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EFFECT OF BROMIDE AND NITRITE ON THE
DEGRADATION OF MONOCHLORAMINE

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INTRODUCTION

Although strong kinetic and UV spectrophotometric evidence\textsuperscript{1,2} supports the existence of N-bromo-N-chloramines, no definitive proof exists for the production of NHBrCl as a major product in the decomposition of monochloramine (NH\textsubscript{2}Cl) in the presence of bromide according to the mechanism proposed by Trofe et al.\textsuperscript{1}

\begin{equation}
\text{NH}_2\text{Cl} + H^+ \xrightarrow{\text{Kp}} \text{NH}_3\text{Cl}^+
\end{equation}

\begin{equation}
\text{NH}_3\text{Cl}^+ + \text{Br}^- \xrightarrow{\text{slow}} \text{NH}_3\text{Br}^+ + \text{Cl}^-
\end{equation}

\begin{equation}
\text{NH}_2\text{Cl} + \text{NH}_3\text{Br}^+ \xrightarrow{\text{fast}} \text{NHBrCl} + \text{NH}_4^+
\end{equation}

If NHBrCl is produced then the rate of monochloramine disappearance given by (4),

\begin{equation}
- \frac{d[\text{NH}_2\text{Cl}]}{dt} = 2k'\text{Kp}[\text{NH}_2\text{Cl}][H^+][\text{Br}^-]
\end{equation}

might be decreased if another substance was present that preferentially reacted with an NHBrCl precursor, e.g. NH\textsubscript{3}Br\textsuperscript{+}. Since HOBr might also be hypothesized as a product of step (2), nitrite was chosen as an initial candidate as it is easily oxidized by free halogens\textsuperscript{3} and much more slowly by chloramines\textsuperscript{4}.

Conventional spectrophotometric methods cannot be easily used to measure monochloramine in the presence of both nitrite and bromide because of the resulting complex spectra. Instead an approach was taken which related monochloramine disappearance to total oxidant loss.
Previous work on the degradation of monochloramine in the presence of bromide\(^5\) has shown that under certain conditions bromine containing oxidant products rapidly decompose. A reaction of \(\text{NHBrCl}\) involving another species \(R\) producing nitrogen gas and halide ions as found for other halomine decompositions\(^6,7\) is suggested.

\[
R + \text{NHBrCl} \quad \overset{k''}{\longrightarrow} \quad \text{N}_2 + \text{Cl}^- + \text{Br}^- \quad \text{(unbalanced)}
\]  

Inclusion of the above reaction into the mechanisms proposed by Trofe et al.,\(^1\) yields equation (6) showing that the rate of monochloramine disappearance may be approximated by the rate of total oxidant decay.

\[
\frac{d[\text{TOX}]}{dt} \approx \frac{d[\text{NH}_2\text{Cl}]}{dt}
\]  

Therefore the effect of nitrite on monochloramine disappearance in the presence of bromide might be evaluated by simply measuring total oxidant concentration with time.

EXPERIMENTAL PROCEDURES

All reagent solutions were prepared with chlorine demand free water (CDFW) obtained by chlorinating distilled, deionized water and then dechlorinating with UV radiation. Stock buffer solutions of reagent grade \(\text{Na}_2\text{HPO}_4\) and \(\text{NaH}_2\text{PO}_4\) were filtered through a 0.45 um millipore filter, chlorinated and then dechlorinated with UV radiation. Stock solutions of reagent grade \(\text{NaBr}, \text{NaNO}_2,\) and \((\text{NH}_4)_2\text{SO}_4\) were also filtered.
prior to use. Sodium hypochlorite was prepared by sparging ultrapure chlorine gas through a solution of sodium hydroxide. A 75 mM solution of monochloramine (total nitrogen to chlorine mole ratio of approximately 2.5:1.0) was obtained by the slow addition of sodium hypochlorite to a vigorously stirred solution of excess ammonium sulfate buffered to pH 9.1.

The experiments were conducted in either a light-proof 0.5 or 1.0 liter flask maintained at 25°C by immersion in a thermostatted water bath. The experiments were initiated by adding an appropriate aliquot of monochloramine to a temperature equilibrated flask containing 0.25 M phosphate reaction media prepared using CDFW by appropriate addition of stock NaBr, NaNO₂, (NH₄)₂SO₄ and phosphate buffer salts. Samples were periodically withdrawn for total oxidant analysis. Initial monochloramine concentrations were measured using both the DPD-FAS titrimetric method⁸ and by UV spectrophotometry at 245 nm. Both methods compared within ± 2%.

A procedure based on the DPD-FAS titrimetric method⁸ was used to measure total oxidant in the presence of nitrite, and "estimated bromamines" and total oxidant in the absence of nitrite.⁸⁻¹¹ A modification involved use of a more concentrated DPD buffer with immediate and rapid titration with FAS. Based on the results of a previous study⁵, experimental conditions were chosen in which the rate of total oxidant decay in the monochloramine-bromide mixtures appeared to be approximately equal to the rate of monochloramine disappearance.

Samples were periodically withdrawn in a few experiments and dechlorinated with sodium thiosulfate. The UV spectra of the
dechlorinated samples was measured from 250 to 400 nm using a 10 cm cell. Nitrite was also measured using the diazotization method. 8

The rate of total oxidant loss was evaluated in three types of experiments; monochloramine plus nitrite, monochloramine plus bromide, and monochloramine plus nitrite and bromide. The concentration of one species was varied while the others were held constant. In the presence of both nitrite and bromide, pH was varied from 7.2 to 8.0 with the initial reactants ranging from 0.5 to 4 mM monochloramine, 20 to 80 mM excess total ammonia, 0.25 to 1.5 mM nitrite, and 2 to 60 mM bromide. In the absence of nitrite, pH was varied from 7 to 7.8, bromide varied from 10 to 80 mM, and excess ammonia and initial monochloramine held constant at 20 and 2.0 mM respectively. Pseudo first order rate constants were evaluated from a linear regression of \(-\ln [\text{TOX}]/[\text{NH}_2\text{Cl}]_0\) vs time plots for ordinate values lying between values 0.1 and 2.0.

RESULTS AND DISCUSSION

The rate of total oxidant decay in the presence and absence of nitrite (experiments of BRN-1 and 12 Br-1 respectively) subsequent to a brief initial lag period appeared to be first order (Figure 1) following a relationship given by equation (7),

\[
-\ln \frac{\text{[TOX]}}{[\text{NH}_2\text{Cl}]_0} = -kt
\]

in which TOX is the total oxidant residual, \([\text{NH}_2\text{Cl}]_0\) (by DPD) is the initial monochloramine dose, and \(k\) is a pseudo first order rate

constant. The marked linearity ($r^2 > .99$) over an 86% decay in total oxidant observed in all experiments suggests the applicability of eqn. (7) in describing a large fraction of the oxidant decay. Relationship (7) applied in the absence of nitrite was expected since relationships (4) and (6) were thought to apply.

Termination of the lag period illustrated in Figure 1 was interpreted as coinciding with the onset of approximate steady-state decay of bromine containing oxidant products. It is for this reason all data were regressed between ordinant values of 0.1 to 2.0 to obtain the pseudo (apparent) first order rate constant.

The addition of nitrite appeared to increase the rate of TOX decay substantially and was independent of the initial monochloramine concentration (Table I). If the observed increase in the decay rate were a result of a simple (1:1 stoichiometric) parallel oxidation of nitrite, a marked curvilinear behavior and monochloramine dependence would be observed since initial monochloramine is in sufficient excess to cause a significant depletion of nitrite. Total oxidant decay in the presence of only nitrite was found to be negligible in comparison to the greatly accelerated rates observed when bromide was added. A previous study\textsuperscript{12} investigating the kinetics of monochloramine degradation in the presence of nitrite alone also indicated that at experimental conditions used in the study reported, no significant oxidant loss should be expected. Clearly the observed effect involves some complex interaction between bromide, nitrite and monochloramine.

A significant nitrite concentration appears to remain after a large total oxidant loss even though nitrite is decreasing with time as shown
by the decrease in the predominant peak at $355^{13}$ nm measured after dechlorination of samples taken from experiment 2BRN-1 (Figure 1). Scans taken at 2, 18, and 37 minutes correspond to a decrease in total oxidant of 2, 63, and 86% (a decrease of 0.04, 1.26, and 1.72 mM as monochloramine) respectively. The minimum nitrite concentrations at these times (as measured by the diazotization method) was 0.46, 0.36 and 0.34 mM respectively. Clearly, a considerable fraction of the initial 0.5 mM nitrite has not been consumed.

The apparent first order rate of total oxidant decay increases linearly with initial nitrite concentration (Figure 3). Above approximately 10 mM bromide, total oxidant decay in the presence of 0.5 mM nitrite and 20.0 mM excess ammonia becomes linearly related to bromide concentration (Figure 4). The results suggest that the bromide dependence is independent of nitrite and equal to that observed in the absence of nitrite.

Ammonia concentration has a slight effect on the rate of total oxidant decay (Table 2). The apparent first order rate constant decreased by about 20% for an eight fold increase in excess ammonia at the conditions specified. It is believed that as ammonia concentration increases relationship (6) becomes less valid.

The total oxidant decay rate increased in direct proportion with hydrogen ion concentration over a pH range of 7.2 to 8.04 (Figure 5). A similar pH dependence was observed over a pH range of 7.0 to 7.8 in the absence of nitrite.
Proposed Reaction Kinetics

It appears that the pseudo first order total oxidant decay constant can be expressed as the sum of two functions, (eqn. 8) when bromide is in considerable excess.

\[ \bar{k} = k_1[H^+][NO_2^-] + k_2[H^+][Br^-] \]  

Under the assumption that equation (6) is applicable, relationship (8) is consistent with a reaction mechanism involving two parallel reactions for which the rate of disappearance of monochloramine is given by equation (9).

\[ \frac{d[NH_2Cl]}{dt} = k_1[NH_2Cl][H^+][NO_2^-] + k_2[NH_2Cl][H^+][Br^-] \]  

The first term in equation (9) describes a reaction involving bromide, nitrite and monochloramine. The nitrite concentration appears relatively constant over the experimental conditions used. The second term in equation (9) is consistent with the mechanism and rate expressions developed for the degradation of monochloramine in the presence of bromide alone (e.g. relationships (1) through (6)).

The rate constant \( k_2 \) was found to be \( 5.46 \pm 0.25 \times 10^7 \text{ L}^2 \text{ moles}^{-2} \text{ min}^{-1} \) from a plot of the observed first order rate constant, \( \bar{k} \), versus \([H^+][Br^-]\) determined in the absence of nitrite as shown in Figure 6. This value compares closely with the value of \( 5.8 \pm 0.35 \times 10^7 \text{ L}^2 \text{ moles}^{-2} \text{ min}^{-1} \)
min$^{-1}$ reported by Trofe et al.$^{14}$ for the reaction at 25°C but in 0.20 M phosphate buffer. The rate constant $k_1$ evaluated from a plot of $k - k_2[H^+][Br^-]$ vs $[H^+][NO_2^-]$ (Figure 7), was found to be $1.80 \pm 0.11 \times 10^9$ L$^2$ moles$^{-2}$ min$^{-1}$.

The first term in equation (9) cannot be attributed to a simple 1:1 stoichiometric oxidation of nitrite by monochloramine. The observed relatively small nitrite loss might be attributable to a reaction involving the decomposition of bromine containing species and not the parallel reaction indicated.

A catalytic effect on the decomposition or reduction of any bromine containing products does not seem likely, since the rate of total oxidant decay in the absence of nitrite should be limited by steps (2) and (3). A simple nitrite reaction with or catalyzed decomposition of an activated complex formed in step (2) is also not indicated since a bromide dependant mechanism would probably be involved.

A reaction in which nitrite catalyses the oxidation of bromide but with bromide not involved in a rate limiting step is consistent with the first term of the empirical reaction expression (9). The mechanism might involve the reaction of monochloramine and nitrite to produce an intermediate that in turn oxidizes bromide in a fast step. A bromamine which then rapidly decomposes, and nitrite would be products.

CONCLUSIONS

The observed results cannot be explained in terms of a simple interaction with the monochloramine-bromide reactions occurring in the absence of nitrite. Clearly, the presence of nitrite did not decrease
the rate of oxidant decay and thus did not provide evidence for the production of NHBrCl.

The results indicate that relatively small concentrations of nitrite can greatly accelerate the degradation of monochloramine in the presence of bromide. It does not appear that nitrite is being significantly consumed in a 1:1 stoichiometric oxidation by monochloramine. If the effect of nitrite is catalytic then these results suggest that the presence of nitrite may also accelerate other oxidation-reduction reactions. For example, nitrite may play an important role in oxidant decay in partially nitrified sewage effluents where both monochloramine and nitrite may be present. If not a complex oxidation-reduction possibly involving bromide as a catalyst is indicated. The results also suggest that the presence of other potentially oxidizable species may affect oxidant decay in a manner not attributable to a simple parallel oxidation.

ACKNOWLEDGEMENTS

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REFERENCES


Table I. Pseudo First Order Rate Constants with Respect to Initial Monochloramine Concentration at 25\degree C, pH = 7.5, [Br\textsuperscript{-}]\textsubscript{o} = 20.0 mM, [N\textsubscript{t}]\textsubscript{x} = 20.0 mM and [NO\textsubscript{2}\textsuperscript{-}]\textsubscript{o} = 0.50 mM.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>[NH\textsubscript{2}Cl]\textsubscript{o} (mM)</th>
<th>k \times 10^2 (min\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6BRN-2</td>
<td>0.51</td>
<td>5.5 ± 0.2\textsuperscript{a}</td>
</tr>
<tr>
<td>6BRN-3</td>
<td>1.0</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td>2BRN-1</td>
<td>2.0</td>
<td>5.7 ± 0.1</td>
</tr>
<tr>
<td>6BRN-1</td>
<td>4.0</td>
<td>5.8 ± 0.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} ±95\% confidence level indicated.
TABLE II. Pseudo First Order Rate Constants with Respect to Excess Ammonia Nitrogen Concentration at 25°C, pH = 7.5, \([Br^-]_o = 20.0\) mM, \([NO_2^-]_o = 0.50\) mM and \([NH_2Cl]_o = 2.0\) mM.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>([N_T]_x) (mM)</th>
<th>(\bar{k} \times 10^2) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5BRN-3</td>
<td>10.0</td>
<td>5.9 ± 0.1(^a)</td>
</tr>
<tr>
<td>2BRN-1</td>
<td>20.0</td>
<td>5.7 ± 0.1</td>
</tr>
<tr>
<td>5BRN-1</td>
<td>40.0</td>
<td>5.3 ± 0.1</td>
</tr>
<tr>
<td>5BRN-2</td>
<td>80.0</td>
<td>4.8 ± 0.1</td>
</tr>
</tbody>
</table>

\(^a\) ±95% confidence level
FIGURE CAPTIONS

1. Effect of 0.50 mM nitrite on the determinations of the pseudo first order rate constant at pH = 7.5, $[\text{Br}^-]_0 = 20.0$ mM, $[\text{N}_t]^x = 20.0$ mM, and $[\text{NH}_2\text{Cl}]_0 = 2.0$ mM.

2. Ultraviolet spectra indicating a significant nitrite concentration during reaction at pH 7.5 of 2.0 mM NH$_2$Cl in the presence of 0.50 mM NO$_2^-$, 20.0 mM Br, and 20.0 mM excess ammonia nitrogen.

3. Effect of nitrite on the pseudo first order rate constant determined at pH = 7.5, $[\text{Br}^-]_0 = 20.0$ mm, $[\text{N}_t]^x = 20.0$ mm, and $[\text{NH}_2\text{Cl}]_0 = 2.0$ mM.

4. Effect of bromide on the pseudo first order rate constant in the absence and presence of 0.50 mM nitrite at pH = 7.5, $[\text{N}_t]^x = 2.0$ mM, and $[\text{NH}_2\text{Cl}]_0 = 2.0$ mM.

5. Effect of hydrogen ion concentration on the pseudo first order rate constants in the absence and presence of 0.50 mM nitrite at pH 7.5, $[\text{N}_t]^x = 20.0$ mM, $[\text{Br}^-]_0 = 20.0$ mM, and $[\text{NH}_2\text{Cl}]_0 = 2.0$ mM.

6. Determination of rate constant $k_2$.

7. Determination of rate constant $k_1$. 
Figure 1. Effect of 0.50 mM nitrite on the determinations of the pseudo first order rate constant at pH = 7.5, [Br\(^-\)]\(_0\) = 20.0 mM, [NH\(_2\)Cl]\(_0\) = 2.0 mM, and [NT\(_x\)] = 20.0 mM.
Figure 2. Ultraviolet spectra indicating a significant nitrite concentration during reaction at pH 7.5 of 2.0 mM NH₄Cl in the presence of 0.50 mM NO₂⁻, 20.0 mM Br, and 20.0 mM excess ammonia nitrogen.
Figure 3. Effect of nitrite on the pseudo first order rate constant determined at pH = 7.5, [Br\(^-\)]\(_0\) = 20.0 mM, [N\(_T\)]\(_x\) = 20.0 mM, and [NH\(_2\)Cl] \(_0\) = 2.0 mM.
Figure 4. Effect of bromide on the pseudo first order rate constant in the absence and presence of 0.50 mM nitrite at pH = 7.5, $[N_t]_x = 2.0$ mM, and $[\text{NH}_2\text{Cl}]_o = 2.0$ mM.
Figure 5. Effect of hydrogen ion concentration on the pseudo-first order rate constants in the absence and presence of 0.50 mM nitrite at pH 7.5, $[N_t]_x = 20.0$ mM, $[Br^-]_o = 20.0$ mM, and $[NH_2Cl]_o = 2.0$ mM.
Figure 6. Determination of rate constant $k_2$. 

$$[\text{NH}_2\text{Cl}]_0 = 2.0\text{mM}$$
$$[\text{NT}]_x = 20.0\text{mM}$$

slope = $k_2 = 5.46 \times 10^7 (L^2\text{mole}^{-2}\text{min}^{-1})$

(95% C.L. ± 0.25 x $10^7$)

$$[\text{H}^+] [\text{Br}^-]_0 \times 10^{10} \text{ (moles}^2/L^2\text{)}$$
Figure 7. Determination of rate constant $k_1$. 

\[ \text{slope} = k_1 = 1.80 \times 10^9 \text{ (L}^2 \text{ moles}^{-2} \text{ min.}^{-1}) \]

\[ (95\% \text{ C.L. } \pm 0.11 \times 10^9) \]
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