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# THE KINETICS OF CHLORINE-AMMONIA REACTIONS IN SEA WATER

Annual Report June 1, 1977 to May 31, 1978

> J. Donald Johnson G. W. Inman, Jr.

University of North Carolina

Prepared for U. S. Nuclear Regulatory Commission

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# ABSTRACT

By employing stopped-flow techniques, rate constants were determined for the reactions of hypochlorous acid with bromide and ammonia in solutions at different pH's and salinities. Values for the specific rate constants at 25°C are  $k_1 = 3.8 \times 10^3$  and  $k_2 = 3.1 \times 10^6$  liters/ mole-sec respectively for the following reactions:

HOC1 + Br<sup>-</sup> 
$$\xrightarrow{k_1}$$
 HOBr + C1<sup>-</sup>  
HOC1 + NH<sub>3</sub>  $\xrightarrow{k_2}$  NH<sub>2</sub>C1 + H<sub>2</sub>O

Using the differential rate equations for each reaction, the relative formation rates were computed for a range of pH's, salinities and ammonia nitrogen concentrations. The results should be useful in predicting the nature of halogen substitution on ammonia nitrogen in estuarine waters.

As a complement to the kinetic runs, speciation experiments were done with full strength chlorinated sea water enriched with ammonia. The resultant solutions were analyzed by UV spectroscopy, amperometric Litration and a membrane electrode. At low ammonia nitrogen and high initial chlorine concentrations, hypobromous acid and tribromamine formed. As the ratio of Cl<sub>2</sub> to N was decreased, some dibromamine was observed and at ratios less than 1:1, monochloramine formed and eventually predominated.

Preliminary experiments were also done to determine a rate constant for the oxidation of bromide by monochloramine. Results showed that even in full strength sea water the reaction was quite slow (t  $_{1/2}$   $^{\circ}$ 28 hours for [NH<sub>2</sub>Cl]° < 5.0 mg/l as Cl<sub>2</sub>). The reaction was found to be pH dependent and yielded an unidentified product with a UV absorbance peak near 220 nm.

#### SUMMARY

Chlorination of ammonia-rich estuarine waters may produce monochloramine, the bromamines or a mixture of the haloamines depending on pH, temperature, salinity, chlorine dose and ammonia concentration. Monochloramine is toxic to aquatic life primarily because of its persistence and is a poor fouling control agent. The bromamines, though intrinsically no less toxic, decay rapidly and are effective antifoulants. The predominance of either bromamines or monochloramine is determined by the competitive reactions of free chlorine with ammonia and naturally occurring bromide. The bromide concentration of saline waters normally follows the salinity, therefore the rate of hypobromous acid formation and also bromamine formation is enhanced by high salinities. Lower salinity estuarine waters generally contain more ammonia and favor the formation of monochloramine. It was the objective of the proposed research to precisely determine the ammonia-to-salinity ratios required to favor either bromamines or monochloramine. This was accomplished by determining rate constants, using stopped-flow techniques, for the respective reactions of hypochlorous acid with bromide and ammonia under a variety of experimental conditions. Rate equations have been derived and values found for the specific reaction rate constants are k, = 3.8 X  $10^3$  and  $k_2 = 3.1 \times 10^6$  liters/mole-sec for the respective reactions:

> HOC1 + Br<sup>-</sup>  $\xrightarrow{k_1}$  HOBr + C1<sup>-</sup> HOC1 + NH<sub>3</sub>  $\xrightarrow{k_2}$  NH<sub>2</sub>C1 + H<sub>2</sub>O

Using the differential rate equations for each reaction, the relative formation rates were computed for a range of pH's, salinities and ammonia nitrogen concentrations. A plot was then constructed which would enable one to predict the probability of bromamine formation versus monochloramine formation at a given salinity, ammonia-nitrogen concentration and pH.

In order to determine the major components of the total residual oxidant concentration in sea water containing ammonia, a number of qualitative speciation experiments were carried out. Filtered sea water

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obtained from the North Carolina coast was enriched with different amounts of ammonia and chlorinated with 2.5 and 5.0 mg/l as Cl<sub>2</sub> of sodium hypochlorite. The resultant solutions were analyzed by UV spectroscopy, amperometric titration and a halogen membrane electrode. At very low ammonia concentrations, tribromamine and hypobromous acid formed and at high ammonia concentrations a mixture of monochloramine and dibromamine was observed. The monochloramine component was stable throughout the 45 min observation period, whereas tribromamine decomposed rapidly. The threshold ammonia concentration for monochloramine ver: e formation appeared to be at 0.4 to 0.5 mg/l NH<sub>3</sub>-N for a chlorine dose of 2.5 mg/l in full strength sea water. This observation was in qualitative agreement with predictions based on rate constants determined from our stopped-flow kinetic runs.

Preliminary experiments were also done to determine a rate constant for the oxidation of bromide by monochloramine by monitoring the UV absorbance at 245 nm,  $\lambda_{max}$  for NH<sub>2</sub>Cl. Results indicated that in full strength sea water the reaction would be quite slow with an estimated half-life greater than 20 hours. The reaction was found to be pH dependent and yielded an unidentified product with a UV absorbance peak near 220 nm.

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# THE KINETICS OF CHLORINE-AMMONIA REACTIONS IN SEA WATER

I. Introduction

#### A. Background

Chlorine is commonly used as a biocide in the condenser systems of power plants employing either fresh or saline water as a coolant. The chemical mechanisms involved in this process and the products formed are of interest because of the potential toxicity 1,2 of the chlorinated effluent and from the standpoint of fouling control efficiency." Most of the reactions are rapid and the mechanisms complex, particularly so if amino-nitrogen and organics are present. If estuarine or sea water is chlorinated, the free chlorine, primarily HOCL, will react rapidly with naturally occurring bromide to produce hypobromous acid, HOBr, and hypobromite ion, OBr.4,5 If ammonia is present it may compete for the free chlorine and form monochloramine, NH2C1.6 Ammonia, commonly present in estuarine waters, has a low molecular weight compared to chlorine such that only 0.2 mg/l ammonia nitrogen is equivalent, on a 1:1 molecular basis, to 1.0 mg/1 chlorine. Hypobromous acid may also react with ammonia to form the bromamines, where the degree of bromine substitution on nitrogen will be determined primarily by pH and the chlorine to ammonia ratio. The following schematic diagram shows the major reaction pathways and possible products in chlorinated ammonia-rich sea water.



Monochloramine is the least desirable of the above products because of its persistence and high chronic toxicity to various forms of marine life. Because it is a relatively weak oxidant it is also a poor fouling control agent. The bromamines, though not intrinsically less toxic. are not persistent because of their greater reactivity towards reducing agents and an ability to undergo autodecomposition. Bongers et al<sup>9</sup> have demonstrated the effectiveness of bromamines as condenser antifoulants in low-salinity high ammonia estuarine water disinfected with bromine chloride. They also observed that the residual oxidants or bromamines formed from bromine chloride and the ammonia present decayed more rapidly than those produced by chlorination of that same water. Similar results were found by Hergott et al 10 in a survey of chlorination practices at five power plants around the San Francisco Bay area. The slowest decay of residual oxidant was observed in the cooling waters of lowest salinity. The most rapid decay occurred in high salinity waters where most of the oxidant was identified as a bromine residual. Bongers concluded that bromine chloride may be a desirable alternative to chlorine in many situations. However, depending on the chlorine dose, pH, ammonia content and salinity of a cooling water, it may not be necessary to employ the more expensive bromine chloride since chlorine may produce identical results.

# B. Research Objectives

The above work and calculations based on past laboratory kinetic studies<sup>11</sup>, <sup>12</sup> indicate that there is a critical ammonia-to-salinity ratio where monochloramine formation begins to predominate over hypobromous acid and subsequent bromamine formation. In order to predict this point for a given coolant water, a reliable set of rate equations must be known that can, as a minimum, account for changes in salinity, pH, temperature and ammonia concentration. Therefore, the primary objective and a logical first step in developing a kinetic model for sea water chlorination has been to determine rate constants for the formation of HOBr and NH<sub>2</sub>Cl under a variety of pH and salinity conditions. Further research objectives have been to determine the chemical speciation of chlorinated ammonia-

enriched sea water samples and determine the stability of monochloramine, the most persistent and toxic product.

#### II. EXPERIMENTAL

#### A. Reagents

#### Chlorine Demand-Free Water

The procedure for preparing demand-free water is described in detail elsewhere.<sup>13</sup> This water was used to rinse all glassware, to prepare stock solutions and as a diluent in all aqueous solutions.

# Sea Water

All sea water used in these experiments was obtained from Onslow Bay near the sea buoy, 3 miles south of Morehead City, North Carolina, at flood tide on July 16, 1977. Samples were taken in acid-washed polyethylene containers and immediately returned to Chapel Hill, stored at 4°C and filtered through 0.45 µm Millipore filters. The pH was 8.10  $\pm$  0.05, total organic carbon 2.2 mg/l and the salinity 33°/... the ammonia concentration was less than 0.01 mg/l ammonia nitrogen as determined by adding ~2 mg/l bromine solution and observing the UV absorbance at 258 nm,  $\lambda_{max}$  for NBr<sub>3</sub> ( $\epsilon = 5000$ ).

### Artificial Sea Water

A concentrated stock solution of bromide-free artificial sea water was prepared according to the formula of Kester et al.<sup>14</sup> The composition and concentration of each component are given in Table 1. This stock was used in the preparation of reactant solutions for kinetic runs involving the formation of monochloramine. Fischer Certified A.C.S.grade reagents were used with the exception of sodium chloride which was biological grade containing less bromide and other impurities. The stock was filtered (.45  $\mu$ m), chlorinated to 5 mg/l as Cl<sub>2</sub> and then irradiated with UV light to eliminate any reducing agents.

### Ammonia Chloride Solutions

Stock ammonium chloride solutions were prepared by the addition of appropriate amounts of Fisher Certified A.C.S.-grade ammonium chloride in demand-free water and diluting to volume.

# Table 1

Composition of the artificial sea water stock solution used to prepare reactant solutions of different ionic strengths.  $\mu$  (formal) = 0.99, chlorinity = 27.8 °/ $_{\circ\circ}$ , salinity = 50.3 °/ $_{\circ\circ}$  and specific gravity = 1.06 at 25°C.

Component	Mass(g)	Molarity (at 25°C)	Molality
NaC1	70.50	0.638	0.602
Na2SO4	11.36	0.0423	C.0399
MgCl <sub>2</sub> ·6H <sub>2</sub> O	31.38	0.0816	0.0771
CaCl <sub>2</sub> ·2H <sub>2</sub> O	4.20	0.0151	0.0143
NaHCO3	0.593	0.0037	0.0006
H20	1882.		

# Sodium Hypochlorite Solutions

Hypochlorite stock solutions were prepared by diluting Fisher Reagentgrade sodium hypochlorite (5%). Their titers were determined by amperometric titration.

# Dibromamine Solutions

Solutions of NHBr<sub>2</sub> used to calibrate the halogen membrane electrode were prepared by adding 150 ml of 80.5  $\mu$ M HOBr to 150 ml of 400  $\mu$ M NH<sub>4</sub>Cl buffered at pH 7 with 0.01 M phosphate. The concentrations of NHBr<sub>2</sub> were determined from the absorbance at 232 nm,  $\lambda_{max}$  for NHBr<sub>2</sub>, ( $\epsilon = 1900$ ). Under these conditions all of the total oxidant consisted of dibromamine as confirmed by amperometric titration and UV absorbance.

# Buffer Solutions

A potassium phosphate buffer stock (-0.10  $\underline{M}$  in PO<sub>4</sub>) was prepared by adding enough 0.2  $\underline{M}$  KH<sub>2</sub>PO<sub>4</sub> to 500 ml of 0.2  $\underline{M}$  K<sub>2</sub>HPO<sub>4</sub> until the desired pH was obtained. The reagents were Mallinckrodt Analytical Reagentgrade K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O and fisher Primary Standard KH<sub>2</sub>PO<sub>4</sub>. The stock was filtered (0.45  $\mu$ m), chlorinated and irradiated with UV light in order to eliminate trace amounts of reducing agents.

#### Sodium Chloride Solution

A 2.00 M stock solution of NaCl was prepared from Fisher Biological-

grade sodium chloride and demand-free water. The solution was filtered, chlorinated and irradiated. This stock was used in the preparation of reactant solutions for all kinetic runs to measure the rate of hypobromous acid formation.

## Potassium Bromide Solutions

All KBr solutions were prepared from Fisher-Certified A.C.S.-grade potassium bromide.

#### Monochloramine Stock Solutions

Stock solutions of monochloramine (25 mM) were prepared by mixing an appropriate amount of NaOCl stock to a solution of NH<sub>4</sub>Cl buffered at pH 8.75, and diluting to 100 milliliters. The ammonia to chlorine ratio was maintained at 2.0:1. Stocks were prepared in this manner prior to each experiment and the NH<sub>2</sub>Cl concentration determined spectrophoto-metrically from the absorbance at 245 nM. Stock concentrations prepared in this manner were consistently 25 mM.

#### Sodium Hypobromite Solutions

Hypobromite solutions were prepared by mixing stoichiometric amounts of NaOCl stock with potassium bromide stock and allowing 24 hours for the reaction to go to completion. The pH was adjusted to 11.2 with 0.25 N sodium hydroxide and the stock stored in the dark. The resulting concentration was determined spectrophotometrically from the absorbance at 329 nm,  $\lambda_{max}$  for OBr<sup>-</sup>.

### B. Methods

#### Total Oxidant Concentrations

Total oxidant concentrations were determined by amperometric titration using phenylarsine oxide as a titrant according to a procedure in Standard Methods.<sup>15</sup> However, the KI was always added first to the diluent water and the pH 4 buffer added immediately prior to adding the sample aliquot.

### Tribromamine and Hypobromous Acid-Hypobromite

The concentrations of NBr<sub>3</sub> and HOBr + OBr<sup>-</sup> were determined from the UV absorbance at 258 nm,  $\lambda_{\rm max}$  for NBr<sub>3</sub>, and from total oxidant concentration in a manner described elsewhere.<sup>13</sup>

#### Dibromamine

The concentration of NHBr, in solutions containing no excess bromine was measured with an amperometric membrane electrode. A detailed description of the construction, properties and use of this device are given by Johnson et al.<sup>16</sup> When +350 mV is applied across the probe's gold working electrode and Ag/AgCl reference electrode, a number of halogen compounds are selectively reduced and will produce a current proportional to their concentrations. 17,18 The sensitivities (milliamperes-liter/equivalent) are given in Table 2 for a number of halogen compounds. If no excess halogen is present in sea water containing ammonia, only NH2Br, NHBr2, NH2Cl and NHCL2 are likely to be encountered. Since  $NH_2C1$  produces no reduction current<sup>16</sup> at +350 mV, the membrane electrode may be used to measure the sum of NHBr,, NHCl, and NH,Br concentrations. For the ammonia: halogen ratios employed in this study, the major contribution to the electrode response was expected to come from NHBr2. Dichloramine was a possible interference but produces a very small response and is normally only present at low pH.<sup>19</sup> The probe is also 17 times more sensitive to NHBr, than to an equivalent amount of NH, Br.

A Delta Scientific Model 8324 "Chlorine"Analyzer was modified so that +350 mV could be applied to the electrode. The electrometer output of the Analyzer was then calibrated using NHBr<sub>2</sub> solutions. The calibration curve shown in Figure 1 was obtained from data taken before and after the sea water chlorination runs. The NHBr<sub>2</sub> concentrations were determined spectrophotometrically by monitoring the absorbance at 232 nm,  $\lambda_{max}$  for NHBr<sub>2</sub>.

# Monochloramine

The concentration of NH<sub>2</sub>Cl ( $\epsilon$  = 455) was determined from the absorbance at 245 nm by correcting for the contribution of NHBr<sub>2</sub> ( $\epsilon$  = 1300 at



Figure 1. Calibration curve of the membrane electrode response to  $\ensuremath{\mathsf{NHBr}}_2$  .

245 nm).<sup>20</sup> When the NHBr, concentration was large in comparison to NH2C1, the UV method was found to be inadequate. In this case the  $\rm NH_2Cl$  concentration was calculated as the difference in the equivalent NHBr, concentration and the total oxidant concentration.

lable 2.	Membrane Electrode	Sensitivities	to Various	Halogen	Species
Compound		X = C1			X = Br
NX3		48			70
NHX <sub>2</sub>		0.2			27
NH2X		0.0			1.6
HOX		6.6			5.0

<sup>a</sup>In milliamperes-liter/equivalent at an applied potential of 337 mV vs Ag/AgC1 with a Millipore Fluorcoore microporous-type FG047 membrane.

# C. Procedures

# Chemical Speciation in Chlorinated Sea Water

Two sets of experiments were carried out wherein sodium hypochlorite was added to filtered Onslow Bay sea water spiked with ammonium chloride. In the first set the initial chlorine dose was held constant at 5.0 mg/1 as Cl<sub>2</sub> (70.5 µeq/1 as oxidizing halogen) and the initial ammonia concentrations were varied from 0.075 to 3.16 mg/1 as ammonia nitrogen. In a second set of experiments the initial concentrations of chlorine and ammonia were halved. The initial conditions and results of these sixteen experiments are summarized in Appendix A. The sea water pH of 8.1 was unaltered by the addition of either hypochl(r te or ammonia chloride.

Prior to each run a baseline scan from 300 to 220 nm was run on a Cary 14 recording spectrophotometer with sea water in both sample and reference beams. The response of the electrode was also zeroed using sea water. A run was begun by adding an appropriate amount of concentrated hypochlorite stock (~250 mg/1) to 300 ml of sea water containing the desired ammonia concentration. During this addition the solution was stirred rapidly with a magnetic stirrer. An aliquot was immediately removed into a 10-cm quartz cell and a scan done from 300 to 220 nm.

The spectral scan was repeated at 3, 5, 10, 15, 20, 30 and 40 min. Immediately after removing a sample for UV analysis, the membrane electrode was lowered into the stirred solution and current response recorded every minute for 10 min and every 5 min thereafter. At 1, 5, 10, 20 and 40 min, 10-ml aliquots were withdrawn for determination of total oxidant concentrations. The electrode response, total oxidant values and absorbances at the wavelengths of interest were plotted as a function of time. The concentrations of individual compounds were calculated as described above under Methods.

# Bromide Oxidation by Hypochlorous Acid

Twenty-three sets of stopped-flow kinetic runs were carried out to determine the effect of pH, ionic strength and temperature on the rate of hypobromous acid formation. All runs were done under pseudo-first order conditions where the bromide concentration was fifteen times the initial hypochlorite concentration. The experimental data for these runs are tabulated in Appendix B. Reactant solutions were prepared in the following manner. All bromide solutions were prepared by diluting to 100 ml a mixture of encugh 2 <u>M</u> NaCl to obtain the desired ionic strength, 10 ml of 0.10 <u>M</u> phosphate buffer and 10 ml of 0.05 <u>M</u> KBr. When necessary the pH was adjusted to the desired value by the addition of dilute (0.025 N) NaOH or HCl. Runs were done at five salt concentrations, 0.05, 0.10, 0.20, 0.35 and 0.50 molar.

In a similar manner, all hypochlorite solutions were prepared by diluting to 100 ml a mixture of NaCl, 10 ml of 0.10 <u>M</u> phosphate buffer and 10 ml of 3.2 X 10<sup>-3</sup> <u>M</u> hypochlorite solution. Portions of these solutions were then introduced into the reservor syringes of an Aminco-Morrow Stopped Flow apparatus and allowed to equilibrate at the run temperature. A run was initiated by pressing a drive button which simultaneously activated the drive syringes and initiated the data acquisition process. A detailed description of the stopped-flow apparatus and its operational procedures are given by Reich<sup>21</sup> and Morrow.<sup>22</sup> The reaction of HOCl with Br to produce HOBr was monitored by observing the change in light intensity at 292 nm,  $\lambda_{max}$  for OCl . Hypochlorite,

OC1<sup>–</sup>, was in equilibrium with HOC1 and therefore the rate of bromide oxidation was proportional to the loss of OC1<sup>–</sup>. The source and detection system consisted of a Beckman DU monochromator, a Power Designs Model 1565 photomultiplier tube, amplification circuitry and a data acquisition system associated with a Raytheon 706 computer. Light intensity changes were converted to current changes, voltages and finally digitized by an analog-to-digital converter. A more detailed discussion of the relationships between light intensity, current, voltage and absorbance are given by Braddock.<sup>23</sup> Because absorbance changes were always less than 0.10, observed rate constants could be computed from linear regressions on ln (V-V<sub>w</sub>) or ln (A-A<sub>w</sub>) versus time.<sup>23</sup>

# Kinetics of Monochloramine Formation

Twenty-five sets of runs were done to determine the effect of pH and ionic strength on the rate of monochloramine formation in artificial sea water. The results are tabulated in Appendix C. Since there is some rate data available<sup>12</sup> on the fresh water kinetics of this reaction, it was decided to proceed directly with experiments employing an artificial sea water medium. However, because of discrepencies between our initial findings and the earlier work of Morris<sup>12</sup>, it was decided to repeat some fresh water runs under conditions similar to those employed by Morris. Runs were also done using phosphate buffers as had been done with the bromide work. However, due to problems with Mg(HPO,) precipitation at high pH, phosphate was eliminated. Buffers proved to be unnecessary as the pH's of reactant solutions could be adjusted prior to mixing with only dilute NaOH and HCl. Reactant solutions were prepared in a manner identical to that used for the bromide oxidation runs with three exceptions. Artificial sea water stock was substituted for the NaCl stock, 10 ml of 0.05 M NH, Cl were substituted for the KBr and no phosphate buffer was added. Five salt concentrations were used resulting in total ionic strength values of 0.031, 0.056, 0.106, 0.206 and 0.406. This covered a salinity range from 1 to 20 °/00. The reaction was monitored by following the appearance of monochloramine at 245 nm. observed rate constants were calculated from linear regressions on ln ( $\Delta A$ ) versus time, where  $\Delta A = A_{m} - A$  for an appearance. These calculations and those for the formation of hypobromous acid were performed by a computer program written in PL-1 for the IBM system 370 at the University of North Carolina at Chapel Hill.

# The Decomposition of Monochloramine in the Presence of Bromide

The oxidation of bromide ion by monochloramine was studied under pseudofirst order conditions by mixing buffered solutions of monochloramine and potassium bromide where the bromide was present in large excess. Solutions were maintained at pH's from 7.1 to 7.9 with phosphate buffer and the spectrometer cell holders were thermostated at 25°C with a constant temperature bath. The excess ammonia concentration in the reaction solutions varied from 0.69 mM to 0.91 mM. Initial concentrations of NH2C1 and Br for all runs were 0.75 mM (53 mg/l as Cl2) and 16.0 mM (1280 mg/1) respectively which gave a 22:1 molar ratio of [Br]°:[NH,C1]°. The ionic strength, 0.020 + 0.004, of the reaction solutions was determined by the phosphate buffer. The reaction was initiated by adding an appropriate volume (usually 3 to 4 ml) of 25 mM monochloramine stock to a stirred and thermostated solution of 16 mM KBr and buffer. A 4 ml aliquot was withdrawn into a 1 cm quartz cell and a series of repetitive scans made from 350 to 200 nm using a Cary Model 219 dual-beam spectrophotometer. Absorbance data was then taken at two wavelengths, 245 and 232 nm, which are  $\lambda_{max}$  for NH<sub>2</sub>Cl and NHBr<sub>2</sub>. A computer program was used to calculate the concentrations of monochloramine and dibromamine by solving two simultaneous equations in two unknowns.

# III. Results and Discussion

# A. Chemical Speciation in Chlorinated Sea Water

Raw data for a given speciation experiment consisted of a series of UV spectral scans, total oxidant concentrations and the response of a halogen membrane electrode all obtained at times ranging from 1 to 40 minutes. For the sake of brevity, only the more representative absorbance and concentration-time curves are presented here.

Figure 2 shows the time-dependence of the UV absorbance of chlorinated sea water for an initial chlorine:ammonia molar ratio of 6.25 and 0.16 mg/l ammonia nitrogen. The peak near 250-260 nm is due to NBr<sub>3</sub> with a slight contribution from HOBr. The formation and rate of disappearance of NBr<sub>3</sub> at pH 8.1 and the given chlorine:ammonia ratio are in qualitative agreement with results obtained previously in freshwater.<sup>13</sup> Figure 3 shows the time-dependence of total oxidant concentration, electrode response and concentrations of NBr<sub>3</sub> and HOBr + OBr<sup>-</sup>, increases initially since it is a product of NBr<sub>3</sub> decomposition. The relatively high electrode response is produced because the electrode is calibrated to NHBr<sub>2</sub> while the solution consists almost entirely of NBr<sub>3</sub>, which has a greater sensitivity than either HOBr or NHBr<sub>2</sub> as shown in Table 2.

An example of data from a run in which ammonia was in excess and also present at a high concentration (2.0 mg/1) is given in Figures 4 and 5. In Figure 4, the peak near 240-250 nm becomes more pronounced with time and suggests the presence of monochloramine ( $\lambda_{max} = 245$  nm) and also one or more levs stable compounds. Dibromamine is the only known haloamine capable of producing the observed electrode response when ammonia is present in excess at high pH. However, the lack of a distinct peak at 232 nm.  $\lambda_{max}$  for NHEr<sub>2</sub>, prevents a positive identification based solely on the UV data. Monobromamine ( $\lambda_{max} = 278$  nm) can be present only in low concentrations since the absorbance near 280 nm. is small relative to that near 245 nm. It is also observed only at higher ammonia:bromine ratics.<sup>7,20</sup> The decay curves attributed to NH<sub>2</sub>Cl and NHBr<sub>2</sub> are shown in Figure 5. After an initial decrease in the concentration of NHBr<sub>2</sub>, both



Figure 2. Time dependence of the UV spectrum of chlorinated, ammonia-enriched sea water. The initial chlorine and ammonia nitrogen concentrations were 5.0 and 0.16 mg/l respectively.



Figure 3. Concentration-time curves for NBr<sub>3</sub>, HOBr + OBr and total oxidant for an initial chlorine dose of 5.0 mg/l in sea water containing 0.16 mg/l ammonia nitrogen. The electrode response (meter reading X 28 X  $10^{-6}$ ) is also shown.







Figure 5. Concentration-time curves for  $NH_{2}Cl$ , total oxidant concentration and electrode response for an<sup>2</sup> initial chlorine dose of 5.0 mg/l and 2.0 mg/l ammonia nitrogen.

halogen species appear to be stable with NH<sub>2</sub>Cl comprising 75% of the total oxidant present. In estuarine water containing weak reducing agents, the bromamine portion would likely disappear leaving the more inert monochloramine.

The concentration-time data from each run were used to construct the plots shown in Figures 6 and 7 wherein the concentrations in mg/1 as Cl, of each component as plotted against the logarithm of initial ammonia concentration. These plots show the composition of the total oxidant concentration for a particular initial ammonia concentration at 1 and 30 minutes after chlorination. The chlorine dosage is constant and the ammonia: halogen ratio increases from left to right. The left-hand portion of each plot represents the condition of excess halogen added beyond that required to completely oxidize ammonia while the right-hand side represents a situation with ammonia in excess. At a 1.5 - 1.7 molar ratio of halogen to ammonia, conditions are favorable for redox rather than substitution reactions. Near this point, often referred to as the breakpoint, the total oxidant concentration decreases rapidly with time. The rigures show that at low ammonia concentrations and halogen: ammonia ratios greater than 3, NBr, is the principal bromamine present. Tribromamine is stabilized by acid pH and an excess of hypobromous acid. At pH 8.1 it is unstable even at a relatively high halogen: ammonia ratio (12.5) and after 30 min has decreased to 0.42 mg/l from an initial 3.55 mg/l. At this point HOBr and OBr, which are also products of NBr, decomposition, are the major constituents of the total oxidant concentration. At higher ammonia concentrations there is less free bromine and NBr, decomposes more rapidly. This is evident by noting the NBr, concentrations at 1 and 30 min when the initial chlorine: ammonia molar ratio is about 3:1. After 30 min, NBr, was undetectable by its UV absorbance.

At a relatively high ammonia concentration, ~0.5 mg/l, and a 1:1 molar ratio of chlorine:ammonia,dibromamine forms and decomposes rapidly as shown in Figures 6 and 7. At 1.0 mg/l ammonia nitrogen, monochloramine was detected from its UV adsorbance at 245 nm. At ammonia nitrogen



Figure 6. Composition of the total oxidant concentration at 1 min as a function of ammonia concentration. The chlorine dose is a constant 5 mg/1.



Figure 7. Composition of the total oxidant concentration at 30 min as a function of ammonia concentration. The chlorine dose is a constant 5 mg/l.

levels less than 1.0 mg/l it was difficult to measure NH<sub>2</sub>Cl because of interferences from dibromamine absorbance. This limitation was the determining factor in choosing chlorine dosages and nitrogen levels for these experiments. At higher nitrogen levels monochloramine was easily observed and was also stable.

An additional experiment was performed to confirm the presence of monochloramine in chlorinated sea water. Two sea water samples containing 1.0 mg/1 ammonia nitrogen were dosed with equivalent amounts (70.5 ueq/1, 2.5 mg/1 as Cl<sub>2</sub>) of hypochlorite and hypobromite and their UV spectra scanned from 210 to 290 nm. The chlorinated sample gave a broad and stable maximum near 240-250 nm after several hours whereas the brominated sample produced a maximum near 230 nm that decreased rapidly in a manner characteristic of dibromamine solutions.

These data show that monochloramine will form and eventually predominate in full strength chlorinated sea water when the ammonia nitrogen level is at least 1 mg/1. However, this does not answer the question of whether or not monochloramine would be formed at lower ammonia concencrations and lower chlorine doses more typical of cooling water chlorination practices. In order to answer this question and to determine the current limits of sensitivity of our present analytical methods, another set of runs were carried out at half the initial ammonia concentrations and chlorine dose. The major characteristics of UV absorbance and concentration-time curves were not substantially different from those of the previous experiments with the possible exception of a slower initial decomposition rate. Speciation plots are shown in Figures 8 and 9 at the respective times of 1 and 30 minutes. Because the nitrogen levels were lower for these runs, the concentration of labile oxidant or what was thought to be dibromamine, comprised a greater percentage of the total oxidant concentration than in the earlier runs. This happened simply because there was less ammonia to compete with bromide for the hypochlorous acid. However, all of the total oxidant could not be accounted for solely by the presence of dibromamine. In each run there was a fraction (10-20  $\mu$ eq/1 or 0.3-0.7 mg/1 as Cl<sub>2</sub>) of total oxidant that did not vary greatly during the course of a particular run, but did increase



Figure 8. Composition of the total oxidant concentration at 1 min as a function of ammonia concentration. The chlorine dose is a constant 2.5 mg/l.



Figure 9. Composition of the total oxidant concentration at 30 min as a function of ammonia concentration. The chlorine dose is a constant 2.5 mg/1.

when the ammonia concentration was increased. This fraction's observed stability is consistent with the known properties of monochloramine. Only at the highest initial ammonia concentration (1.6 mg/1 ammonia nitrogen) could monochloramine be detected by its UV absorbance. The concentrations of dibromamine and monochloramine measured during these runs are near the limits of selectivity and sensitivity for our present detection methods. UV spectral measurements in chlorinated sea water were particularly difficult because of a high and changing background absorbance. The effect was more noticeable at higher halogen: nitrogen ratios, when there was excess halogen over that required to form a monohaloamine. The baseline shift was always negative with the effect of underestimating concentrations. A possible explanation is that excess halogen was reacting with some organic components of sea water and changing the UV absorption charactteristics. We hope to minimize this problem in the future by using cleaner Gulf Stream sea water for some of the speciation experiments.

B. Bromide Oxidation by Hypochlorous Acid

The proposed mechanism<sup>11</sup> for the oxidation of bromide ion by hypochlorous acid is:

HOCI 
$$\xrightarrow{\kappa_1}$$
 OCI  $\xrightarrow{\kappa_1}$  H<sup>+</sup> (1)

 $HOC1 + Br^{-} \xrightarrow{1} HOBr + C1^{-}$  (2)

In order to test its validity an expression must be derived for the observed rate constant in terms of the reaction rate constant  $k_1$  and all reaction variables. The rate of bromide disappearance is also equal to the rate of disappearance of total oxidizing chlorine and the rate of appearance of total oxidizing bromine. Therefore,

$$\frac{dBr}{dt}T = \frac{-d[Br]}{dt} = \frac{-dCl_T}{dt} = k_1 [HOC1][Br] \frac{\gamma_o \gamma \pm}{\gamma_{Br}}, \quad (3)$$

where  $Cl_T = [HOC1] + [OC1]$ ,  $Br_T = [HOBr] + [OBr]$ , and  $\gamma_o$  and  $\gamma_{Br}$  are the respective activity coefficients for HOC1 and the activated complex. The activity coefficients of the single charged species, Br and OC1 are assumed to equal  $\gamma^{\pm}$ . Since we monitor the disappearance of OC1, it is desirable to express  $Cl_T$  and HOC1 in terms of OC1. This may be done by
using the thermodynamic acid dissociation constant,  $K_a^{24,26}$  for hypochlorous acid where,

$$K_{a} = \frac{[OC1^{-}] [H^{+}] \gamma \pm \gamma}{[HOC1] \gamma_{o}} H , \qquad (4)$$

$$[HOC1] = \frac{[OC1^{-}] [H^{+}] \gamma \pm \gamma}{K_a \gamma_{\phi}} H$$
(5)

and 
$$Cl_{T} = [OC1^{-}] (1 + [H^{+}] \gamma \pm \gamma_{H} / K_{a} \gamma_{o}).$$
 (6)

Substituting (5) and (6) into (3) and also making these simplifying assumptions that  $\gamma_o = 1$  and  $\gamma \pm = \gamma_{\rm Br}$  yields the following differential rate equation:

$$\frac{-d[OC1^{-}]}{dt} = \frac{k_1 [OC1^{-}] [Br^{-}]}{1 + K_a / [H^{+}] \gamma_H \gamma^{\pm}}$$
(7)

A further substitution is necessary since  $[H^+]$  is monitored using a pH electrode with a saturated calomel reference. The hydrogen-ion activity is given by  $a_{H} = [H^+]\gamma_{H}$  and is related to the operational activity measured with a pH electrode by j:

$$\tilde{a}_{\rm H} = j a_{\rm H} = j \gamma_{\rm H} [{\rm H}^+], \qquad (8)$$

where j depends upon the difference in liquid junction potentials between standard buffer and the saline solution. If [H<sup>+</sup>] is related to  $\tilde{a}_{H}$ , the rate equation then becomes

$$\frac{-d[oc1^{-}]}{dt} = \frac{k_1 [oc1^{-}][Br^{-}]}{1 + K_0 f/\tilde{a}_{\mu} \gamma^{\pm}} .$$
(9)

Under a given set of run conditions at constant pH, temperature, ionic strength and a large excess of bromide, the integrated form of (9) is

$$\ln [OC1^{-}] = \frac{-k_{I} [OC1^{-}][Br^{-}]}{1 + K_{a} f / \tilde{a}_{H}^{-} Y^{\pm}} - \ln [OC1^{-}]^{\circ}, \qquad (10)$$

where  $[0C1^-]^\circ$  = the initial hypochlorite concentration. A plot of In  $[0C1^-]$  versus time should yield a straight line with a slope equal to  $-k_{obs}$  where,

$$k_{obs} = \frac{k_1 [Br]}{1 + K_a j / \tilde{a}_H \gamma^{\pm}}$$
(11)

In practice, a voltage proportional to the concentration of hypochlorite

was measured as a function of time (see Figure 10) and the slope determined by performing a linear regression on the logarithm of  $\Delta V$ ,  $V-V_{\infty}$ , versus time. A sample plot is shown in Figure 11, where the regression was done for 80% completion.

As conditions are varied from run to run,  $k_{obs}$  becomes a function of bromide concentration, temperature, pH and ionic strength. Temperature primarily affects  $k_1$  according to the activation energy of the reaction. The dissociation constant,  $K_a$ , the activity coefficient,  $\gamma \pm$ , and j also change with temperature. (See Appendix D for temperature dependence of  $K_a$  and j) A change in ionic strength affects  $\gamma \pm$  and this has been accounted for in our calculation by Davies' equation<sup>27</sup> where,

$$\log \gamma t = \left[ A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\sqrt{\mu} \right]$$
(12)

and A = 1.825 X 10<sup>6</sup> (78.3 X T)<sup>-3/2</sup> and  $\mu$  is the formal solution ionic strength. A test of the validity of equation (11) is a plot of  $k_{obs}$ versus  $[3r^{-}]/(1 + K_a j/\tilde{a}_H \gamma \pm)$  as shown in Figure 12, where  $K_c = K_a j/\gamma \pm$ . The slope, 3.8 X 10<sup>3</sup> liters/mole-sec, of chis plot is equal to  $k_1$ , the reaction rate constant for the formation of hypobromous acid at 25°C. This value is somewhat higher than the 3.0 X 10<sup>3</sup> liters/mole-sec obtained by Farkas et al<sup>11</sup>  $\rho$  high pH. A possible explanation for this is an increased rate of bromide oxidation by the ion pair, NaOC1, which should react as rapidly as HOC1.

The temperature dependence of  $k_1$  was determined by plotting ln  $k_1$  versus 1/T for four different temperatures as shown in Figure 13. There was a small dependence with an Arrhenius activation energy of approximately 1.5 kcal. A complete expression for the rate constant is,

$$k_1 = 4.7 \times 10^4 e^{-1500/RT}$$
 liters/mole-sec, (13)

where the Arrhenius factor,  $Z = 4.7 \times 10^4$ , was determined from the intercept, ln (Z), of Figure 13.

## C. The Kinetics of Monochloramine Formation

Morris and Weil<sup>12</sup> studied the kinetics of monochloramine formation in low ionic strength solutions and concluded that the following mechanism was most consistent with their data:



Figure 10. A typical plot of amplifier output voltage versus time for the formation of hypobromous acid. The concentration of OCl is proportional to V-V<sub>w</sub> where V<sub>w</sub> is the voltage at t = infinity or complete reaction.



Figure 11. A plot of the natural logarithm of V-V versus time for the disappearance of OC1 where the slope =  $-k_{obs}$ .









HOC1 
$$\stackrel{K_a}{\longleftarrow}$$
 OC1  $\stackrel{+}{\rightarrow}$  H<sup>+</sup> (14)

$$HOC1 + NH_3 \xrightarrow{\kappa_2} NH_2C1 + H_2O$$
 (15)

The rate of monochloramine appearance is equal to the rate of disappearance of total uncombined chlorine according to the equation,

$$\frac{-dCl}{dt}T = \frac{dM}{dt} = k_2 [HOC1][NH_3] \gamma_{\circ} \gamma_N / \gamma_M, \qquad (16)$$

where  $Cl_T = [HOC1] + [OC1^-]$  and  $M = [NH_2C1]$ . Since our reaction variables are total chlorine, total ammonia nitrogen, pH and ionic strength a differential rate equation containing only these variables must be derived. The concentration of hypochlorous acid may be expressed in terms of  $Cl_T$ ,  $K_a$  and  $[H^+]$  by using the equilibrium expression (4) to give:

$$[HOC1] = C1_{T} / (1 + K_{a} \gamma_{o} / [H^{\dagger}] \gamma_{H} \gamma^{\pm})$$
(17)

and a similar equation for the ammonia concentration is:

$$[NH_{3}] = N_{T} / (1 + K_{b} \gamma_{N} / [OH^{-}] \gamma \pm \gamma_{OH}), \qquad (18)$$

where values of  $K_b$  were determined by Bates and Pinching.<sup>28</sup> Substituting (17) and (18) into (16) and using the expression for  $K_w$ ,<sup>29</sup> the ionization constant of water, gives

$$\frac{dM}{dt} = \frac{k_2 N_T Cl_T \gamma_{\circ} \gamma_N / \gamma_a}{(1 + K_a \gamma_{\circ} / [H^+] \gamma_H \gamma_{\pm}) (1 + K_b [H^+] \gamma_H / K_w \gamma_{\pm})}$$
(19)

Again the simplifying assumptions are made that the activity coefficients of uncharged species are unity ( $\gamma_o = \gamma_N = \gamma_M = 1$ ) and the activity coefficients of singly charged species are equal ( $\gamma \pm = \gamma_{NH_4^+} = \gamma_{OC1^-}$ ). If the hydrogen-ion activity, [ $H^+$ ]  $\gamma_H$ , is expressed in terms of operational activity according to equation (5) the differential rate equation becomes:

$$\frac{dM}{dt} = k_2 N_T Cl_T/B, \qquad (20)$$

where,  $B = (1 + K_a j/\tilde{a}_H \gamma^{\pm})(1 + K_b \tilde{a}_H/K_w j \gamma^{\pm})$ . If total oxidizing chlorine is conserved then at any time during the reaction  $M = [NH_2C1] = C1_T^\circ - C1_T$ , where  $C1_T^\circ$  is the initial chlorine concentration. The final monochloramine concentration should also equal  $C1_T^\circ$ . Therefore

$$C1_{T} = M_{or} - M = \Delta M, \qquad (21)$$

where,  $M_{\omega}$  is the monochloramine concentration at t = infinity. By substituting (21) into (20) the rate equation becomes

$$\frac{dM}{dt} = \left(\frac{k_2 N_T}{B}\right) (M_{\infty} - M)$$
(22)

Integrating this equation over the limits  ${\rm t_1}$  to  ${\rm t_2}$  and  ${\rm M_1}$  to  ${\rm M_2}$  gives the integrated form of the rate equation

$$\ln (M_{\infty} - M_2) = \frac{\kappa_2 - \kappa_T}{B} (t_2 - t_1) + \ln (M_{\infty} - M_1), \quad (23)$$

provided  ${\rm N}_{\rm T}^{>>}~{\rm Cl}_{\rm T}^{\,\circ}$  as was the case for all of our kinetic runs. Since  $M_1$ ,  $t_1$ ,  $M_\infty$ ,  $k_2$  and B are all constant for a given set of run conditions and  $\Delta M$  is proportional to  $\Delta A$  or  $\Delta V$ , a plot of ln  $\Delta A$  versus  $\Delta t$  will give a value of  $k_{obs}$  from its slope where slope =  $-k_{obs} = -k_2 N_T/B$ . A sample plot is shown in Figure 14. The best value for k, may be determined by plotting  $k_{obs}$  versus  $N_T^{B}$  as shown in Figure 15. In all cases the ionic strength medium was artificial sea water wherein the salinity was varied from 1 to 20°/ ... The pH range covered was relatively narrow (7.4 to 8.2) but is probably typical of estuarine conditions. Data was not included from runs were phosphate buffers had been used. A linear regression on the data of Figure 15 gave a value of 3.1 X 10<sup>6</sup> liters/mole-sec for  $k_2$ . Since this is considerably less than the 6.2 X 10<sup>6</sup> value obtained by Morris and Weil<sup>12</sup> for low ionic strength solutions containing no extra salts, we decided to replicate Morris' original ionic strength conditions as closely as possible in some stopped-flow runs. Values for k2 obtained from three runs at pH 9 and 10.0 ranged from 1.9 to 2.3 X 10<sup>6</sup> liters/mole-sec or about one-third of Morris and Weil's value. At this point, the stopped-flow apparatus was "calibrated" by determining a rate constant for the well known carbonate reaction employing the initial conditions of Berger and Stoddart. A rate constant of 18.5 sec<sup>-1</sup> was measured at 22.9°C. This fell between the 16.6 sec<sup>-1</sup> calculated from the thermal data of Berger and Stoddart and the 19.3 sec<sup>-1</sup> from optical data of Dalyiel.<sup>31</sup> Clearly the stopped-flow apparatus was functioning well within an experimental error of 10%. Morris and Weil worked at lower concentrations and apparently used no injection system to control the mixing process. Their mixing procedure consisted



Figure 14. A plot of ln ( $\Delta A$ ) versus time where  $\Delta A = A_{\infty} - A$  for the appearance of monochloramine. The slope =  $-k_{obs}$ .



Figure 15. A plot of k versus  $N_T/B$  for all kinetic runs at 25°C and salinities 1 to 20°/... The slope is k<sub>2</sub>, the reaction rate constant for the formation of monochloramine.

of simultaneously pouring the solutions together into a beaker. Therefore one would expect substantial variation among their observed rate constants, but this was not the case. They also monitored hypochlorite disappearance and monochloramine appearance by their UV absorbances as well as total and uncombined chlorine using a modified orthotolidinearsenite procedure. There was agreement among these methods on the measured values of k ... However, they were unable to carry out runs in the pH region between 6.5 and 10.0 due to the rapidity of the reaction. Another major point of difference between both procedures was that Morris and Weil worked at a much lower concentration of initial hypochlorite and a lower ratio of nitrogen to chlorine. Their  $N^{\circ}_{T}:Cl^{\circ}_{T}$ ratio was about 2:1 where ours was 15:1. Assuming no error 1. ther procedures implies that there may be a heretofore unnoticed ammonia concentration effect on the kinetics of monochloramine formation. The simple mechanism of equations (14) and (15) may be insufficient to completely describe the rate of monochloramine formation. Clearly, more experiments are needed wherein the initial ammonia concentrations gradually approach the initial hypochlorite concentration. A variation of k<sub>2</sub> with excess ammonia concentration would mean that the reaction is not exactly first order with respect to NH2.

D. The Decomposition of Monochloramine in the Presence of Bromide Initial experiments have been done to investigate the oxidation of bromide ion by monochloramine. Typical plots of  $NH_2Cl$  versus time,  $NHBr_2$ versus time, and the natural logarithm of  $NH_2Cl$  versus time are shown in Figures 16, 17, and 18, respectively. A linear regression on the log plots gave the observed rate constants where slope =  $-k_{obs}$ . Table 3 summarizes the results of these initial experiments. From Table 3, it can be seen that the rate of oxidation of bromide ion by monochloramine is highly dependent upon pH. At pH 7.89, the half-life if 63 minutes whereas at pH 7.10 the corresponding half-life is reduced to 10 minutes. It is not known at this time whether hydrogen ions act catalytically to increase the rate of the reaction or that lower pH conditions favor the formation of an intermediate that in turn reacts with monochloramine.







Figure 17. The concentration of dibromamine versus time.



Figure 18. A plot of ln [NH<sub>2</sub>Cl] versus time at 25°C where slope =  $-k_{obs}$ .

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Experiment Number	pН	[N <sub>T</sub> ] mM	k <sub>obs</sub> (min <sup>-1</sup> )	t <sup>1</sup> 2 (min)
2M-Br-2	7.89	0.69	1.1 X 10 <sup>-2</sup>	63
2M-Br-3	7.34	0.91	$4.3 \times 10^{-2}$	16
2M-Br-4	7.35	0.80	$4.6 \times 10^{-2}$	15
2M-Br-5	7.36	0.82	$4.6 \times 10^{-2}$	15
2M-Br-6	7.10	0.86	$6.9 \times 10^{-2}$	10

Table 3: Observed Rate Constants for the Oxidation of Bromide

(Temperature = 25°C, [NH<sub>2</sub>C1]° = 0.75 mM, [Br]° = 16.0 mM, [Br]° NH<sub>2</sub>C1]° = 22:1)

These preliminary runs indicate that the oxidation of bromide by monochloramine may be very slow in sea water. For full strength sea water at pH 8.1 where the monochloramine concentration is less than 5 mg/l as Cl<sub>2</sub>, the half-life would be greater than 20 hours assuming no loss through demand reactions.

During the course of these early experiments the spectral scans of the low pH solutions (pH 7.1 to 7.3) showed a peak between 220 to 225 nm as illustrated in Figure 19. A peak in this region could not be readily explained by the presence of dibromamine since its  $\lambda_{max}$  occurs at 232 nm.<sup>20,32</sup> Other haloamines that absorb in this region are dichloramine (NHCl<sub>2</sub>) and trichloramine (NCl<sub>3</sub>) which have absorbance maxima at 206 nm and 220 nm, respectively.<sup>33</sup> The formation of these two compounds was not probable since the total ammonia:halogen molar ratio (N<sub>T</sub>:X<sub>T</sub>) was greater than one during the reactions. Also the formation kinetics of NHCl<sub>2</sub> and NCl<sub>3</sub> are slow in the pH region 7.10 to 7.90.<sup>33,34,19</sup>

Another possible explanation for the apparent absorbance peak at 220 nm may be a bromide ion effect. As the monochloramine reacts with the 'romide ion the concentration of bromide in the sample cell decreases while the bromide concentration in the reference cell remains constant. At the end of the reaction the net decrease in bromide ion is equal to the amount of monochloramine reacted. Figure 20 shows a spectrophoto-metric scan of a 0.80 mM bromide solution. Bromide ion absorbs strongly



Figure 19. A UV spectrum of a mixture of monochloramine and bromide at pH 7.1 at 20 minutes









in the lower UV where a large change occurs between 210 and 225 nm. This absorbance, if not blanked out, may affect the spectrum of the reaction solution. The absorbance at any wavelength due to the difference in bromide ion between the reference and sample cells can be expressed as follows.

$$\Delta A_{Br} = \varepsilon_{Br} b \Delta [NH_2C1]$$
(24)  
where:  
$$\varepsilon_{Br} = molar absorbtivity at wavelength \lambda,b = cell path lengthand \Delta [NH_2C1] = amount NH_2C1 reacted (moles/liter)$$

This absorbance correction was made on two runs and Figure 21 shows the results as applied to the spectrum obtained for run number 2M-Br-6. When correcting for the bromide ion effect the peak apparently disappears. One discrepancy still arises after correcting for the bromide ion difference between the reference and sample cells. If dibromamine were the only reaction product one would expect to see a noticeable shoulder in the spectrum near 230 nm. A typical spectrum, illustrated in Figure 19, shows a valley around 230 nm rather than a shoulder which would confirm the presence of dibromamine. At this stage of our investigation, NHBr<sub>2</sub> cannot be precisely identified as a principle reaction product of the reaction between monochloramine and bromide.

#### IV. Conclusions and Future Plans

### A. Chemical Speciation in Chlorinated Sea Water

A mixture of bromamines and monochloramine formed in full-strength chlorinated sea water when the ammonia nitrogen was greater than 0.5 mg/1 and the chlorine dose less than 2.5 mg/1. UV absorbance data and membrane electrode response suggested that dibromamine was the predominale bromamine present. However, at this time, the presence of dibro mamine in chlorinated ammonia rich sea water cannot be confirmed due to the lack of a well-defined peak at 232 nm,  $\lambda_{max}$  for NHBr<sub>2</sub>. Monobromamine could not be detected in any experiments by its UV absorbance at 278 nm. At very high ammonia concentrations (> 0.5 mg/1 NH3-N) and after thirty minutes to an hour, monochloramine was detected as the major component of the total oxidant concentration. This is in agreement with the initial results first reported to us by Morris Roberts of the Virginia Institute of Marine Science on the chlorination of estuarine water. Substantial NH\_Cl formation may also occur at lower nitrogen levels, ~0.3 mg/1, provided ammonia remains in excess. For ammonia nitrogen levels less than 0.4 mg/1 and sufficiently large chlorine doses, tribromamine and hypobromous acid were the major products. Tribromamine was unstable at the sea water pH of 8.1 and decomposed rapidly.

Future experiments will be carried out with both clean sea water and saline water samples taken in the vicinity of operational power generating stations. For some of these experiments the initial chlorine dose will be 1 mg/l. The principal research tool will be the Cary Model 219 spectrophotometer which offers an order of magnitude increase in sensitivity over the Model 14 used in our earlier speciation runs.

B. The Competitive Formation Kinetics of Hypobromous Acid and Monochloramine in Ammonia-Rich Sea Water

The respective rate equations, (3) and (16), for the formation of HOBr and NH<sub>2</sub>Cl share a first-order dependence on HOCl, the hypochlorous acid concentration. Therefore, the relative initial rates of HOBr formation or bromide oxidation and NH<sub>2</sub>Cl formation are independent of initial

chlorine dose provided the molar ratio of ammonia to chlorine is greater than one. As shown previously by Gorchev and Morris,  $^{32}$  the relative rate may be expressed by the following equation which is a result of dividing (3) by (16):

$$R_{\mathbf{r}} = \left(\frac{dB\mathbf{r}}{dt}T\right) \cdot \left(\frac{dM}{dt}\right) = \frac{k_1 [HOC1][B\mathbf{r}] \gamma_{\circ} \gamma \pm / \gamma_B \mathbf{r}}{k_2 [HOC1][NH_3] \gamma_{\circ} \gamma_N / \gamma_M},$$
(25)

which reduces to

$$R_{r} = \frac{k_{1} [Br]}{k_{2} [N_{T}]} (1 + K_{b} a_{H}/K_{w} j \gamma^{\pm}), \qquad (26)$$

where each variable has been defined in previous sections. For R values greater than one, hypobromous acid formation is favored and for values less than one, monochloramine formation is most probable.  $R_r$  is affected by pH, temperature, salinity and ammonia nitrogen. At 25°C values for k, and k, are 3.8 X 10<sup>3</sup> and 3.1 X 10<sup>6</sup> liters/mole-sec as determined in the past year's study. The bromide concentration of ocean and estuarine waters typically follows the salirity and therefore may be expressed as  $[Br] = (0.24 \times 10^{-4} \text{ moles/liter} - g/kg) \times \text{salinity since}$ sea water of salinity 35  $^{\circ}/_{\circ\circ}$  contains 6.8 X 10<sup>4</sup> µg/liter bromide.<sup>35</sup> The activity coefficient,  $\gamma^{\pm}$ , of singly charged OC1 or NH<sub>4</sub> may be calculated from the Davies equation if the ionic strength is known. The ionic strength,  $\mu$ , of sea water (chlorinity 19°/...) is 0.7 and based on this, the ionic strength of diluted sea water can be related to salinity by  $\mu = 0.0204/g/kg$  X salinity where salinity = 1.80655 X chlorinity.<sup>36</sup> Using these relationships with equations (26) and (12) it becomes possible to calculate values of R\_ at different pH's, temperatures, salinities and total ammonia nitrogen concentrations. A useful way of presenting the effect of different variables on R, is to hold two variables, pH and temperature, constant. Consider one variable, say solinity, as an independent variable and determine ammonia nitrogen values that give R = 1. An example of such a plot is shown in Figure 22. Each line represents combinations of ammonia nitrogen and salinity values that give  $R_{1} = 1$ or an equal probability of forming hypobromous acid and monochloramine at the particular pH at 25°C. Combinations that fall below a line produce conditions favorable to the formation of hypobromous acid and hence the bromamines, whereas a combination falling above a line is likely



Figure 22. A plot of ammonia nitrogen and salinity values that give  $R_r = 1$  or an equal probability of forming HOBr or NH<sub>2</sub>Cl at a particular pH. Combinations falling above a pH line produce conditions favorable to the formation of NH<sub>2</sub>Cl whereas combinations below a line are conducive to HOBr formation.

to produce monochloramine. An additional assumption regarding the graph is that the chlorine dose cannot be so large that a 1:1 molar ratio of C1:N is exceeded. On a weight basis this corresponds to a chlorine concentration of 5 times the ammonia nitrogen concentration. A plot such as Figure 22 should prove useful in predicting in a very qualitative way the type of substitution, either chlorination or bromination, that would occur in a given saline water. As an example, for full strength sea water at pH 8.1 with approximately 0.3 - 0.4 mg/1 ammonia nitrogen, one would predict on the basis of Figure 22 that a mixture of monochloramine and bromamines would occur. Indeed this is in qualitative agreement with our earlier speciation experiments. At higher ammonia nitrogen concentrations, 0.5 to 1.0 mg/1, monochloramine would be expected to predominate as was also observed in previous experiments.

The next logical step in the development of rate equations and a model for the chlorine-amponia-bromide system is to determine rate constants for the bromamine formation reactions. However, before this can be done, the following questions must be answered about the monochloramine and hypobromous acid formation kinetics:

- (1) Why is there a discrepency between our results and those of Morris and Weil?<sup>12</sup> If both results are to be believed, then the reaction is not purely first order with respect to ammonia.
- (2) What is the rate of hypobromous acid formation in real ammonia-free sea water? Since our first kinetic runs were carried out in a phosphate-buffered system, it is desirable to obtain data from a more realistic system. This will be relatively simple for the bromide oxidation reaction since there should not be any interfering reactions provided no ammonia were present. It would also be desirable for monochloramine, but unfortunately the naturally occurring bromide precludes this.

Therefore our future plans are to carry out the experiments necessary to answer the above questions and then proceed to gather data on the

### bromamine formation kinetics.

C. The Decomposition of Monochloramine in the Presence of Bromide Initial experiments to investigate the oxidation of bromide ion by monochloramine show that the rate of the reaction is pH dependant. At pH 7.0, the reaction is approximately six times faster than at pH 7.9. In general, the monochloramine oxidation of bromide ion is much slower than the oxidation of bromide ion by hypochlorous acid. If the chemical conditions of the cooling waters are such that the formation of monochloramine is favored then the subsequent oxidation of bromide ion by the monochloramine may become important.

Future work will include a comprehensive study of the kinetics of the reaction, including the effects of pH, ionic strength, temperature, and initial concentration of reactants. We will also carry out runs with real seawater and attempt to better qualify and quantify the reaction products resulting from the reaction. Finally, we will try to develop an adequate description of the reaction mechanism based both on a theoretical and empirical basis and incorporate the mechanism into our overall scheme of important chlorination reactions taking place in sea water.

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## Publications Resulting From This Research

J. W. Inman and J. D. Johnson, "The Effect of Ammonia Concentration on the Chemistry of Chlorinated Sea Water", in <u>Water Chlorination:</u> <u>Environmental Impact and Health Effects</u>, <u>Vol. 2</u>, R. L. Jolley, Ed. (Ann Arbor, Mich.: Ann Arbor Science, 1978).

# Appendix A

Concentration-Time Data For Chemical Speciation Experiments

## Table A-1

Oxidant Speciation in Ammonia-enriched Chlorinated Sea Water

pH = 8.10, T =	25°C, Sal	inity = 3	5°/00,	Total	Organic	Carbon	= 2	mg/1
	Chlorine ]	Dose = $2.$	5  mg/1	added	as NaOCI			-

Run Number	C1/N (Molar	N/C1 ratio)	[NH <sub>3</sub> -N] (mg/1)	, initial (µ molar)	Time (min)	Oxidan TOX	HOBr + OBr	(mg/1 NBr <sub>3</sub>	as CJ 2) NHBr
					1.0	2.02	1.24	0.79	
FS-25-1	11.4	0.088	0.043	3.08	5.0	1.06	0.48	0.59	-
			1.5050		10.0	0.95	0.54	0.41	-
		and the part		Association (1996)	20.0	0.73	0.46	0.28	-
					30.0	0.58	0.36	0.22	-
			+		1.0	2.17	1.14	1.02	
				1	2.5	1.98	1.15	0.84	
FS-25-2	6.25	0.160	0.079	5.64	5.0	1.72	1.13	0.59	1. A 4
					10.0	1.40	1.06	0.34	
		1	1		20.0	1.06	0.89	0.16	1 C H.
					30.0	0.85	0.74	0.10	
			1		1.0	1.31	<0.01	0.92	0.38
- 11 AG		1.	1		2.5	1.11	0.06	0.46	0.58
FS-25-7	3.13	0.319	0.158	11.3	5.0	0.87	0.17	0.28	0.42
					10.0	0.60	0.18	0.09	0.33
		1	1	1	20.0	0.42	0.19	-	0.23
					30.0	0.30	0.07	-	0.24
			1		1.0	1.01	0.17	0.63	0.20
- 1. J. M. M.					2.5	0.78	0.23	0.35	0.20
FS-25-8	2.48	0.403	0.198	14.2	5.0	0.46	0.18	0.16	0.13
					10.0	0.34	0.28	0.01	0.05
		1.1.1.1.1		1	20.0	0.27	0.27	÷ i÷	-
	12 C 11 C 1	11		1	30.0	0.15	0.15	-	

Run Number	Cl/N (Molar	N/Cl ratio)	[NH <sub>3</sub> -N] (mg/1)	, initial (µ molar)	Time (min)	Oxidant TOX	Concentr NHBr <sub>2</sub>	ations (mg NH <sub>2</sub> Cl (di	/1 as Cl <sub>2</sub> ) fference)
	10.557				1.0	1.61	1.291	0.32	
	1.1.1.1				2.5	1.38	1.04	0.34	
	1				5.0	1.11	0.63	0.48	
FS-25-3	1.58	0.63	0.313	22.3	10.0	0.73	0.23	0.50	
	1 3		1		20.0	0.46	0.05	0.41	
	1.0				30.0	0.29		0.29	
	1				1.0	1 09	1 7/2	0.95	
	1.1.1.1				2.5	1.90	1.74	0.25	
FS-25-4	0.00	1 01	0 4 98	25.5	5.0	1.00	1.52	0.33	
	0.55	1.01	0.490	33.5	10.0	1.70	1.20	0.50	
	1 1 2				20.0	1.40	0.92	0.46	
		1.1.1		1.11	30.0	0.70	0.39	0.32	
					1.0	1.08	1 / 52	0.52	
	1				2.5	1 01	1.43	0.53	
FS-25-5	0.496	2.02	0,995	71.0	5.0	1.91	1.20	0.71	
	1			1	10.0	1.63	0.78	0.02	
	1				20.0	1.31	0.60	0.03	
	1 - 1				30.0	1,13	0.50	0.64	
					1.0	1 70	1 252	0.14	0 703
					2.5	1.65	1.25	0.46	0.78
FS-25-6	0.313	3.19	1.58	113	5.0	1 61	0.86	0.50	0.60
					10.0	1.46	0.71	0.74	0.39
			1.		20.0	1 23	0.57	0.74	0.32
	1				30.0	0.89	0.50	0.67	0.42
				1	1 30.0	0.09	0.50	0.39	0.50

Table A-1 continued

(1) Dibromamine concentration calculated from absorbance data.

(2) Dibromamine calculated from electrode data.

(3) Calculated from the absorbance at 245 nm.

Run C1/N		N/C1	N/C1 [NH <sub>3</sub> -N], initial		Time	Oxidant Concentrations (mg/1 as Cl)				
Number	(Molar	ratio)	(mg/1)	(µ molar)	(min)	TOX	HOBr + OBr	NBr 3	NHBr 2	
					1.5	4.49	3.35	1.15		
12.04	Real Providence	N		1.1.6	5.0	3.91	3.08	0.83	-	
FS-5-1	12.5	0.080	0.075	5.35	10.0	3.56	2.92	0.64	-	
				1.000 A.	20.0	2.40	3.07	0.33	-	
	6.433				40.0	3.30	3.16	0.14	-	
10.00					1.5	4.37	2.52	1.84	-	
					5.0	4.11	3.09	1.02	-	
FS-5-2	6.25	0.160	0.160	11.4	10.0	3.73	3.07	0.66	-	
					20.0	3.35	3.01	0.33	-	
		1.1.1		5	40.0	2.48	2.33	0.15	1.75	
					1.0	3.40	0.13	1.63	1.64	
		1.1.1.1.1			5.0	2.64	0.69	0.58	1.38	
FS-5-3	3.13	0.319	0.315	22.5	10.0	2.30	1.00	0.22	1.32	
					20.0	1.80	-		-	
					40.0	1.50		+		
1					1.0	2.20	-	1.04	1.19	
		1.1.1.1	1.1.1.1.1.1		5.0	1.10	-	0.19	0.99	
FS-5-9	2.47	0.405	0.400	28.6	10.0	0.90	-	0.01	0.79	
	1.1.1.1.1.1.1				20.0	0.85	-	-	0.58	
1.1.1.1.1.1.1.1	1.5	1			40.0	0.64		-	0.51	

Table A-2 Oxidant Speciation in Ammonia-enriched Chlorinated Sea Water





# IMAGE EVALUATION TEST TARGET (MT-3)



# MICROCOPY RESOLUTION TEST CHART







# IMAGE EVALUATION TEST TARGET (MT-3)



# MICROCOPY RESOLUTION TEST CHART



Run	C1/N	N/C1	[NH3-N	], initia:	Time	Oxidant	Concentrat	ions (mg/l as Cl_)
Number	(Molar	ratio)	(mg/1)	(v molar)	(min)	TOX	NHBr 2	NH <sub>2</sub> C1 <sup>2</sup>
					1.0	3.73	3.46	이 아이들 말했다. 이 아이들은
					5.0	0.67	0.52	
FS-5-4	1.57	0.637	0.63	45.0	10.0	0.63	0.31	그 옷을 넣는 물건이 많을
					20.0	0.37	0,11	
					40.0	0.25		상태 정치 같은 것
					1.0	4.90	3.08	0.74
					5.0	4.22	1.75	1.51
FS-5-5	1.00	1.00	1.00	71.4	10.0	3.48	1.57	1.03
					20.0	2.60	1.23	0.80
					40.0	1.64	0.75	0.92
					1.0	5.50	1.74	3.19
					5.0	5.32	1.29	3.46
FS-5-6	0.500	2.01	2.00	143	10.0	5.00	1.18	3.30
					20.0	4.40	1.05	3.02
					40.0	3.90	0.81	3.25
					1.0	4.50	0.84	3.66
					5.0	4.23	0.63	3.71
FS-5-8	0.313	3.20	3.16	226	10.0	4.11	0.48	3.59
					20.0	3.86	0.44	3.36
					40.0	3.40	0.30	3.00

.....

Table A-2 continued

# Appendix B

Kine~ic Data for the Oxidation of Bromide by Hypochlorous Acid
# Table B-1

# Bromide Oxidation by HOC1

# $T = 25.2 \pm 0.2^{\circ}C$ [Br]° = 2.5 X 10<sup>-3</sup>M(200 mg/1 as Br) [HOC1]° + [OC1<sup>-</sup>]° = 0.158 X 10<sup>-3</sup> M (11.2 mg/1 as C1<sub>2</sub>)

Set	<u>рН</u>	[C1](Molar)	Average k (sec <sup>1</sup> ) <sup>obs</sup>	s.d.	Error from pH	Total Error (±)
6-A	8.07	0.05	1.58	0.02	0.08	0.10
В	8.06	0.10	1.71	0.04	0.09	0.13
С	8.09	0.20	1.51	0.04	0.08	0.12
D	8.08	0.35	1.41	0.04	0.07	0.11
Е	8.07	0.50	1.43	0.03	0.07	0.10
7-A	7.82	0.05	2.87	0.18	0.11	0.29
В	7.83	0.10	2.86	0.15	0,11	0.26
С	7.83	0.20	2.60	0.10	0.10	0.20
D	7.85	0.35	2.85	0.05	0.10	0.15
E	7.86	0.50	2.41	0.13	0.10	0.23
8-A	7.52	0.05	4.16	0.11	0.12	0.23
В	7.52	0.10	4.04	0.15	0.12	0.27
С	7.54	0.20	4.01	0.24	0.12	0.36
D	7.56	0.35	3.79	0.11	0.11	0.22
Е	7.57	0,50	3.54	0.40	0.11	0.51
9-A	7.21	0.05	5.75	0.15	0.12	0.27
В	7.22	0.10	5.87	0.21	0.16	0.37
С	7.24	0.20	5.44	0.23	0.11	0.33
D	7.24	0.35	5.40	0.45	0.11	0.56
E	7.24	0.50	5.37	0.81	0.11	0.92
0-A1	8.16	(T=20.6°C)	1.19	0.02	0,06	0.08
В	8.15	$(T=14.4^{\circ}C)$	1.09	0.02	0.05	0.07
C	8.16	(T=30.8°C)	1.36	0.02	0.07	0.09

(1) [C1<sup>-</sup>] = 0.10 Molar

Appendix C

Kinetic Data for the Formation of Monochloramine in Artificial Sea Water

# Table C-1

# Monochloramine Formation

Т	= 25.1 :	± 0,1°C, [N	$H_4C1]^\circ = 2$	.5 X 10 <sup>-3</sup> <u>M</u> , [0	C1 <sup>-</sup> ]° =	0.16 x	10 <sup>−3</sup> <u>M</u>
Set	рH	Salinity g/kg	μ (molal)	Average k (sec <sup>-1</sup> ) <sup>obs</sup>	s.d.	pH Error	Total Error
11-A	8.93	1.76	0.035	70.6	1.9	0.7	2.6
В	8.96	3.01	0.060	65.2	1.0		1.7
С	9.00	5.52	0.110	59.8	1.3	11	2.0
D	9.02	10.5	0.210	57.2	0.5	**	1.2
Е	8.46	20.6	0.410	56.6	3.2		3.9
12-A	7.49	1.51	0.031	50.1	0.3	#	1.0
В	7.57	2.81	0.056	43.9	2.5		3.2
С	7.42	5.32	0.106	41.0	0.9	11	1.6
D	7.44	10.4	0.206	31.1	0.1		0.8
Е	7.46	20.4	0.406	28.8	0.7		1.4
13-A	7.80	1.51	0.031	63.3	1.3		2.0
В	7.83	2.81	0.056	59.0	1.0		1.7
С	7.85	5.32	0.106	55.4	0.8	17	1.5
D	7.87	10.4	0.206	50.7	2.4		3.1
Е	7.88	20.4	0.406	48.2	1.2	11	1.9
14-4	8.17	1.51	0.031	71.2	1.2	0.3	1.5
	8.17	2.81	0.056	-	-	11	-
	8.20	5.32	0.106	65.9	2.0		2.3
υ	8.20	10.4	0.206	57.3	1.7		2.0
E	8.21	20.4	0.406	51.8	0.8	"	1.1
15-A	10.88	no added	0.003	1.97	0.05	0.04	0.09
В	10.02	salts	11	12.2	0.3	0.7	1.0
С	8.89		11	66.5	2.9	0.7	3.6

#### Appendix D

# Temperature Dependence of $K_a$ , $K_b$ , $K_w$ and j

Values for  $\rm K_a,$  the dissociation constant for hypochlorous acid, were calculated from the following equation which was derived empirically by Morris.  $^{24}$ 

$$pK = 300.0/T - 10.0686 + 0.0253 T$$
,

where  $pK_a = -\log K_a$ . An equation for  $K_b$ , the dissociation constant for ammonia, was derived by fitting the data of Bates and Pinching<sup>28</sup> to the following cubic equation:

 $pK_b = 28.2937 - T (0.21263 - T (6.39648 \times 10^{-4} - T \times 6.4175 \times 10^{-7}))$ An equation for K<sub>w</sub>, the dissociation constant for water, was derived in

a similar manner from the data of Harned and Geary.<sup>29</sup>

$$pK_{T} = 59.6786 - T (0.3420 - T (8.6388 \times 10^{-4} - T \times 7.7315 \times 10^{-7}))$$

The temperature dependence of j was determined from the relationship,

 $\log j = -(Ej_{+} - Ej_{+}) F/2.303 RT = -\Delta EF /T,$ 

where  $E_{jt}$  and  $E_{jb}$  are the calculated junction potentials for sea water solutions and phosphate buffer solution against a saturated KCl reference electrode filling solution.<sup>25,26</sup>

#### GLOSSARY

<u>Units for Oxidant Concentrations</u> - The concentrations of oxidants such as  $Cl_2$ , HOC1, HOBr, NBr<sub>3</sub>, NH<sub>2</sub>C1, etc. are typically expressed as milligrams/liter, moles/liter, equivalents/liter and microequivalents/ liter (µeq/1). Since all oxidants mentioned in this report are derived from chlorine or hypochlorite doses, they are always expressed as milligrams/liter (mg/1) as  $Cl_2$ . One mg/1 of  $Cl_2$  is equivalent to 14.1 X 10<sup>-6</sup> moles/liter of HOC1, because 1 mole of  $Cl_2$  hydrolyzes to give 1 mole of HOC1 according to the reaction;

$$H_{2}O + C1_{2} \iff HOC1 + C1^{-} + H^{+}$$

The molar concentration of HOCl equivalent to 1 mg/l of  $Cl_2$  is calculated as follows:

 $\frac{1 \text{ mgCl}_2}{1 \text{ tter}^2} \times \frac{1 \text{ mole } Cl_2}{70.91_6} \times \frac{1 \text{ g}}{Cl_2} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{1 \text{ mole } HOC1}{1 \text{ mole } Cl_2} = 14.1 \text{ 10}^{-6} \text{ mole } HOC1/1 \text{ iter}$ 

One mole of HOC1 is also equivalent to one mole of HOBr so that 14.1 X  $10^{-6}$  moles/liter (14.1 µM) HOBr is also equivalent to 1 mg/1 of Cl<sub>2</sub> on a molar or equivalent basis. Equivalents/liter is a measure of a compound's potential oxidizing ability. The halogens in Cl<sub>2</sub>, Br<sub>2</sub>, HOC1, HOBr, NBr<sub>3</sub>, NHEr<sub>2</sub>, NH<sub>2</sub>Cl, etc. are in the +1 oxidation state and are typically reduced to the -1 state when a redox reaction occurs. Because a 2 electron change takes place, there are 2 equivalents per mole of Cl<sup>+1</sup> or Br<sup>+1</sup>. Therefore, 1 mg/1 of Cl<sub>2</sub> is equivalent to 28.2  $\times$  10<sup>-6</sup> equivalents/liter. One mole of NBr<sub>3</sub> has an equivalent concentration 6 times its molar concentration since there are 3 Br<sup>+1</sup> atoms per molecule. In this report the oxidant concentrations were usually expressed as mg/1 as Cl<sub>2</sub> for the chemical speciation experiments and as molarities for the kinetic runs.

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