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THE KINETICS OF CHLORINE-AMMONIA REACTIONS IN SEA WATER

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Quarterly Report

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I. INTRODUCTION

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During this period the rate of monochloramine formation was further characterized as a function of pH, ionic strength and ammonia concentration. Work was begun on the first Annual Report and our stopped-flow apparatus and associated equipment were ordered after receiving formal notice of the Contract's continuation in September. Further work was also done to identify the reaction products of monochloramine with bromide.

II. EXPERIMENTAL

A. The Kinetics of Monochloramine Formation

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The experimental procedures followed during this period were identical to those described in our first Annual Report.¹

B. The Decomposition of Monochloramine in the Presence of Bromide

Most reagents and stock solutions were identical to those described in the first Annual Report.¹ Different solution compositions and experimental procedures are covered in the Results and Discussion section.

III. RESULTS AND DISCUSSION

A. The Kinetics of Monochloramine Formation

Fourteen additional sets of stopped-flow kinetic runs were carried out to determine the effects of pH, temperature, ionic strength and ammonia concentration on the rate of monochloramine formation in artificial sea water solutions. The results are summarized in Table 1.

The Effect of pH. The effect of changing pH at a constant ionic strength and temperature (25°C) is presented in Figure 1. The results are similar to those obtained by Weil and Morris² who extrapolated their low and high pH data to determine the effect of intermediate pH's. The work presented here is the first known attempt to measure the very rapid rates of monochloramine formation over the pH range 7.0 to 10.0. As shown in the plot, the rate of monochloramine formation from armonia and hypochlorous acid reaches a maximum between pH 8.2 and 8.6 and rapidly falls off on either side of these values. The solid points represent experimentally observed rate constants for a series of stopped-flow runs and the curve was fitted to these data with a reaction rate constant of 2.8 \pm 0.2 x 10⁶ liters/mole-sec. This value is approximately one half the value of 6.2 x 10⁶ liters/mole-sec obtained by Morris and Weil. At first it was thought that this disagreement was due to the difference in ionic strength conditions for both sets of data. This was not the case. since our work (sets 18-A, 22-A,B,C) showed that in solutions of very low ionic strength such as those employed by Morris, the rate constant would be expected to decrease rather than increase. An increase would be necessary to account for the discrepancy. However, their conditions also differed from ours in regard to the initial reactant concentrations. Their initial ammonia concentrations covered the range 1.4 to 7.2 x 10^{-5} M whereas ours were considerably higher at 2.5 to 7.5 x 10^{-3} M. Their experiments were also carried out under second order conditions whereas ours were also carried out under pseudo-first order conditions. If both sets of data are accurate then the source of the difference between rate constants may have been due to the rather large difference in

initial ammonia concentrations. In order to test this hypothesis some additional kinetic runs were carried out and the results are discussed in the following section.

Order with Respect to Ammonia Concentration. In runs 20-A and 20-B the respective ammonia concentrations were doubled and tripled. From this rather limited amount of data an estimate of the reaction order was obtained by plotting $\ln (k_{obs})$ versus $\ln (N^{\circ}/B)$ as shown in Figure 2, where N° is the initial ammonia concentration and B has been defined in a previous report. The order was found to be 0.8, not 1.0 as expected. As the following discussion explains, the 0.8 value is consistent with both sets of data. if the true order is assumed to be 0.8 then it is possible to extrapolate either our own or Morris' data to different ammonia concentrations. Based on our new data, the initial reaction rate at any initial ammonia concentration may be expressed with the equation,

$$v = k \cdot [N^{\circ}]^{0.8} \cdot C,$$
 (1)

where $v = d[NH_2Cl]/dt$ and C is a constant at any given pH, temperature, hypochlorite concentration and ionic strength. The initial rate over a small range of ammonia concentrations may be expressed by the first order expression,

$$v_{\mathbf{x}} = k_{\mathbf{x}} \cdot \mathbf{N}_{\mathbf{x}}^{\circ} \cdot \mathbf{C}, \qquad (2)$$

which was employed in the present work and by Morris. Since (1) is valid at any ammonia concentration, then

$$k_{x} \cdot N_{x}^{\circ} \cdot C = k \cdot [N_{x}^{\circ}]^{0.8} \cdot C$$

$$k = k_{x} \cdot [N_{x}^{\circ}]^{0.2}$$
(3)

If N and N^o_b represent the respective ammonia concentrations for our kinetic runs and those of Morris, then

or

TABLE 1

Monochloramine Formation

$T = 24.9 \pm 0.2^{\circ}C$, $[NH_4C1]^{\circ} = 2.5 \times 10^{-3} M$, $[OC1^{-3}]^{\circ} = 0.16 \times 10^{-3} M$

Comments	Set	pH	μ (molal)	Average k _{0bs} (sec ⁻¹	s.d.	pH Error	Total Error	$k_1 \ge 10^{-6}$ (liters/ mole-sec)	N°/B x 10 ⁵
Carbonate reaction to test accuracy of stopped-flow apparatus	16-17			18.5	(16.6-19	.3 from	data of	Berger ⁷ and	Dalziel ⁸)
No added salts	18-A	9.88	0.003	31.1	2.0	0.7	2.7	1.79	1.74
Constant ionic	19-A	6.78	0.20	16.8	2.6	0.7	3.3	3.33	0.504
strength, pH	В	7,23	0.20	30.2	0.5		1.2	2.87	1.05
varled	С	7.83	0.20	51.7	2.1		2.8	2.86	1.81
	D	8.92	0.20	49.0	1.8		2.9	2.75	1.78
	E	9.96	0.20	13.3	0.5	"	1.2	2.66	0.498
[NH C1]° x 2	20-A	10.02	0.205	21.7	0.4	0.7	1.1	2.40	0.904
" x 3	В	9.97	0.207	32.4	0.4	"	1.1	2.16	1.50
Temperature	21-A	9.48	T=30.8°C	33.0	5.6	0.7	6.3	2.91	1.13
varied	В	9.76	20.3°C	16.9	0.4		1.1	2.46	0.690
$(\mu = 0.20)$	С	9.91	15.3°C	11.8	0.2	"	0.9	2.20	0.538
Ionic strength varied	22-A	8,71	0.006	70.9	7.6	0.5	8.1	2.36	3.00
over a low salinity	В	8.79	0.020	70.0	2.6		3.1	2.67	2.62
range	С	8,83	0.063	62.2	3.1	"	3.6	2.80	2.23
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 $B = (1 + K_a j / \tilde{a}_H \gamma \pm) (1 + K_b \tilde{a}_H / K_w j \gamma \pm)$

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Figure 1. Observed rate constants for the formation of monochloramine as a function of pH. Solid points are experimental data and the curve was calculated for a reaction rate constant of 2.8 x 10⁶ liters/mole-sec.





$$k = k_{a} \cdot [N_{a}^{\circ}]^{0.2} = k_{b} \cdot [N_{b}^{\circ}]^{0.2}, \qquad (4)$$

where k_a and k_b are the respective first order rate constants determined over a narrow range of ammonia concentrations. One rate constant may now be calculated in terms of another since

$$k_b = k_a [N_a^\circ] 0.2/[N_b^\circ]^{0.2}$$
 (5)

By substituting $k_a = 2.8 \times 10^6$ liters/mole-sec $N_a = 2.5 \times 10^{-3} M$ and $N_b = 5.0 \times 10^{-5} M$ (an average of Morris' initial ammonia concentrations) into (5) a value of 6.1 x 10^6 liters/mole-sec was calculated for k_b . This value is in agreement with the constant determined experimentally by Morris. Therefore, what was initially thought to be a discrepancy between rate constants was a function of the different ammonia concentrations employed in each study and a reaction order that is not exactly 1.0 but 0.8 with respect to ammonia. This means that the first order mechanism for the formation of NH₂Cl may not be valid over a wide range of ammonia concentrations. Any model that attempts to predict the speciation of chlorinated waters containing ammonia should correct the first order to a first order constant with equation 4.

The Effect of Ionic Strength or Salinity. Figure 3 shows the effect of varying ionic strength on the observed rate constant at 25°C and a relatively constant pH (8.7 to 8.9). The data for this plot were taken from runs 15-C, 19-D, and 22-A,B and C. The observed effect is a decrease in the value for k_{obs} as the ionic strength or salinity is increased. At salinities above 2.0 the effect is adequately accounted for in our model using Davies' equation to estimate activity coefficients. This can be seen in Figure 2 where there is a good agreement between calculated and experimental points at high ionic strengths. At salinities below 2.0 and ionic strengths less than 0.02 the fit is not as good. The model predicts a k_{obs} that is too large. Perhaps a more correct way of reviewing this is to say that a model based on the low ionic strength data would not account for the data at high ionic strength and would predict a k_{obs} that was too low. Evidently there is an additional effect of



Figure 3. Dependence of the observed rate constant on the ionic strength. Circles are calculated values and solid points are experimental values.

increasing ionic strength that causes an increase in the formation rate and hence an increase in k_{obs} . This may be due in part to additional production of NH₂Cl by the reaction of ammonia with ion pairs such as NaOCl or Mg(OCl)₂. It is not a large effect and could be ignored in saline waters where the salinity is greater than $2^{\circ}/_{\circ \circ}$. Figure 4 is a plot of k_{obs} versus N°/B for all kinetic was carried out to date wherein the salinity was greater than $2.5^{\circ}/_{\circ \circ}$. Figure 5 is an identical plot with the addition of data from the lower salinity runs. These plots represent a test of the rate equation or model used in correlating our kinetic data. Although application of the model is best restricted to salinities above $2^{\circ}/_{\circ \circ}$, it may be adequate for predicting the speciation of chlorinated waters over a wide pH range.

<u>Temperature Dependence</u>. Figure 6 is a plot of $\ln k$ versus $^{1}/T$ and shows the temperature dependence of the reaction rate constant from 15 to 30°C. An activation energy of 3080 cal was calculated from the slope.

B. The Decomposition of Monochloramine in the Presence of Bromide

1. Results

In the past four months our research has been directed towards identifying the principle reaction products obtained when reacting millimolar concentrations of monochloramine with an excess of bromide ion. In our previous Annual Report¹ it was shown that when reacting monochloramine with excess bromide ion a UV spectrum was obtained that exhibited a peak near 225 nanometers (nm). It was noted that none of the known haloamines have absorbance maxima that could explain the presence of the apparent peak. We also postulated that the peak may have been an artifact in the spectrum caused by the difference in bromide ion concentrations between the reference and sample cells as the reaction proceeded. Attempts have now been made to positively identify the principle reaction product and correlate the observed UV spectrum to the product.



Figure 4. A test of the rate equation where k is plotted versus N°/B (see reference 1) for $S > 2.5^{\circ}/_{\circ\circ}$.







Figure 6. Temperature dependence of k, the reaction rate constant for the formation of monochloramine

<u>Voltammetric Scans</u>. Voltammetric scans were done on solutions of dibromamine (~100 μ M) and the reaction mixture of monochloramine (0.45 mM) and bromide ion (16 mM). Temperature was maintained at 14°C and the solutions were buffered at pH 6.8. A three electrode cell was employed using a rotating platinum electrode (RPE) as the working electrode, a saturated colomel electrode as the reference, and a platinum foil auxiliary electrode. The actual electronic apparatus and experimental cell design are described elsewhere.³

Figure 7 is a normalized plot of microamps diffusion current per micromole of oxidant (μ Amp/ μ MOx.) versus millivolts applied. The solid line represents the response of a solution of ~100 μ M NHBr₂. The dashed line represents the response from a solution of monochloramine (0.45 mM) and an excess of bromide ion (16 mM). The dibromamine concentrations were calculated during the scan from UV data absorbance obtained from the Cary 219 spectrophotometer. This method was described previously.¹ The current response for the solution mixture was divided by the corresponding dibromamine concentrations and the normalized data points plotted.

The voltamagrams are similar in response over the range of 800 to 100 millivolts applied. In the region from 100 mv to 0 mv the monochloramine/bromide ion solutions response increases dramatically. It is spectulated that this increase in response is due to the reduction of monochloramine present in the solution as well as the reductions of dibromamine at these applied voltages. Voltammetric scans of monochloramine indicate that it will begin to produce sizeable diffusion current when the voltage applied is less than +100 millivolts.⁴

It is reasonable to spectulate from these experiments that dibromamine or a haloamine with very similar electrochemical properties is the principal reaction product when monochloramine is reacted with an excess of bromide ion.



Ether Extraction Experiments. The solubilities of the three chloramines in ethyl ether vary considerably and this property has been exploited as a separation method.⁵ Monochloramine is slightly soluble in ether while dichloramine is highly soluble and trichloramine is readily soluble. While specific data on the solubility of the three bromamines in ether is lacking, it seems plausible that the bromamine solubilities are roughly equivalent to their respective chloramine counterpart. The bromamines have been formed in ether and their UV spectra characterized.⁶ Therefore ether extractions seemed to be a promising technique for the identification of reaction products formed in haloamine reactions. In addition to its high affinity for dibromamine, ether also rejects the excess bromide ion during the extraction process, thereby removing a potential interference in the UV spectrum below 2.5 nm.

Ether Extractions of Reaction Mixtures of Monochloramine and Excess

Bromide Ion. Monochloramine (1.5 mM) was reacted in an aqueous solution of excess bromide ion (32 mM) buffered at pH 7.0. After 15 minutes 50 ml of the reaction solution was placed in a separatory funnel with 50 ml of ethyl ether. The funnel was shaken gently for 1 minute and the ether phase drawn off and a sample run in the Cary 219. Figure 8 is the UV spectrum acquired from the ether extraction solution. Note the pronounced peak at 218 nm and the broad peak around 250 nanometers. Next, a similar extraction procedure was made on pure solutions of dibromamine and monochloramine. Fifty ml of 2.1 mM monochloramine stock was extracted into 50 ml of ether and a UV spectrum obtained for the extract. Figure 9 shows the spectrum with a peak at 254 nanometers. Similarly, a 0.40 mM solution of dibromamine was extracted into ether and the spectrum shown in Figure 10 was obtained for the extract. A peak for dibromamine appears at 234 nm and a slight hump at 290 nm indicating the presence of monobromamine in the extract. The observed λ_{max_e} for dibromamine at 234 nanometers agrees with that obtained by Gorchev.

Bromination of Monochloramine and Ether Extraction. A 0.72 mM solution of monochloramine was reacted with 0.50 mM solution of hypobromous acid (HOBr) at pH 7.0 with an excess of ammonium ion (6.75 mM). After 1 minute







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Figure 9. Ether extraction spectrum of 2.0 mM monochloramine stock solution.



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a 25 ml aliquot was extracted into 25 ml of ethyl ether and a UV spectrum was obtained as shown in Figure 11. The extraction solution exhibits a well defined peak at 218 nanometers.

<u>Chlorination of Monobromamine and Ether Extraction</u>. Hypochlorite ion (2.5 mM) was reacted with approximately 0.6 millimoles of monobromamine (NH₂Br) at pH 8.5 in excess ammonia (50 mM). After 30 seconds a 25 ml aliquot was extracted into 25 ml of ether and once more a UV spectrum was obtained as shown in Figure 12. Two UV maxima were observed, one at 250 nm, corresponding to monochloramine, and the other at 220 nm as in previous extractions.

Ether Extraction of a Solution Mixture of Monochloramine and Monobromamine. An experiment was conducted to measure the relative reactivity of monochloramine and monobromamine with each other and to try to obtain a UV spectrum of the solution extracted into ether. A reaction mixture of monochloramine (0.54 mM) and monobramamine (0.75 mM) in an excess of ammonia (100 mM) buffered at pH 9.0 was allowed to react for 100 minutes. A 25 ml aliquot was extracted into 25 ml of ether and a UV spectrum obtained for the extract. Figure 13 shows a peak corresponding to monochloramine and monobromamine mixture.

2. Discussion

The UV spectra obtained in the previously described ether extraction experiments indicate that when monochloramine is reacted with excess bromide ion a compound is formed that has a UV maximum near 220 nm in ether. This compound is probably not dibromamine as previously suspected since λ_{max} for dibromamine is around 235 nm in ether. It was also found that this compound could be formed by reacting hypobromous acid with monochloramine, and also by reacting hypochlorite ion with monobromamine. In all three cases the UV spectra of the ether extract showed a well defined peak at 220 ± 2 nm.







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The compound responsible for the 220 nm peak has not been positively identified, but we hypothesize that it may be bromochloroamine (NHBrCl). The experimental evidence indicates that the compound is formed when (1) hypobromous acid reacts with monochloramine, (2) hypochlorite ion reacts with monobromamine and (3) monochloramine reacts with excess bromide ion.

<u>Case 1: Hypobromous Acid Reacting with Monochloramine</u>. When hypobromous acid reacts with monochloramine in the presence of excess ammonia, two possible competing reactions can be envisioned.

 $2HOBr + NH_3 \rightarrow NHBr_2 + 2H_2O$ (1) known HOBr + NH_2Cl + NHBrCl + H_2O (2) hypothesized

The ether extract for such a reaction mixture indicated that little or no NHBr₂ was formed as a peak corresponding to NHBr₂ at 234 nm was absent in the ether extraction spectrum (see Figure 11). Thus if reaction (2) does indeed occur it must be faster than reaction (1) as written. It is hypothesized that reaction (2) is the principle reaction and NHBrCl is responsible for the peak at 220 nm in the ether extract.

<u>Case 2: Chlorination of Monobromamine</u>. Approaching the same system from a slightly different aspect we can analyze the experimental evidence acquired from the chlorination of monobromamine. The UV spectrum of the ether extract showed a well defined peak for monochloramine at 250 nm and the unknown peak at 220 nm (see Figure 12). Two possible reactions that may occur in such a system are:

HOC1 +	NH ₂ →	NH ₂ C1 + H	H ₂ 0	(3)	known
HOC1 +	NH ₂ Br →	NHBrC1 +	H ₂ 0	(4)	hypothesized

Clearly, reaction (3) is responsible for the peak observed at 250 nanometers, the formation of bromochloroamine in reaction (4) is again hypothesized to be responsible for the peak observed at 220 nanometers.

<u>Case 3: Reaction of Monochloramine with Bromide Ion.</u> When reacting monochloramine and excess bromide ion it was found that the principle reaction product exhibited a UV maximum at 220 nm when extracted into ether (see Figure 8). One possible reaction pathway to explain the peak at 220 nm is hypothesized below:

$$NH_2C1 + Br = \frac{810w}{H_2O} + HOBr + NH_3 + C1$$
(5)

$$HOBr + NH_2C1 \xrightarrow{fast} NHBrC1 + H_2O$$
(6)

The final product is proposed to be bromochloroamine as in Case 1 and Case 2.

An additional pathway that has been hypothesized to explain the formation of NHBrCl and the 220 nm peak is :

$$NH_2C1 + Br \longrightarrow NH_2Br + C1$$
 (7)

$$NH_2Br + NH_2C1 \longrightarrow NHBrC1 + NH_3$$
 (8)

However, this mechanism is probably not responsible for the observed 220 nm peak since no such peak was obtained when a solution of monochloramine and monobromamine was extracted into ether (see Figure 13).

It should be emphasized that the foregoing analysis of the various haloamine reactions are speculative. The hypothesis that bromochloramine (NHBrCl) is responsible for the 220 nm peak observed in the reaction extracts needs to be substantiated by a more definitive analyical technique.

IV. CONCLUSIONS AND FUTURE PLANS

A. Rapid Formation Kinetics

The kinetics of monochloramine formation have now been studied over a range of salinities and pH's typical of natural waters. A rate equation has been developed that will mathematically describe the rate of NH2Cl production from pH 7 to 11, at salinities greater than 2 %..., and at temperatures from 15 to 30°C. The one remaining area that may require some attention is the effect of ammonia concentration. Our most recent data indicate that the order is not 1.0 but 0.8 with respect to ammonia. In order for our rate equation to be accurate at all ammonia concentrations it is necessary to apply an empirical correction to the rate constant before extrapolation. Although it would be desirable to support this correction with a suitable mechanism, a large number of additional kinetic runs would be needed to do this. We therefore plan to postpone such work until we obtain our own stopped-flow system and can more efficiently perform the experiments and process data. Our efforts can now be shifted to such experiments that can be performed in our own laboratory. These include a study of the formation of hypobromous acid in sea water samples under second order conditions and halogen speciation experiments at low (~ 1 mg/1) chlorine concentrations.

B. The Decomposition of Monochloramine in the Presence of Bromide When monochloramine reacts with bromide ion a product is formed that exhibits a UV absorbance maximum at 220 nm in both aqueous solutions and ether extracts. Since no peak was observed near 232-235 nm, it is unlikely that dibromamine was present in concentrations approaching those of the unknown product. The compound has been tentatively identified as NHBrCl, although a definitive analysis is needed. Future work will involve the use of mass spectrometry to help determine the speciation of these reaction mixtures. We will also continue to measure the reaction rates of monochloramine and bromide ion as a function of pH and reactant concentrations. A reaction rate constant will be determined and a mechanism postulated.

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