Use of a Rotating Ring Disc Electrode to Study Fast Bromine Demand Reactions

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A rotating ring disc electrode (RRDE) was used to study the fast reactions of electrochemically produced bromine with three different model compounds and one natural water sample. One of the three test compounds, ammonia, exhibited slow, pseudo first-order kinetics while two of the test compounds, $NaAsO_2$ and phenylarsine oxide, exhibited rapid second-order kinetics. Interpretation of the pseudo first-order data yielded a specific rate constant for the reaction of HOBr and NH_3 of $8.1 \times 10^7 \, M^{-1} s^{-1}$, in agreement with published results. Interpretation of the second-order data showed that the minumum detectable concentration of substrate was on the order of $1 \times 10^{-6} \, M$ and the rate constant for bromine reacting with As(III) approached the upper limit of our RRDE system. The natural water sample collected from the Patuxent River exhibited a rapid second-order bromine demand, similar to As(III). Analysis of the RRDE data suggested a family of naturally occurring reactants with a concentration of $2 \times 10^{-5} \, M$, and a reaction rate constant in excess of $10^7 \, M^{-1} s^{-1}$. This method provides a useful way of studying very fast reactions responsible for oxidant demand in chlorinated or brominated estuarine and marine waters.

KEY WORDS: Chlorination, rotating ring-disc electrode, bromine, seawater, phenylarsine oxide, oxidant demand.

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INTRODUCTION

Large amounts of oxidative biocides are introduced into natural
waters from a variety of anthropogenic sources, including electric
power plants and waste treatment plants. The fate of these oxidants
is of environmental concern. In estuarine and marine waters, various
primary biocides (e.g. Cl_2, $BrCl$, O_3) generate bromine oxidants by
reaction with Br^- in seasalt. Experience by many workers has shown
that the applied dose of oxidant passes through a complicated decay
process.[1-7] Understanding the chemical reactions that occur in the
rapid initial phase of this decay has yet to be achieved, and new
experimental approaches are needed to study this problem.

   The purpose of this paper is to explore the feasibility of using a
platinum rotating disc electrode (RRDE) to study the rapid decay of
oxidized bromine in natural waters. The basic idea is to generate
oxidized bromine species electrochemically at the central disc
electrode and then measure at the annular ring the bromine that
survives chemical decay. The transit time from disc to ring varies
with rotation speed and can range from tenths of a second to
milliseconds.[8]

   We will first show that it is possible to obtain useful kinetic
information with the RRDE system by presenting data on three
systems; the reaction of bromine with ammonia, the reaction of
bromine with sodium arsenite, and the reaction of bromine with
phenylarsine oxide (PAO). Then we will show that it is possible to
observe and partially characterize the reaction of bromine with
components of natural estuarine waters.

METHODS

To gather kinetic information from an RRDE experiment, data are
required in the form of a ring current vs. disc current diagram. To
obtain this information, two completely independent circuits are
used. The disc circuit systematically controls the amount of bromine
generated at the disc while the ring circuit measures the bromine
remaining after transit from disc to ring. In our apparatus, the
voltage supplied to the platinum disc electrode (vs. a platinum
reference electrode) was controlled by a variable d.c. power supply

with a maximum output of three volts. The value of the disc current was obtained by measuring the voltage drop across a series resistor with a differential amplifier. The output of the differential amplifier was sent to an Apple II computer. With this arrangement, the disc current could range from 0 to 300 microamps. Simultaneously, the ring voltage was held constant at $+0.4$ volts vs. a sleeve-type saturated calomel electrode by a Metrohm polarizer (model E585) and the corresponding ring current was monitored. All oxidized bromine species (except OBr^-) are reduced to bromide at this potential. The ring current was converted to a corresponding output voltage by the potentiostat and this output voltage was also sent to the computer. The disc current vs. ring current data were sent to a floppy disc file for storage.

At the start of an experiment, enough Baker reagent grade NaBr(s) was added to 100 mL of water to give the desired bromide concentration (usually 0.1 to 0.5 M). Sodium acetate was added as a buffer, where noted. The final pH was adjusted through dropwise addition of HCl or NaOH. After several disc current scans were obtained from the electrolyte blank, a small aliquot of the desired test compound was added to the electrolyte solution. Sequential disc current scans were again obtained. Two of the test compounds were of reagent grade (Baker NH_4Cl and Fisher $NaAsO_2$) and the third test compound (phenylarsine oxide) was purchased as a standardized solution from Hach Chemical Co. In the experiments with natural water, NaBr(s) was added directly to a known volume of natural water, thus minimizing dilution.

It was not necessary to deaerate the solutions because O_2 does not interfere with the detection of bromine.[9] Electrochemical oxidation of bromide to bromine has a current efficiency very near 100%.[10]

The mechanism of oxidation of bromide at a platinum electrode has been studied extensively.[11-15] Molecular Br_2 is the initial form of oxidized bromine, but in strong Br^- solutions, much of this is transformed to Br_3^- and some undergoes rapid hydrolysis to form HOBr. The pseudo first-order rate constant for hydrolysis of Br_2 is $110 s^{-1}$.[16] This translates into a reaction half-life of 0.0063 s. If five half-lives constitute essentially complete reaction, then equilibrium speciation is achieved 0.032 s downstream of the disc electrode. This is a lower limit, because buffer catalysis may cause the reaction to occur even faster.[17,18] Given the geometry of our RRDE, the transit

time of solution from disc to ring at 400 rpm is approximately one order of magnitude greater (0.330 s). The transit time at 4900 rpm is approximately the same order of magnitude (0.027 s).

RESULTS

In a pure NaBr solution containing no bromine consuming components, the ring electrode collects a specific fraction of the bromine generated by the disc.[19] This specific fraction, called the collection efficiency (N_0), can be predicted from the geometry of the electrode[19] and is equivalent to the slope of the ring current vs. disc current diagram (as shown in Figure 1).
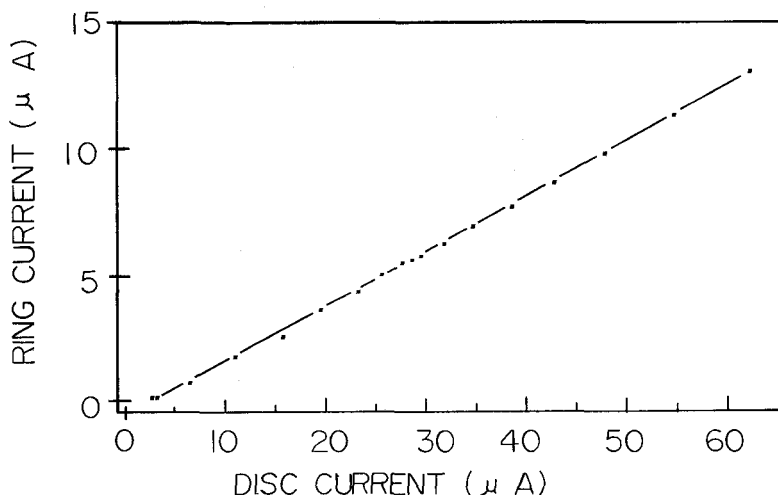
FIGURE 1   Ring current vs. disc current diagram for 0.1 M NaBr at pH 6.0. Rotation speed, 400 rpm (6.67 Hz).

In Table I are presented measurements of N_0 at six rotation speeds in three solutions, each consisting of 0.1 M NaBr in distilled water. Vertical comparison of the numbers provides evidence of satisfactory reproducibility in the electrochemical apparatus. Horizontal comparison of the numbers reveals a small (ca. 10%) decline in collection efficiency with increasing rotational velocity, contrary to RRDE theory. The theoretical value of the collection

TABLE I

Calculated collection efficiency for three blanks, at six rotation speeds each.[a]

	Rotations per minute					
	400	900	1600	2500	3600	4900
I.	0.214	0.208	0.203	0.198	0.194	0.192
II.	0.216	0.212	0.209	0.205	0.201	0.202
III.	0.208	0.202	0.196	0.188	0.185	0.180
Ave.	0.213	0.207	0.203	0.197	0.193	0.191
S.D.	0.004	0.005	0.007	0.009	0.008	0.011
Rel. Error	±2%	±2%	±3%	±5%	±4%	±6%

[a]All solutions are 0.1 M Br and pH 6.0. The theoretical value for the collection efficiency is 0.220.

efficiency, calculated from the geometry of the electrode, is also given in Table I and is in good agreement with the observed values.

In the presence of a bromine consuming component (such as NH_3 or As(III)), the ring electrode collects a smaller fraction of the bromine generated by the disc owing to chemical reactions.[20, 21] The response of the ring current as the disc current is increased, (i.e. the shape of the ring current vs. disc current diagram) depends on the kinetics of the chemical reaction occurring in transit, and there are two ideal limiting types of ring current vs. disc current responses. A linear relationship indicates a pseudo first-order decay of bromine in transit from disc to ring. Both bromine and substrate coexist in the hydrodynamic layer, and bromine suffers a relatively slow attrition in transit from disc to ring. An example of a pseudo first-order ring current vs. disc current diagram is shown in Figure 2. The second limiting type of ring current vs. disc current relationship is curvilinear, and represents second-order kinetics. In this case, the reaction between bromine and reducing agents is so fast that coexistence of bromine and reducing components is excluded in the hydrodynamic layer. A bromine dominated zone exists near the disc and the ring electrode does not detect bromine until this bromine dominated zone expands, with increasing disc current, to reach the ring electrode. An example of second-order kinetics is shown in Figure 3. The reaction of ammonia with bromine follows pseudo first-order kinetics while the reaction of As(III) with bromine follows second-order kinetics.
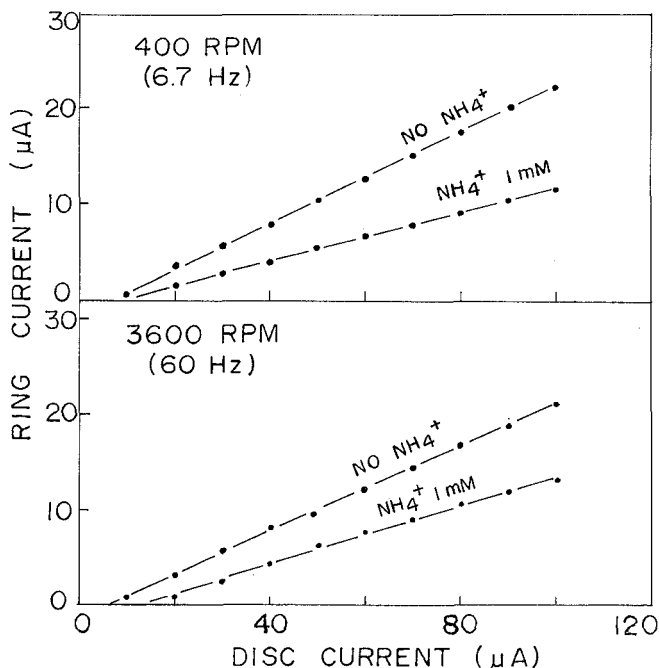
FIGURE 2 Ring current vs. disc current diagrams at two rotation speeds for solutions containing 0.5 M NaBr, 0.1 M Na-acetate, at pH 6.0 with and without 10^{-3} M NH$_4$Cl. These diagrams illustrate psuedo-first order behavior. Reaction of bromine with ammonium lowers the observed slope. The degree of lowering is less at higher rotation velocities because less time is available for reaction during transit of bromine from disc to ring.

Ammonia plus bromine

Data from several ammonia test solutions of different pH and bromide concentration are presented in Table II. The solution conditions, and corresponding equilibrium speciation data, are also summarized. Kinetic collection efficiencies (N_k), which are the slopes of the ring current vs. disc current diagrams under pseudo first-order conditions, were obtained at six different rotation speeds between 400 rpm and 4900 rpm. Specific details of the data reduction procedure are outlined elsewhere,[22] however, graphical analysis of the kinetic current efficiency data according to the model of Albery[20] gave the pseudo first-order rate constants sumarized in Table II.
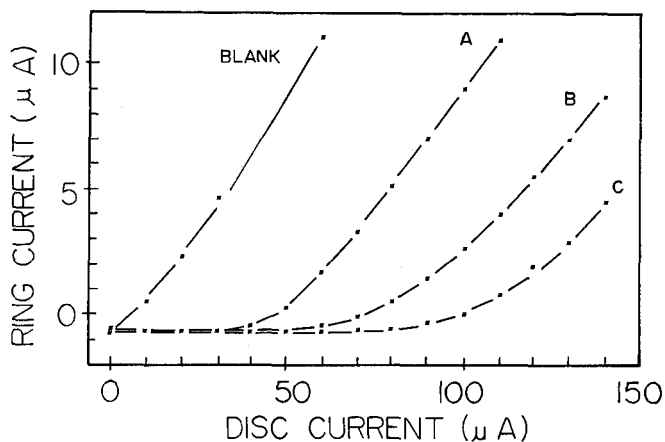
FIGURE 3 Ring current vs. disc current plot for solutions containing 4.7×10^{-5} M $NaAsO_2$, 0.2 M NaBr, and 1.0 M H_2SO_4. Curve A: rotation speed 400 rpm. Curve B: rotation speed 1600 rpm. Curve C: rotation speed 3600 rpm. The curve labelled Blank is for a solution containing NaBr but no $NaAsO_2$.

TABLE II

Experimental conditions and observed rate constants fot the study of the reaction of Bromine and Ammonia with RRDE.[a]

		Conditions[b]			Rate constants[c]	
pH	Br^-	α_{HOBr}	α_{OBr^-}	α_{Br_2}	k_1 (s^{-1})	k_2 $(M^{-1}-s^{-1})$
6.1[d]	0.5	1.61×10^{-3}	5.05×10^{-6}	1.05×10^{-1}	0.34	8.8×10^5
6.0	0.5	1.28×10^{-3}	3.19×10^{-6}	1.05×10^{-1}	0.12	1.9×10^5
6.0	0.1	2.20×10^{-2}	5.50×10^{-5}	3.61×10^{-1}	1.4	2.3×10^6
6.5	0.1	6.64×10^{-2}	5.25×10^{-4}	3.44×10^{-1}	11	5.6×10^6
7.0	0.1	1.83×10^{-1}	4.57×10^{-3}	3.00×10^{-1}	92	1.5×10^7

[a]Except as noted below, all solutions contain 1×10^{-3} M NH_4^+ and 0.1 M sodium acetate. Data collected at six rotation speeds between 400 and 4900 rpm.
[b]The alpha value for species X is defined by $\alpha_X = X/\sum Br_{ox}$, where $\sum Br_{ox} = M_{Br_3} + M_{Br_2} + M_{HOBr}$. The measurements were made at room temperature (i.e. $23 \pm 3°C$). Equilibrium constants calculated from data in ref 25.
[c]The rate constants are defined by $-d(\sum Br_{ox})/dt = k_1 \sum Br_{ox} = k_2(NH_3^0) \sum Br_{ox}$.
[d]$NH_4^+ = 5 \times 10^{-4}$ M; no acetate.

The pseudo first-order rate constants, k_1, were converted to second-order rate constants, k_2, according to equation 1 to allow comparison with published second-order rate constants.

$$k_2 = \frac{k_1 [\text{H}^+]}{K_a [\text{NH}_3]} \qquad (1)$$

K_a is the acid dissociation constant for the ammonium ion ($10^{-9.26}$) and [NH_3] is the total amount of ammonia nitrogen initially added.

The observed second-order rate constant for the reaction of ammonia plus bromine represents the sum of several individual reactions; with each part of the summation corresponding to a reaction with a specific type of bromine oxidant. This is shown in Eq. 2.

$$k_2 = k_{\text{HOBr}} \alpha_{\text{HOBr}} + k_{\text{OBr}^-} \alpha_{\text{OBr}^-} + k_{\text{Br}_2} \alpha_{\text{Br}_2} + k_{\text{Br}_{-3}} \alpha_{\text{Br}_{-3}}. \qquad (2)$$

Careful inspection of this set of ammonia data reveals that the observed second-order rate constant follows most closely the speciation of HOBr. A plot of k_2 vs. αHOBr, as shown in Figure 4, yields a slope equal to the specific rate constant for the reaction of NH_3 and HOBr. The slope of $8.1 \times 10^7 \, \text{M}^{-1} \text{s}^{-1}$ compares quite favorably with the value of $7.5 \times 10^7 \, \text{M}^{-1} \text{s}^{-1}$ reported by Wajon.[23] The zero intercept of this line suggests that only the reaction of NH_3 and HOBr is important in this pH range. Other possible reactions such as NH_3 and OBr^- or NH_3 and Br_2 must be insignificant.

As(III) plus bromine

Both sodium arsenite and phenyl arsine oxide exhibited second-order ring current vs. disc current behavior, as illustrated for NaAsO_2 in Figure 3. These second-order titration curves can be divided into three regions. The first region shows no ring current as the disc current is increased. This represents the region where the coulombically controlled bromine flux is less than the hydrodynamically controlled As(III) flux and all of the bromine is consumed in chemical reaction at the disc surface. At some particular disc current, the flux of bromine just equals the flux as As(III). This critical disc current is used to calculate the concentration of As(III) in the bulk
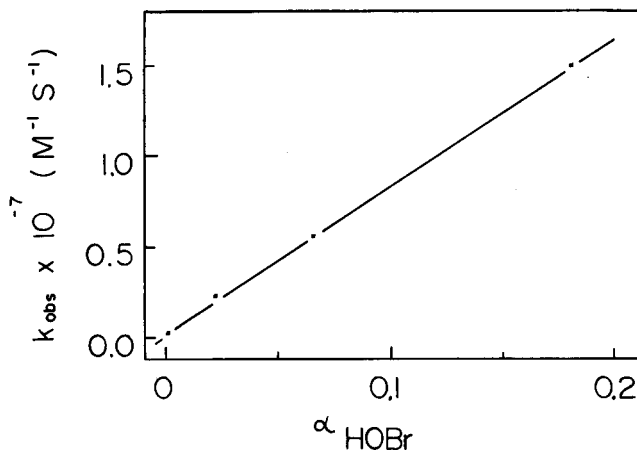
FIGURE 4 Plot of k_2 vs. α_{HOBr}; data from Table II. The slope, which is the rate constant for the reaction $HOBr + NH_3 \rightarrow NH_2Br + H_2O)$, is $8.1 \times 10^7 \, M^{-1} s^{-1}$.

of the solution. As the current is increased further, a bromine dominated zone forms near the disc surface, and with increasing current, it spreads and eventually reaches the inside radius of the ring. When the bromine dominated zone contracts the ring, current begins to flow in the ring circuit. The curved portion of the ring current vs. disc current diagram represents the progress of the bromine dominated zone across the ring; the curvature contains the kinetic information. In the final region, the bromine dominated zone has extended beyond the outer radius of the ring and the slope of the line in this region is equal to the theoretical collection efficiency.

The method of data treatment below follows Albery and Hitchman,[24] which can be consulted for details. To extract the second-order rate constant, the linear portion of the titration curve was extrapolated to zero ring current. The value of the disc current at this point I_{do} was related to the kinetic disc current (I_{dk}) via Eq. (3).

$$I_{dk} = 0.84 \, I_{do} \tag{3}$$

The constant in Eq. (3) was derived from the dimensions of the electrode. After the kinetic disc current was found from Eq. (3), the corresponding kinetic ring current was determined from the curve.

The kinetic ring current was then related to the second-order rate constant through Eq. (4).

$$k_2 = \frac{1.80 \, w^{3/2}}{I_{rk}} \qquad (4)$$

where w is the angular velocity of the electrode and the constant represents a collection of terms including the radius of the ring, the assumed diffusion coefficient of the electroactive species (10^{-5} cm^2/sec), and the kinematic viscosity of solution (10^{-2} cm^2/sec). In addition, the concentration of substrate was found from I_{do}, according to Eq. (5).

$$C_b = \frac{0.021 \, I_{do}}{w^{1/2}} \qquad (5)$$

Again w is the angular velocity and the constant represents a collection of geometric and hydrodynamic terms. The calculated concentration and calculated rate constant results for the two As(III) test compounds are summarized in Table III.

TABLE III

Summary of the As(III) results.

Compound	Actual conc.	Calc. conc.[a]	Calc. rate constant[b]
PAO	2.3×10^{-5}	2.2×10^{-5} M	1×10^{7} L/mol-sec.
NaAsO$_2$	4.7×10^{-5}	6.5×10^{-5} M	9×10^{5} L/mol-sec.

[a]Calculated concentration values are the average obtained at six rotation speeds, according to Eq. (5).
[b]Rate constant values are based in Eq. (4).

The calculated concentration values in Table III represent averages over six different rotation speeds between 400 and 4900 rpm. The calculated value for the concentration of substrate agreed fairly well in the case of PAO, but the concentration of NaAsO$_2$ was moderately overestimated. Based on these and subsequent experiments, the detection limit for the concentration of bromine reactive substrate was estimated at 1×10^{-6} M. The calculated rate constant values were averaged over six different rotation

speeds. The NaAsO$_2$ had a rate constant of $10^6 \, M^{-1} s^{-1}$ and the PAO was an order of magnitude greater. The value given by Albery and Hitchman[24] for the reaction of As(III) and bromine was near $10^6 \, M^{-1} s^{-1}$.

Natural waters

Three aliquots of an estuarine water sample were tested with the RRDE apparatus. The sample was collected from Solomons Island, MD on 25 April, 1983 and had an estimated salinity of 10 g/kg. This Patuxent River water sample clearly exhibited second-order behavior, as shown in Figure 5, so analysis of the data followed the As(III) example. The calculated concentration and rate constant values were averaged over six rotation speeds between 400 and 4900 rpm and are shown in Table IV. According to the concentration calculations, the substrate (or family of substrates) responsible for the rapid oxidant demand is on the order of $2 \times 10^{-5} \, M$.
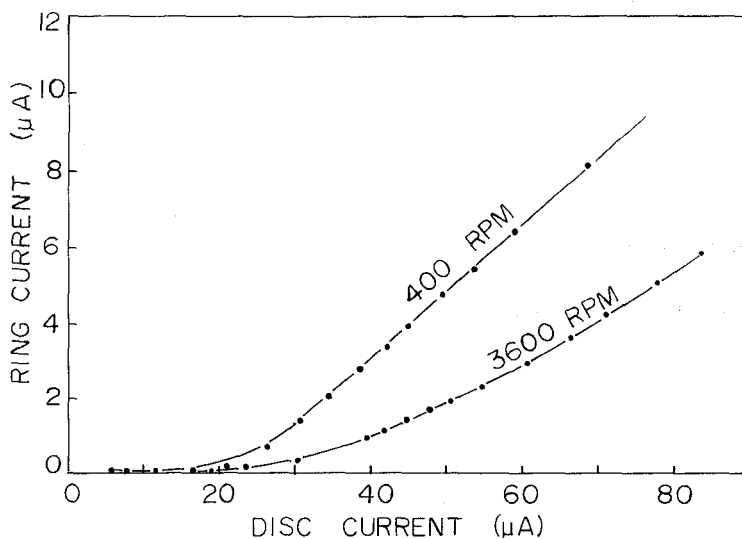
FIGURE 5 Ring current vs. disc current diagram for a natural estuarine water sample at two rotation speeds. Salinity approximately 10 g/kg, pH 7.5; enough solid NaBr was added to the sample to raise the Br$^-$ concentration to 0.1 M. The experiment was done at room temperature $(23 \pm 3°C)$.

TABLE IV

Triplicate determinations of the calculated concentration and rate constant data for a Patuxent Estuary sample.[a]

	I	II	III
Ave conc.	1.8×10^{-5} M	1.9×10^{-5} M	1.8×10^{-5} M
S.D.	0.5×10^{-5} M	0.6×10^{-5} M	0.5×10^{-5} M
Ave rate const.	1.8×10^{7} L/mol-sec.	1.0×10^{7} L/mol-sec.	1.1×10^{7} L/mol-sec.
S.D.	2.2×10^{7} L/mol-sec.	1.0×10^{7} L/mol-sec.	1.0×10^{7} L/mol-sec.

[a]Concentration and rate constant averaged over six rotation speeds between 400 and 4900 RPM. Solution conditions: 0.1 M Br⁻ and pH 7.8.

The rate constant calculations suggest that the rapid oxidant demand reaction has a rate constant on the order of $10^7 \, M^{-1} \, s^{-1}$. The value is approaching the upper limit of RRDE measurement capability,[21] and may be a minimum estimate for the rate constant of the demand reaction.

CONCLUSION

A number of conclusions can be drawn from this series of experiments. Firstly, the observed collection efficiency compares favorably with the theoretical collection efficiency of the rotating disc electrode. Secondly, equilibrium speciation of bromine is attained in transit from disc to ring. Below 4900 rpm, transit times exceed five reaction half-lives of the hydrolysis of Br_2. Thirdly, equilibrium speciation is important with respect to the pseudo first-order reaction of ammonia, particularly because the ammonia data follow the speciation of HOBr rather than OBr⁻ or Br_2. The observed specific rate constant of 8.1×10^7 L/mol-sec for the reaction of HOBr and NH_3 agrees quite well with 7.6×10^7 L/mol-sec as reported in the literature. Surprisingly, however, is the absence of reaction between Br_2 and NH_3. Finally, in comparison to the slower pseudo first-order reactions of ammonia, the As(III) data and the natural water samples follow the faster second-order reaction kinetics. The interpretation of second-order ring current vs. disc current titration curves reveals two parameters: C_b and k. The observed concentrations of various As(III) standards

were within a few percent of the actual amount of As(III) in the test solution. The observed second-order rate constant, only good to an order of magnitude, was representative of the upper limit of RRDE measurement. The rapidity of the second-order reactions implies that the As(III), and the substrates in the natural water responsible for the demand reaction, are reacting with the Br_2 generated at the disc electrode before hydrolysis has a chance to occur.

The implication in natural waters is that Br_2 is consumed by certain substrates in the water long before hydrolysis can convert it to HOBr. Hence, subsequent reaction of HOBr with NH_3 (to form long-lived monobromamine) does not occur.

Acknowledgement

References

1. R. W. Eppley, E. H. Renger and P. M. Williams, *Estuarine and Coastal Mar. Sci.* **4**, 147 (1976).
2. G. T. F. Wong and J. A. Davidson, *Water Res.* **11**, 971 (1977).
3. P. Horstgaard-Jensen, J. Klitgaard and K. M. Peterson, *J. Water Pollut. Control Fed.* **49**, 1832 (1977).
4. G. R. Helz, R. Sugam and A. C. Sigleo, *Environ. Sci. Technol.* **18**, 192 (1984).
5. J. C. Goldman, H. L. Quinby and J. M. Capuzzo, *Water Res.* **13**, 315 (1979).
6. W. R. Haag, *Water Res.* **15**, 937 (1981).
7. R. G. Qualls and J. D. Johnson, *Environ. Sci. Technol.* **17**, 692 (1983).
8. S. Bruckenstein and G. A. Feldman, *J. Electroanal. Chem.* **9**, 395 (1965).
9. H. A. Laitinen and D. E. Woerner, *Anal. Chem.* **27**, 215 (1955).
10. G. Nagy, Z. Feher, K. Toth and E. Pungor, *Anal. Chim. Acta* **100**, 181 (1978).
11. J. Llopis and M. Vazquez, *Electrochim. Acta* **6**, 177 (1962).
12. D. G. Davis and M. E. Everhart, *Anal. Chem.* **36**, 38 (1964).
13. G. Faita, G. Fiori and T. Mussini, *Electrochim. Acta* **13**, 1765 (1968).
14. D. C. Johnson and S. Bruckenstein, *J. Electrochem. Soc.* **117**, 460 (1970).
15. I. Rubenstein, *J. Phys. Chem.* **85**, 1899 (1981).
16. M. Eigen and K. Kustin, *J. Am. Chem. Soc.* **84**, 1355 (1962).
17. A. Lifshitz and B. Perlmutter-Hayman, *J. Phys. Chem.* **65**, 753 (1961).
18. A. Lifshitz and B. Perlmutter-Hayman, *J. Phys. Chem*, **66**, 701 (1962).
19. W. J. Albery and S. Bruckenstein, *Trans. Faraday Soc.* **62**, 1920 (1966).
20. W. J. Albery, M. L. Hitchman and J. Ulstrup, *Trans. Faraday Soc.* **64**, 2831 (1968).
21. W. J. Albery, M. L. Hitchman and J. Ulstrup, *Trans. Faraday Soc.* **65**, 1101 (1969).

22. D. A. Jaworske, *The Kinetics of Rapid Oxidant Consumption: Measurements with a Rotating Ring Disc Electrode* (Ph.D. Dissertation, Univ. of Maryland, College Park, MD, 1983), pp. 363.
23. J. E. Wajon, *Kinetics of N-Bromination Reactions* (Ph.D. Dissertation, Harvard Univ., Cambridge, MA 1980) pp. 205.
24. W. J. Albery and M. L. Hitchman, *Ring-disc Electrodes* (Clarendon Press, Oxford, 1971) pp. 175.
25. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, *Selected Values of Chemical Thermodynamic Properties.* (U.S. Nat. Bur. Standards Tech. Note 270-3, Washington, D.C., 1968) pp. 263.