\[
\text{NH}_4^+ + \text{NHCl}_2 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_3\text{Cl}^+ \quad k_6 = 23.0 \quad \frac{L}{\text{mole hr}} \quad (6)
\]

The redox reactions employed in the first reaction scheme are numbered 7, 8 and 9 below. They are based on the work of Wei\(^7\), with \(I\) standing for an intermediate species and \(P\) for the sum of the end products (\(\text{N}_2,\text{HCl, H}_2\text{O}\)). The rate constant shown for reaction 7 was based on the work of Morris et al.\(^8\) with the constant being pH dependent in accord with their observations. The value of \(k_7\) has been modified somewhat to account for our results. The rate constants for reactions 8 and 9 were set arbitrarily to maintain a very small concentration of \(I\) at all times\(^7\)–\(^9\), and to yield the proper ratio of monochloramine to dichloramine after long contact times.

\[
\text{NHCl}_2 \rightarrow I \quad \text{(slow)} \quad k_7 = [5.5 \times 10^{-9}] / [\text{H}^+] \quad \text{hr}^{-1} \quad (7)
\]

\[
I + \text{NH}_2\text{Cl} \rightarrow P \quad \text{(very fast)} \quad (8)
\]

\[
I + \text{NHCl}_2 \rightarrow P + \text{HOCI} \quad \text{(very fast)} \quad (9)
\]

The results of the reaction scheme above compared poorly with the experimental data. The rate of reaction 6 was obviously much too large. At the low \(M\) ratios in particular, the model was unable to predict the time and magnitude of the peak
dichloramine concentration. In addition, the numerical calculations at such conditions demonstrated that the concentrations of NH₂Cl generally would be governed by an equilibrium expression of the type \([\text{[NH}_2\text{Cl]}^2/\text{[NHCl}_2] \cdot \text{[NH}_3]\] past the peak in dichloramine. Commonly, no such relationship was evidenced with the results of this study. Finally, the computer simulations at pH values of 3.5 to 5.0 and M ratios larger than 0.50 indicated that the distribution of NH₂Cl and NHCl₂ was essentially unaffected by the inclusion of reaction 6.

The model results without reaction 6 were substantially better, especially when the peak dichloramine concentration was less than approximately 2 to 3×10⁻⁵ molar as shown in Fig.3. The predicted peak in dichloramine was generally too great, however, for peak concentrations in excess of approximately 4×10⁻⁴ molar as illustrated in Fig.4. This discrepancy was the most pronounced at the lower pH of 6.6, but it was also noticeable in some of the results obtained at a pH of 7.2. Finally, the discrepancy appeared to be independent of ammonia concentration. Reaction 6 was then eliminated from the model and further adjustments made in the reaction scheme.

**Adjustment of Rate Constants for Reactions 2, 4 and 5**

Increased rates for reaction 4 caused unacceptable discrepancies in the monochloramine results, and a considerably smaller \(k_5\) failed to describe the observed disappearance of NH₂Cl. Likewise, very large rates for \(k_2\) caused too much dependence on the ammonia concentration. It was concluded that the rate constants reported by Gray *et. al.*³ were applicable to this work with minor modifications except for reaction 6, and that at least one more reaction was responsible for the consumption of NH₂Cl and probably NHCl₂ in the peak dichloramine region.
Adjustment of Redox Reactions

A second-order reaction in dichloramine was considered as an additional redox pathway analogous to the one proposed by Cromer et al.\textsuperscript{10} for dibromamine decay. Numerical results of the reaction scheme were improved with this addition but some differences in peak NHCl\(_2\) concentrations still persisted. The observed stability of the residual at very low pH values and the difficulty in having a mechanism for the necessary pH dependency of a 2\textsuperscript{nd} order NHCl\(_2\) reaction prompted the search for another redox pathway.

The alternate path finally adopted was the empirical reaction\textsuperscript{2}

\[
\text{NH}_2\text{Cl} + \text{NHCl}_2 \rightarrow \text{P} \quad k_{10} = 35 \frac{L}{\text{mole hr}}
\]  

with the value for \(k_{10}\) being determined by numerical trial-and-error simulations. This reaction becomes significant in the neighborhood of the peak NHCl\(_2\) concentration, with reaction 7 remaining the most important redox path elsewhere. At low oxidant levels, below 1.5\times10\(^{-4}\)M, the rate of reaction 10 is considerably smaller than that of reaction 7 at all times. For the contact times and concentration ranges used in this work, the model results with the inclusion of reaction 10 are still consistent with the observation of Morris and co-workers\textsuperscript{8} of the independence of the rate of disappearance of NHCl\(_2\) from NH\(_2\)Cl. Also, reaction 10 has the desired pH dependency, becoming very small at low and high pH values. The model with reaction 10 yielded better results than with the assumed second-order reaction in dichloramine alone but some discrepancy still existed at the highest chlorine doses and lowest pH investigated. This is illustrated in Fig.5 which represents the poorest correlation between predicted and observed concentrations in NH\(_2\)Cl and NHCl\(_2\). A more typical fit is shown in Fig.6.
It is believed that the discrepancies of the type shown in Fig. 5 stem from two sources:
inaccuracies in the rate constants not experimentally verified and additional reactions
not included in the model such as a conversion of NH$_3$ and NHCl$_2$ into NH$_2$Cl with a
rate or mechanism different from that reported by Gray and co-workers$^3$ as well as
possibly some nitrite and nitrate production. The formation of small amounts of an
intermediate between NH$_2$Cl and NHCl$_2$ in reaction 5 is also kinetically feasible, based
primarily on the work of Gray et. al.$^3$ concerning the rate limiting step in the dispropo-
portionation of monochlorinated amines with different basicities.

CONCLUSIONS

1- In the absence of free chlorine, the concentration of NH$_3$ does not seem to affect
the rate of disappearance of the residual other than through the formation of
NHCl$_2$ by NH$_2$Cl hydrolysis.

2- The reaction between NHCl$_2$ and NH$_4^+$ to form NH$_2$Cl is either much slower than
reported by Gray et. al.$^3$ or the mechanism is different with a rate limiting step
not involving NH$_3$ or NH$_4^+$.

3- A redox reaction in addition to the first-order decomposition of NHCl$_2$ appears
necessary. Model simulation results indicated that a reaction of the type

\[
\text{NH}_2\text{Cl} + \text{NHCl}_2 \rightarrow P
\]

added to the first-order NHCl$_2$ decomposition can explain the results observed
except at the higher chlorine doses.
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REFERENCES


Figure 1  Typical Experimental Results. Chlorine Dose = 100 mg/L; M ratio = 0.90
Figure 2  Effect of Initial NH\textsubscript{3} on NHCl\textsubscript{2} Concentration. Chlorine Dose = 100 mg/L; Initial pH = 6.64; M ratio = 0.90 (curves 1 and 2); M ratio = 0.05 (curves 3 and 4)
Figure 3  Experiment versus Model Results. Reactions 1-9 with 6 ignored; Chlorine Dose = 25 mg/L; M ratio = 0.25; Initial pH = 6.64
Figure 4  Experiment versus Model Results. Reactions 1-9 with 6 ignored; Chlorine Dose = 100 mg/L; M ratio = 0.90; Initial pH = 6.64
Figure 5  Experiment versus Model Results. Reactions 1-10 with 6 ignored; Chlorine Dose = 100 mg/L; M ratio = 0.90; Initial pH = 6.64
Figure 6  Experiment versus Model Results. Reactions 1-10 with 6 ignored; Chlorine Dose = 25 mg/L; M ratio = 0.25; Initial pH = 6.64
Figure 1. Typical Experimental Results. Chlorine Dose = 100 mg/L; M ratio = 0.90
Figure 2. Effect of Initial NH₃ on NHCl₂ Concentration. Chlorine Dose = 100 mg/L; Initial pH = 6.64; M ratio = 0.90 (curves 1 and 2); M ratio = 0.05 (curves 3 and 4)
Figure 3. Experiment versus Model Results. Reactions 1-9 with 6 ignored; Chlorine Dose = 25 mg/L; M ratio = 0.25; Initial pH = 6.64.
EXPERIMENT VERSUS MODEL RESULTS
REACTIONS 1-9 WITH 6 IGNORED

Chlorine dose = 100mg/L
M ratio = 0.90
Initial pH = 6.64

Figure 4. Experiment versus Model Results. Reactions 1-9 with
6 ignored; Chlorine Dose = 100 mg/L; M ratio = 0.90;
Initial pH = 6.64
Figure 5. Experiment versus Model Results. Reactions 1-10 with 6 ignored; Chlorine Dose = 100 mg/L; M ratio = 0.90; Initial pH = 6.64
Figure 6. Experiment versus Model Results. Reactions 1-10 with 6 ignored; Chlorine Dose = 25 mg/L; M ratio = 0.25; Initial pH = 6.64
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