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THE KINETICS OF CHLORINE-AMMONIA REACTIONS

IN SEA-WATER

Quarterly Report

April 1, 1979 to June 30, 1979

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1624 271

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I. Introduction

During the early part of this quarter, our minicomputer and associated data acquisition hardware arrived and work was begun on the hardware and software interfaces to the stopped-flow spectrophotometer. The culmination of this effort was a PDP-11 assembly language program capable of acquiring data from the photometer output at a rate of 10,000 16-bit words per second. The program also stores data on IBM standard flexible diskettes in a form accessable by high-level languages. Data handling programs were developed in PASCAL to run under RT-11, our minicomputer's disk operating system. Since most of these routines had previously been written in PL-1 to run on an IBM 370, implementation on the mini will represent a considerable savings in computer funds.

A series of kinetic experiments were begun to measure the formation rate of dibromamine under conditions of excess ammonia and neutral pH. The results of experiments to determine the order with respect to initial hypobromous acid concentration are presented in this report.

II. Experimental

A. Reactant Solutions

Reactant solutions were prepared in 250 ml volumetric flasks by diluting stock solutions of sodium hypobromite (10 mM) and ammonium chloride (0.0400 M) to the desired concentrations. Each solution was buffered with phosphate to maintain an ionic strength of 0.033 M and the pH adjusted with 0.1N HCl and 0.1N NaOH. Total Oxidizing bromine was determined amperometrically prior to and after a set of stopped-flow runs.

B. Procedures

Each solution was introduced into the thermostatted (25°C) reservoir syringes of the stopped-flow apparatus and allowed to equilibrate for approximately five minutes. A set of five replicate kinetic runs were immediately performed and the voltage-time data stored on floppy disk media. Sets were done at 232 and 278 nm, absorbance maxima for $NHBr_2$ and NH_2Br.

C. Methods

Relative absorbances or absorbance changes were computed from the raw stopped-flow data by the equation

$$\Delta A = \text{Log} \left\{ \frac{V_\infty - VOS2 + VOS1 \cdot GAIN}{V_2 - VOS2 + VOS1 \cdot GAIN} \right\} \quad , \text{ where VOS1 and}$$

VOS2 are offset voltages of the two operational amplifiers composing the photometer, V_∞ is the output voltage at $t = \infty$ or complete reaction, V_2 is the time dependent output voltage of the final stage and "GAIN" is amplifier gain. If no assumptions are made about reaction stoichiometry or

conservation of oxidizing bromine, the following equation may be used to calculate the rate of dibromamine formation:

$$v_0 = \frac{d[NHBr_2]}{dt} = [\ 1/(\epsilon_{232}^{Di} - \epsilon_{232}^{M} \cdot \epsilon_{278}^{Di} / \epsilon_{278}^{M})\ ] \left\{ -\frac{d(\Delta A_{232})}{dt} - \frac{\epsilon_{232}^{M}}{\epsilon_{278}^{M}} \cdot \frac{d(\Delta A_{278})}{dt} \right\}$$

where ϵ_x^M and ϵ_x^{Di} are the molar absorptivities of NH_2Br and $NHBr_2$ for a 1 cm light path. Since observed absorbance changes at 278 nm were always small relative to those at 232 nm, the second term could be neglected. Therefore the rate of $NHBr_2$ formation was directly proportional to $-d(\Delta A_{232})/dt$. This quantity was used to determine reaction orders from initial rates. The initial formation rate was calculated by fitting an exponential function to the early (~ 10%) part of the ΔA-time curve and extrapolating to zero time.

III. Results and Discussion

Eight sets of runs were done to determine the effect of initial bromine concentration on the initial rate of $NHBr_2$ formation. The concentrations of Br^+ were 0.019, 0.040, 0.102 and 0.190 m$\underline{M}$ (corresponding to 1.3-13.0 mg/1 as Cl_2) and the ammonia concentration was 2.0 m$\underline{M}$ (28 mg/1 N) in all cases. The high ammonia concentration was necessary to prevent "breakpoint" reactions and insure that $NHBr_2$ and NH_2Br were the only bromamines present. The ionic strength and pH were maintained at 0.033 $\underline{M}$ and 7.00 $\pm$ 0.02 respectively by 0.02M phosphate buffer. The times required for complete reaction varied from eight to forty seconds, so there was no interference from the formation of NH_2Br from NH_3 and HOBr, since that reaction is complete in approximately 40 milliseconds under the above conditions. For this reason, the initial bromine concentration was essentially the initial monobromamine concentration. The results of these runs are summarized in Figure 1, wherein the logarithm of the initial rate of $NHBr_2$ formation is plotted against the logarithm of initial bromine (or monobromamine) concentration. The slope of 1.94 is indicative of a reaction that is second order with respect to the initial monobromamine concentration. A rough estimate of the second order, pH dependent rate constant for $NHBr_2$ formation at pH 7.00 and 25°C was computed from the intercept in the following manner. The empirical differential rate law at time zero may be expressed as

$$\left. \frac{d\Delta A_{232}}{dt} \right|_{t=0} = \epsilon v_o = \epsilon k[NH_2Br]^2 \text{ , where } \epsilon = 1/(\epsilon_{232}^{Di} - \epsilon_{232}^{M} \cdot \epsilon_{278}^{Di}/\epsilon_{278}^{M})$$

and k is a second order rate constant. Taking the logarithm of both sides

yield $\ln(d(\Delta A_{232})/dt) = 2 \cdot \ln[NH_2Br]_o + \ln(\epsilon \cdot k)$, where $\ln(\epsilon \cdot k)$ is the intercept from Figure 1. Values for the molar absorptivities of mono- and dibromamine at 232 and 278 nm, based on recent measurements in this laboratory, are $\epsilon_{232}^{Di} = 2000$, $\epsilon_{278}^{M} = 163$ and $\epsilon_{278}^{M} = 324$, which give $\epsilon = 1830$ and a value for k of 1.3×10^3 liters/mole-sec. Unfortunately, a value for ϵ_{278}^{Di} cannot be determined very precisely since it is virtually impossible to obtain a pure aqueous solution of $NHBr_2$ without the presence of either NBr_3 or NH_2Br. However, a fifty percent error in estimating ϵ_{278}^{Di} only introduces a five percent error in ϵ.
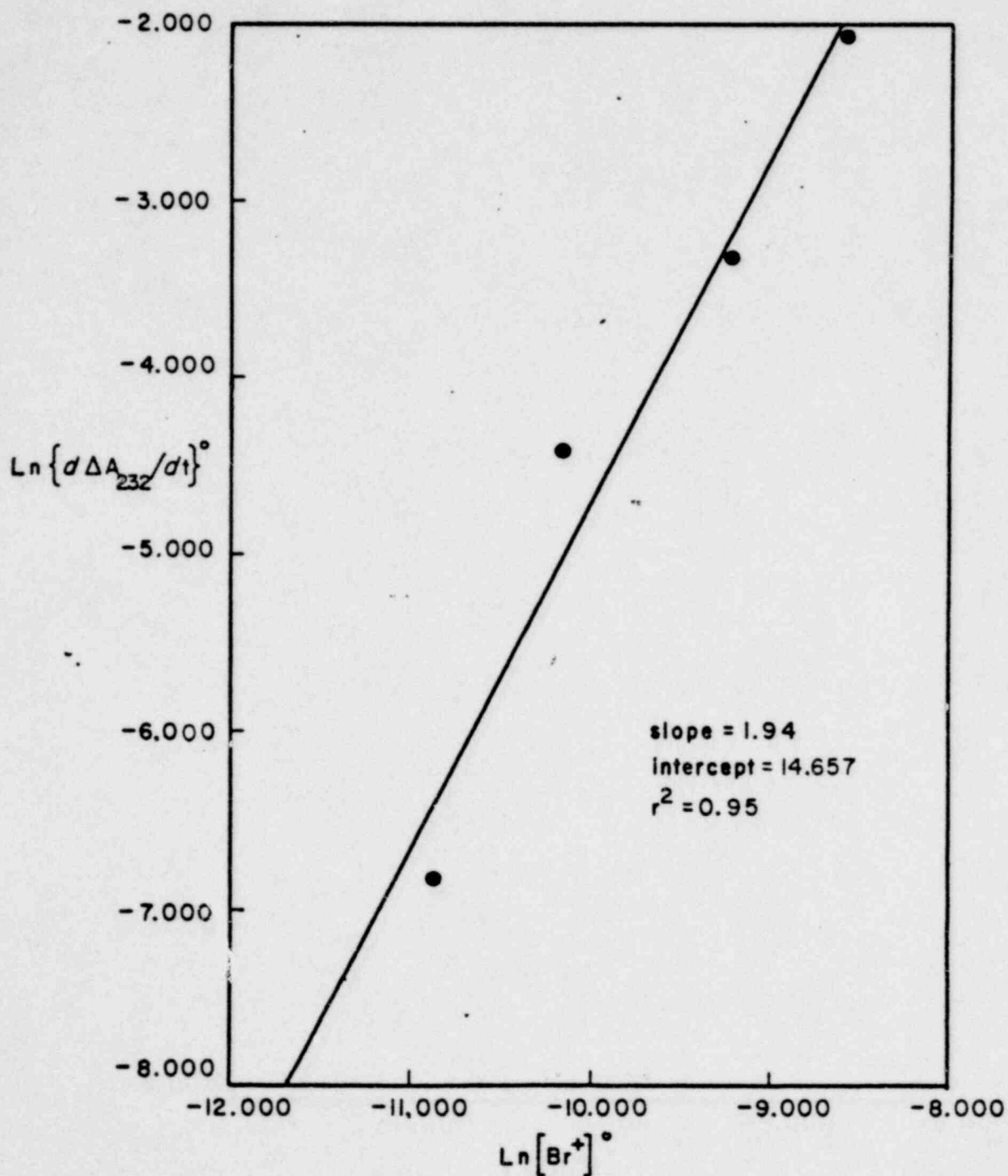
Figure 1. Logarithm of the initial rate of dibromamine formation at 232 nm versus the logarithm of initial bromine concentration. Temperature = 25°C, pH = 7.00 + .02, ionic strength = 0.033$\underline{M}$ (0.02$\underline{M}$ potassium phosphate) and the initial ammonia concentration = 2.0 m$\underline{M}$.

IV. Conclusions and Future Plans

Further experiments to characterize the rate of $NHBr_2$ formation with respect to pH, ammonia concentration, and ionic strength are currently in progress. Hopefully when these experiments are completed it will be possible to calculate specific reaction rate constants and select a reasonable mechanism for the overall reaction. Kinetic runs will also be carried out to measure the rate of NBr_3 and $NHBr_3$ formation in the presence of excess hypobromous acid.