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Equilibrium and Kinetics of Bromine Hydrolysis

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Equilibrium constants for bromine hydrolysis, $K_1 = [\mathrm{HOBr}][\mathrm{H}^+][\mathrm{Br}^-]/[\mathrm{Br}_2(\mathrm{aq})]$, are determined as a function of ionic strength (μ) at 25.0 °C and as a function of temperature at $\mu \simeq 0$ M. At $\mu \simeq 0$ M and 25.0 °C, $K_1 = (3.5 \pm 0.1) \times 10^{-9}$ M^2 and $\Delta H° = 62 \pm 1$ kJ mol^{-1}. At $\mu = 0.50$ M and 25.0 °C, $K_1 = (6.1 \pm 0.1) \times 10^{-9}$ M^2 and the rate constant (k_{-1}) for the reverse reaction of HOBr + H$^+$ + Br$^-$ equals $(1.6 \pm 0.2) \times 10^{10}$ M^{-2} s^{-1}. This reaction is general-acid-assisted with a Brønsted α value of 0.2. The corresponding Br$_2$(aq) hydrolysis rate constant, k_1, equals 97 s^{-1}, and the reaction is general-base-assisted ($\beta = 0.8$).

Introduction

Although equilibrium constants for the hydrolysis of aqueous bromine (eq 1) have been measured by many investigators[1−9]

$$\mathrm{Br_2(aq)} + \mathrm{H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HOBr} + \mathrm{Br}^- + \mathrm{H}^+ \qquad K_1 = k_1/k_{-1} \quad (1)$$

over the past 85 years, considerable disagreement exists about the value of K_1 (Table 1). A few investigators[2,7,8] have reported the temperature dependence for this hydrolysis with $\Delta H°$ values of 48−56 kJ mol^{-1}. There has been no systematic study of ionic strength effects on the equilibrium constant. Accurate characterization of the equilibrium constant with its temperature and ionic strength dependence as well as the corresponding rate constants is important in modeling the fate of atmospheric bromine.[10]

Table 1. Reported Values for Bromine Hydrolysis Equilibrium Constants

10^9K_1, M^2	temp, °C	μ, M	ref
5.2	25.0	0	1
5.8	25.0	0	2
5.8	25.0	0	3
6.9	20	0.10	4
8.8	25.0	0.6[a]	5
9.2	25.0	0	6
12	25.0	∼0.01	7
0.67	20	1.29[b]	8
11	22.0	1.29[b]	9
3.5 ± 0.1	25.0	0	this work
5.3 ± 0.3	25.0	0.10[c]	this work
6.1 ± 0.1	25.0	0.50[c]	this work

[a] Measured in 0.3 M phosphate (total) at pH 6.7. [b] 1.0 M H$_2$SO$_4$. [c] NaClO$_4$ used for ionic strength control.

There are several reasons why this fundamental constant is difficult to measure. Aqueous bromine is quite volatile, hypobromous acid disproportionates slowly (eq 2), and direct

$$3\,\mathrm{HOBr} \rightarrow \mathrm{BrO_3}^- + 2\mathrm{Br}^- + 3\mathrm{H}^+ \qquad (2)$$

dilution of liquid bromine into water is reported to give appreciable amounts of bromate ion.[2] Early measurements[1−3] used conductivity methods to measure the extent of hydrolysis in eq 1, and Liebhafsky's value of 5.8×10^{-9} M^2 for K_1 at 25 °C, $\mu = 0$ M, is widely used. His measurements were made within 2 h, but they are very sensitive to H$^+$ release in eq 2, which could give K_1 values that are too large. Eigen and Kustin[4] used temperature-jump relaxation methods to determine the forward and reverse rate constants (k_1, k_{-1}). Perlmutter-Hayman and Weissman[5] used an indirect kinetic method based on the rate of oxidation of 2-propanol to estimate K_1. Pink[6] used a spectrophotometric method. Pusenok and Mischenko[7] obtained a K_1 value by potentiometric titration of KOBr. Kshirsagar and Field[8] indirectly obtained a K_1 value (0.67×10^{-9} M^2) at 20 °C in 1 M H$_2$SO$_4$ through study of the reaction of Br$_2$(aq) and BrO$_3^-$. Fösterling et al.[9] determined K_1 by combined titrimetric and spectrophotometric measurements in 1 M H$_2$SO$_4$ at 22 °C and reported a value of 11×10^{-9} M^{-2}.

It was our initial intention just to determine K_1 at 25.0 °C with an ionic strength of 0.50 M, so that we could use this value with our kinetic studies at these conditions. Our review of the past experimental procedures indicated that the values determined at $\mu = 0$ M in 1934[2,3] seemed to be more reliable than subsequent work. We elected to use much lower concentrations of [Br$_2$]$_\mathrm{T}$ ([HOBr] + [Br$_2$(aq)] + [Br$_3^-$]) than had previously been used by any investigators in order to minimize the rate of HOBr disproportionation. This rate has been reported to be third-order by some investigators[11,12] and second-order by others.[13,14] The disproportionation is metal ion catalyzed,[15] and HOBr is also subject to photodecomposition.[16] Therefore, we took many precautions in our measurements as outlined in the experimental procedure, and as a result we obtained reproducible K_1 values with good precision. Our levels of [Br$_2$]$_\mathrm{T}$ were 1/100 of those used by Liebhafsky.[2] Our values are a factor of 1.7

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Table 2. Molar Absorptivities for Bromine Species

species	λ, nm	ϵ, M^{-1} cm^{-1}
$Br_2(aq)$	390	175
	266	47
HOBr(aq)	390	6
	266	97
Br_3^-	390	618
	266	40 900

lower than Liebhafsky's value at $\mu = 0$ M. We chose to perform a temperature dependence experiment at $\mu = 0$ M as well as an ionic strength dependence experiment at 25.0 °C.

The kinetics of $Br_2(aq)$ hydrolysis were measured at 20 °C in a landmark paper by Eigen and Kustin.[4] They used temperature-jump relaxation methods to give $k_1 = 110\ s^{-1}$ and $k_{-1} = 1.6 \times 10^{10}\ M^{-2}\ s^{-1}$ at $\mu = 0.10$ M. Citri and Epstein[17] first modified this k_{-1} value to equal $8 \times 10^9\ M^{-2}\ s^{-1}$ and then[17,18] (after what they stated was a more careful analysis of ref 4) changed both values at high acidity to give $k_1 = 68.8/([H^+] + 0.25)$ and $k_{-1} = 5 \times 10^9/([H^+] + 0.25)$. This was done to avoid rate constants that exceeded the diffusion-controlled limit at high aciditities. In these two studies of oscillatory reactions,[17,18] no mention is made of temperature or ionic strength, although more than 40 rate constants are reported. The basis for these corrections for k_1 and k_{-1} is not clear. Lifshitz and Perlmutter-Hayman[19] attempted to estimate k_1 in the presence of phosphate buffer and found the reaction was too fast to measure by their continuous-flow method. The rate constants for the reaction in eq 3, where HA and A^- are general

$$Br_2(aq) + H_2O + A^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HOBr + Br^- + HA \qquad (3)$$

acids and bases, can be measured by the pulsed-accelerated-flow method.[20-22] In this work, we report k_{-2} values for HA $= H_3O^+$, HSO_4^-, and H_3PO_4.

Experimental Section

Procedure for Bromine Hydrolysis Equilibrium Measurements. Deionized, distilled water was boiled to remove CO_2 (final pH 7.0 ± 0.5). When ionic strength adjustment was necessary, $NaClO_4$ solutions (CO_2 free, stored under Ar) were prepared from the recrystallized salt. Aqueous bromine solutions (0.1−0.4 mM) were formed from the dissolution of bromine vapor obtained from $Br_2(l)$. All $Br_2(aq)$ solutions were protected from exposure to light as well as from exposure to ambient air. Spectrophotometric measurements were taken at 390 nm (2 nm band pass) in a 10.0 cm cell to give absorbance readings (±0.001) in the range of 0.11−0.84. The cell was filled with solution such that there was no headspace when capped. Temperature control was maintained by means of a circulating water bath. The temperature of the cell contents was directly measured to ±0.1 °C. At 20−30 °C, the absorbance measurements were made within 19 ± 7 min to avoid significant HOBr disproportionation. For measurements at 6−15 °C, the temperature was increased for a single hydrolysis sample, and the measurements were recorded within 2 h. Immediately after the equilibrium absorbance was determined, the sample in the same cell was acidified with a small amount (0.16−0.28 mL) of $HClO_4$ (70%) to convert reactants to $Br_2(aq)$ without transfer, and the absorbance was again measured. The perchloric acid solution was purged with argon before use to remove trace volatile oxidizing impurities such as Cl_2. The final pH was typically 1.1 where $Br_2(aq)$ was 97.5−99.4% of $[Br_2]_T$. The $[Br_2]_T$ value was adjusted for the dilution factor (0.7 ± 0.2%) and for the [HOBr] content by iteration with the corresponding K_1 value. Three to four sets of measurements were used for each condition. The experimental precision for K_1 for each set was ±2%. Table 2 summarizes the molar absorptivity values at 390 nm that were used for the equilibrium calculations. The $Br_2(aq)$ and HOBr solutions were standardized iodometrically, and the Br_3^- solution was generated from primary standard $KBrO_3$ and excess NaBr in acid.[23] Our HOBr spectrum agreed with earlier reports of $\epsilon_{260} = 100\ M^{-1}\ cm^{-1}$ [24] and with $\epsilon_{390} = 6\ M^{-1}\ cm^{-1}$.[25]

Reagents. Solutions of NaBr and $NaClO_4$ were standardized gravimetrically. Perchloric acid solutions were standardized with NaOH solutions that were in turn standardized against potassium hydrogen phthalate. Solutions for buffer catalysis by $H_3PO_4/H_2PO_4^-$ were prepared from NaH_2PO_4 and $HClO_4$. Solutions of HSO_4^-/SO_4^{2-} were prepared from $NaHSO_4$ and $HClO_4$.

Spectrophotometric Measurements. A Perkin-Elmer Lambda 9 UV−vis−NIR spectrophotometer interfaced to a Zenith 386/20 computer was used to obtain hydrolysis data. Temperature measurements were calibrated with a thermometer certified to meet ASTM specification E1-91a. The cell compartment was flushed with nitrogen gas when operating at temperatures of 15 °C or below to prevent condensation on the cells.

Pulsed-Accelerated-Flow (PAF) Method. A PAF spectrophotometer, model IV,[21,22] was used to obtain kinetic data for Br_2 formation from HOBr, Br^-, and H^+ ($\mu = 0.50$ M, 25.0 °C). The PAF spectrophotometer employs integrating observation[26,27] in the twin-path mixing/observation cell as the flow is decelerated during a 0.5 s pulse to give a linear velocity ramp; 250 measurements are taken as the flow rate in the observation cell changes from 12.0 to 3.0 m s^{-1}.

The kinetics were measured under either pseudo-first-order conditions or pseudo-second-order conditions. First-order rate constants were observed (eq 4) when a partially disssociated aqueous bromine solution

$$\frac{d[Br_2(aq)]}{dt} = k_{obsd}[HOBr] \qquad (4)$$

was reacted with additional H^+ and Br^-, where $k_{obsd} = k_{-1}[H^+][Br^-]$. Under these conditions small amounts of Br_3^- are rapidly formed (eq 5, where $K_{Br} = 16.8\ M^{-1}$ at 25.0 °C, $\mu = 0.5$ M).[23] The rate constants

$$Br_2(aq) + Br^- \overset{K_{Br}}{\rightleftharpoons} Br_3^- \qquad (5)$$

for the forward and reverse reactions in eq 5 are $1.5 \times 10^9\ M^{-1}\ s^{-1}$ and $1 \times 10^7\ s^{-1}$, respectively.[29] Therefore, Br_3^- serves as an indicator for the formation of additional $Br_2(aq)$, and the reactions are monitored at 266 nm. The treatment of the experimental signal to resolve reaction rate constants and mixing rate constants has been described previously.[20,21,28]

Second-order rate constants (eq 6) were observed when a dilute bromine solution was adjusted to $p[H^+]$ 6.9 and then mixed in the PAF

$$\frac{d[Br_2(aq)]}{dt} = k_{obsd}[HOBr][Br^-] \qquad (6)$$

with excess acid, so that $k_{obsd} = k_{-1}[H^+]$. Under second-order equal concentration conditions of HOBr and Br^-, the formation of $Br_2(aq)$ was monitored at 390 nm. The apparent rate constant, k_{app}, was obtained

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Table 3. Experimental Bromine Hydrolysis Equilibrium Constants[a]

temp, °C[b]	μ, M[c]	10^9K_1, M^2	temp, °C[b]	μ, M[c]	10^9K_1, M^2
6.3	0	0.60 ± 0.02	25.0	0	3.5 ± 0.1
10.0	0	0.91 ± 0.01	25.0	0.10	5.3 ± 0.3
14.9	0	1.5 ± 0.1	25.0	0.30	6.8 ± 0.2
19.6	0	2.0 ± 0.1	25.0	0.50	6.1 ± 0.1
20.4	0	2.0 ± 0.2	25.0	0.80	5.0 ± 0.3
25.8	0	3.7 ± 0.1	25.0	1.00	6.2 ± 0.2
30.1	0	5.00 ± 0.03			

[a] $[Br_2]_T = (1-4) \times 10^{-4}$ M, pH = 3.9–4.3, $[Br^-] = (7-10) \times 10^{-5}$ M. [b] ±0.1 °C. [c] $\mu = 0$ refers to no added salt where hydrolysis gives $\mu \simeq 10^{-4}$ M; other μ values are controlled with $NaClO_4$.

by iteration on the X value at different velocities from the absorbance data in eq 7,[26,27] where A_v is the absorbance at a given instantaneous

$$M_{\text{exptl}} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{\ln(X+1)}{X} \qquad X = \frac{k_{\text{app}}C_0 b}{\nu} \tag{7}$$

velocity, A_∞ is the final absorbance, A_0 is the absorbance at time zero, b is the reaction pathlength (0.01025 m), C_0 is concentration, and ν is the solution velocity. The k_{obsd} value can be obtained from the intercept of a double-reciprocal plot of $1/k_{\text{app}}$ vs $1/\nu$ in eq 8, where k_m is a proportionality constant from the mixing rate constant (k_{mix}), where

$$\frac{1}{k_{\text{app}}} = \frac{1}{k_m\nu} + \frac{1}{k_{\text{obsd}}} \tag{8}$$

$k_{\text{mix}} = k_m\nu$.

Solutions used for the PAF experiments were filtered, degassed, and then placed in a water bath at 25.0 °C for at least 20 min before data collection. Three or more PAF runs were averaged to give the observed rate constant. The relative standard deviation for PAF data is typically 5–10%.

Results and Discussion

Equilibrium Constants for Br_2(aq) Hydrolysis. Experimental values for K_1 are determined from spectrophotometric measurements (390 nm) of Br_2(aq) concentrations by using eq 9, where $x = [HOBr] = [Br^-] = [H^+]$ and $x = [Br_2]_T - [Br_2(aq)]$. Any errors in the measurements are magnified by the cubed term. Small absorbance contributions from HOBr and Br_3^- are taken into account in iterative calculations of K_1 and x. The tribromide ion concentration is almost negligible at the low levels of $[Br_2]_T$ used. The $[Br_2]_T$ values were measured after acidification as described in the procedure. Removal of volatile trace species by purging the concentrated perchloric acid was an essential step to give reproducible results with good precision. Table 3 summarizes the K_1 values obtained at μ = 0 M (only the hydrolysis products contribute to the ionic strength so that it is less than 2×10^{-4} M) with temperature variation from 6.3 to 30.1 °C and at 25.0 °C with ionic strength variation from μ = 0 to 1.00 M. These results agreed well with measurements using Liebhafsky's method[2] of Br_2(aq) preparation in place of our procedure to form Br_2(aq).

$$K_1 = \frac{x^3}{[Br_2(aq)]} \tag{9}$$

Effect of Temperature on K_1. The linear plot of $\ln K_1$ against $1/T$ in accord with eq 10 gives $\Delta H° = 62 \pm 1$ kJ mol^{-1} and $\Delta S° = 46 \pm 5$ J mol^{-1} K^{-1}. Our equilibrium constant at 25.0 °C (3.5×10^{-9} M) is a factor of 1.7 smaller than Liebhafsky's value,[2] and our $\Delta H°$ value is larger than his value of 50.9 kJ mol^{-1} (obtained from the corrected value[2b] that he gives for the slope of $\log K_1$ vs $1/T$). However, if we use his data from 0 to 35 °C, we calculate a $\Delta H°$ value of 56.0 ± 0.1 kJ mol^{-1}. His data indicate a small temperature dependence of $\Delta H°$ and can be better fit to eq 11, where the thermodynamic parameters can be evaluated from $A = -(\Delta H° - \Delta C_pT)/R$, $B = \Delta C_p/R$, and $C = (\Delta S° - \Delta C_p \ln T - \Delta C_p)/R$.[30] This treatment gives $\Delta C_p = -280 \pm 110$ J mol^{-1} K^{-1} for Liebhafsky's data. However, eq 11 does not give a significantly better fit of our data where $\Delta C_p = -230 \pm 410$ J mol^{-1} K^{-1}. Although the uncertainty of the ΔC_p value is very large, it is possible that ΔC_p is negative because a large, negative ΔC_p is characteristic for both Cl_2 hydrolysis ($\Delta C_p = -537$ J mol^{-1} K^{-1})[31,32] and the reaction of Br_2(aq) with hydroxylamine ($\Delta C_p = -440$ J mol^{-1} K^{-1}).[33]

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{10}$$

$$\ln K = A/T + B \ln T + C \tag{11}$$

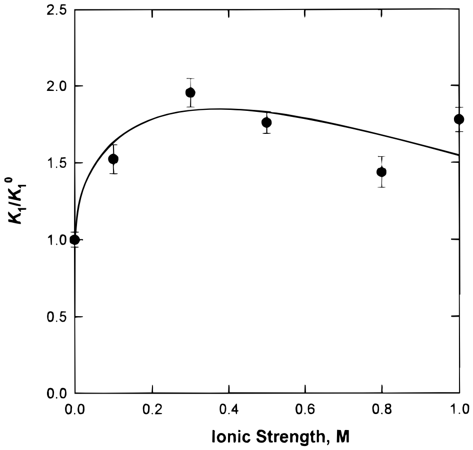

Figure 1. Ionic strength dependence of the bromine hydrolysis equilibrium constant at 25.0 °C. The curve corresponds to the fit of eq 12 for B′ = 0.3.

Ionic Strength Effect on K_1. Table 3 gives the variation of K_1 as a function of ionic strength controlled by $NaClO_4$. The Debye–Hückel–Brønsted treatment[34] predicts the relationship in eq 12, where K_1^o is the value of the equilibrium constant at μ = 0 M and K_1 is for any ionic strength. Figure 1 shows the fit of eq 12 where B′ = 0.3, which is within the range of typical values for this interaction coefficient.[35,36] The B′μ term takes into account the effect of reduced activity of water at high ionic strength conditions.

$$\log K_1 = \log K_1^o + 1.02\left(\frac{\mu^{1/2}}{1 + \mu^{1/2}}\right) - B'\mu \tag{12}$$

Kinetics of Br_2(aq) Formation in Dilute $HClO_4$. The rate expression for reversible bromine hydrolysis is given in eq 13.

$$\frac{-d[Br_2(aq)]}{dt} = k_1[Br_2(aq)] - k_{-1}[HOBr][H^+][Br^-] \tag{13}$$

We adjusted conditions for the PAF studies to make $k_{-1}[HOBr][H^+][Br^-] \gg k_1[Br_2(aq)]$. Under pseudo-first-order

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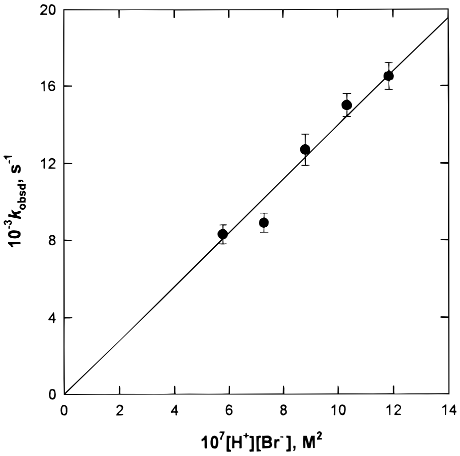

Figure 2. Pseudo-first-order rate constants observed by the PAF method at 266 nm for $Br_2(aq)/Br_3^-$ formation as a function of the product of $[H^+][Br^-]$ concentrations where $[Br_2]_T = 4.0 \times 10^{-4}$ M, $[H^+] = 7.6 \times 10^{-4}$ M, and $[Br^-] = (7.6-15.6) \times 10^{-4}$ M.

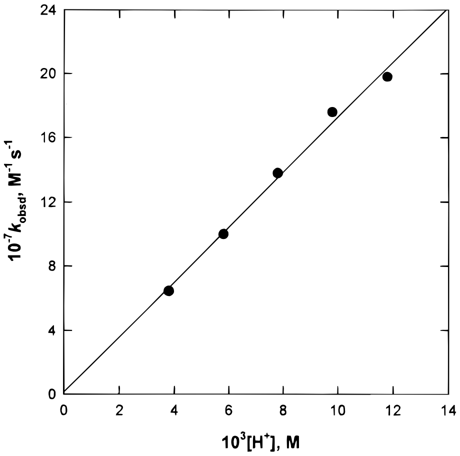

Figure 3. Pseudo-second-order rate constants observed by the PAF method at 390 nm for the formation of Br_2 from HOBr and Br^- with added H^+ where $[HOBr] = [Br^-] = 4.0 \times 10^{-4}$ M and $[H^+] = (3.8-11.8) \times 10^{-3}$ M.

conditions, a dilute solution of aqueous bromine (∼20% dissociated into HOBr) was mixed with H^+ and Br^- in the PAF instrument. The postmixing concentrations were $[Br_2]_T = 4.0 \times 10^{-4}$ M, $[H^+] = 7.6 \times 10^{-4}$ M, and $[Br^-] = (7.6-15.6) \times 10^{-4}$ M. A small, but readily observable, amount of Br_3^- (at 266 nm) forms instantly (eq 5), and the subsequent conversion of the mixture to >99% $[Br_2(aq) + Br_3^-]$ is measured in accord with eq 4 where $k_{obsd} = k_{-1}[H^+][Br^-]$. The reaction consumes 10% of the postmixed $[H^+]$ and 5−10% of the postmixed $[Br^-]$, so the pseudo-first-order condition is valid to about ±5%. The resolved k_{obsd} values were in the range of 8000−16 000 s^{-1} as shown in Figure 2. The resulting k_{-1} value is $(1.4 \pm 0.2) \times 10^{10}$ M^{-2} s^{-1}.

Under second-order conditions, the $Br_2(aq)$ solution was first adjusted to pH 6.9, where it was >99% hydrolyzed to HOBr and Br^-. This solution was reacted with dilute $HClO_4$ in the PAF instrument. The postmixing concentrations were $[HOBr] = [Br^-] = 4.0 \times 10^{-4}$ M and $[H^+] = 0.0038-0.0118$ M. The reaction converted 95−97% of $[Br_2]_T$ to $Br_2(aq)$ and was observed at 390 nm. The resolved second-order rate constants (eq 6) varied from $(6.4 \pm 0.1) \times 10^7$ to $(19.8 \pm 0.1) \times 10^7$ M^{-1} s^{-1} as shown in Figure 3. The resulting k_{-1} value is $(1.7 \pm 0.1) \times 10^{10}$ M^{-2} s^{-1}. By combining both sets of data, we find an average k_{-1} value of $(1.6 \pm 0.2) \times 10^{10}$ M^{-2} s^{-1} at 25.0 °C, $\mu = 0.50$ M, which is in good agreement with Eigen and Kustin's value of 1.6×10^{10} M^{-2} s^{-1} at 20 °C, $\mu = 0.10$ M. The higher temperature in our study will give a larger k_{-1} value, but this is offset by the higher ionic strength which will lower the k_{-1} value. From the equilibrium constant, we calculate $k_1 = 97 \pm 7$ s^{-1} (25.0 °C, $\mu = 0.50$ M) compared to Eigen and Kustin's value of 110 s^{-1} (20 °C, $\mu = 0.10$ M).

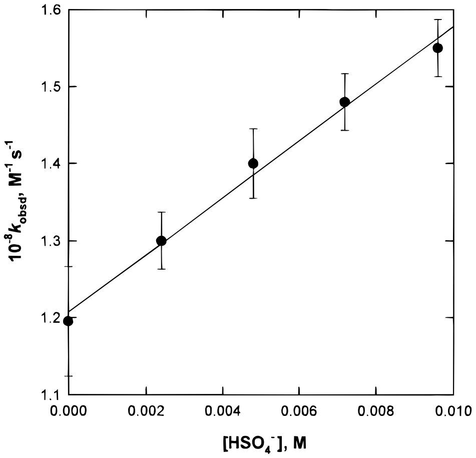

Figure 4. Plot of the observed pseudo-second-order rate constants (eq 15) vs $[HSO_4^-]$ for the reverse reaction of Br_2 hydrolysis in HSO_4^-/SO_4^{2-} buffer. The experimental conditions are as follows: $[Br^-]_0 = [HOBr]_0 = 3.6 \times 10^{-4}$ M, $[H^+] = 7.48 \times 10^{-3}$ M, $\mu = 0.50$ M, 25.0 °C.

Kinetics of $Br_2(aq)$ Formation in HSO_4^-/SO_4^{2-} Buffer. Bromine hydrolysis in the presence of buffer occurs by two pathways (eqs 1 and 3). The reverse reaction was studied under pseudo-second-order conditions with initial postmixing concentrations as follows: $[Br^-] = [HOBr] = 3.6 \times 10^{-4}$ M, $[H^+] = 7.48 \times 10^{-3}$ M, and $[HSO_4^-] + [SO_4^{2-}] = 0.020-0.080$ M. Under these conditions, the terms with k_1 and k_2 in the rate expression are much smaller than terms associated with k_{-1} and k_{-2}. Therefore, the rate expression can be simplified into eq 14. The observed rate constant determined by PAF methods is

$$\frac{d[Br_2]}{dt} = k_{-1}[HOBr][H^+][Br^-] + k_{-2}[HOBr][HA][Br^-] \quad (14)$$

given by eq 15, and the k_{-2} value can be obtained from the slope of the plot k_{obsd} (M^{-1} s^{-1}) vs [HA]. The k_2 value can be

$$k_{obsd} = k_{-1}[H^+] + k_{-2}[HA] \quad (15)$$

calculated by eq 16, where K_a is the dissociation equilibrium

$$k_2 = \frac{K_1 k_{-2}}{K_a} \quad (16)$$

constant of HA. The k_{obsd} values are plotted in Figure 4 for Br_2 formation in the presence of HSO_4^-/SO_4^{2-} buffer. The resulting rate constants at $\mu = 0.50$ M and 25.0 °C with $K_a = 5.49 \times 10^{-2}$ M^{37} are $k_{-2} = (3.7 \pm 0.2) \times 10^9$ M^{-2} s^{-1} and $k_2 = (4.1 \pm 0.2) \times 10^2$ M^{-1} s^{-1}.

Kinetics of $Br_2(aq)$ Formation in $H_3PO_4/H_2PO_4^-$ Buffer. The k_{obsd} values for Br_2 formation in the presence of the $H_3PO_4/H_2PO_4^-$ buffer were determined under second-order condi-

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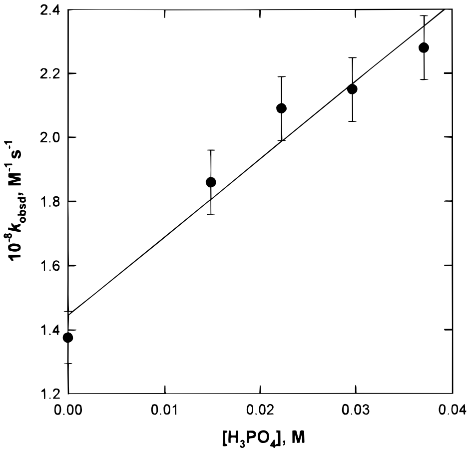
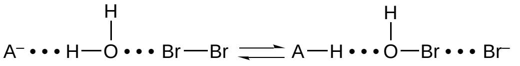


Figure 5. Plot of the observed pseudo-second-order rate constants (eq 15) vs [H_3PO_4] for the reverse reaction of Br_2 hydrolysis in H_3PO_4/$H_2PO_4^-$ buffer. The experimental conditions are as follows: $[Br^-]_0$ = $[HOBr]_0 = 4.0 \times 10^{-4}$ M, $[H^+] = 8.61 \times 10^{-3}$ M, $\mu = 0.50$ M, 25.0 °C.

tions with initial postmixing concentrations as follows: $[Br^-] = [HOBr] = 4.0 \times 10^{-4}$ M, $[H^+] = 8.61 \times 10^{-3}$ M, and $[H_3PO_4] + [H_2PO_4^-] = (4.0-10.0) \times 10^{-2}$ M. Figure 5 shows the plot of k_{obsd} against [HA]. The rate constants at $\mu = 0.50$ M and 25.0 °C with $K_a = 1.46 \times 10^{-2}$ M[38] are $k_{-2} = (2.4 \pm 0.3) \times 10^9$ M^{-2} s^{-1} and $k_2 = (1.0 \pm 0.1) \times 10^3$ M^{-1} s^{-1}.

General-Acid/Base-Assisted Mechanisms. In previous work, we showed general-acid/base-assisted mechanisms for Cl_2 hydrolysis.[31] The general-base-assisted mechanism of the forward reaction for Cl_2 or Br_2 hydrolysis consists of Cl^+ or Br^+ transfer to the oxygen atom of H_2O as it transfers a proton to A^-. Proposed changes as the species pass through the transition state are shown in eq 17 for bromine. The general-acid-assisted mechanism for the reverse reaction involves Br^+ transfer to Br^- as proton transfer occurs from HA to HOBr. The rate constants are proportional to the strength of the acid or base in accordance with the Brønsted−Pedersen relationship (eqs 18 and 19),[39] where p is the number of equivalent protons in acid HA, q is the number of sites that can accept a proton in the conjugate base A^-, α and β are the slopes which reflect the degree of proton transfer in the transition state, and G_A and G_B are constants. The α and β values range from 0 to 1, and theoretically, $\alpha + \beta = 1$.



$$A^- \cdots H{-}\overset{\overset{\displaystyle H}{|}}{O} \cdots Br{-}Br \rightleftharpoons A{-}H \cdots \overset{\overset{\displaystyle H}{|}}{O}{-}Br \cdots Br^- \tag{17}$$

$$\log(k_2/q) = \log G_B - \beta\log(K_a q/p) \tag{18}$$

$$\log(k_{-2}/p) = \log G_A + \alpha\log(K_a q/p) \tag{19}$$

Table 4 summarizes the constants for general-acid/base-assisted Br_2 hydrolysis. Figure 6 shows the plots of $\log(k_{-2}/p)$ and $\log(k_2/q)$ vs $\log(K_a q/p)$ for three acid/base pairs. Linear relationships in Figure 6 confirm the general-acid/base-assisted mechanisms for Br_2 hydrolysis. On the basis of experimental measurements of k_{-2}, α is 0.2 ± 0.1. The value for β becomes 0.8 ± 0.1 using k_2 values derived from k_1 and k_{-2}. The smaller α value compared to the β value shows there is a smaller degree of proton transfer from HA to HOBr in the general-acid-assisted reverse reaction compared to the degree of proton transfer from H_2O to A^- in the general-base-assisted forward reaction.

Table 4. Summary of Constants for the Brønsted−Pedersen Relationship

HA	p	q	pK_a	$10^{-10}k_{-2}$, M^{-2} s^{-1}	k_2, s^{-1}
H_3O^+	3	2	−1.72	1.6 ± 0.2	1.9 ± 0.2[b]
HSO_4^-	1	4	1.26[c]	0.37 ± 0.02	410 ± 20[d]
H_3PO_4	3	2	1.84[e]	0.24 ± 0.03	1000 ± 100[d]

[a] Conditions: 25.0 °C, $\mu = 0.50$ M. [b] $k_2 = k_1/55.5$ (k_1 = water path). [c] Reference 37. [d] $k_2 = K_1k_{-2}/K_a$. [e] Reference 38. Obtained from data interpolation of pK_a values ranging from $\mu = 0$ to 1.1 M at 25.0 °C.

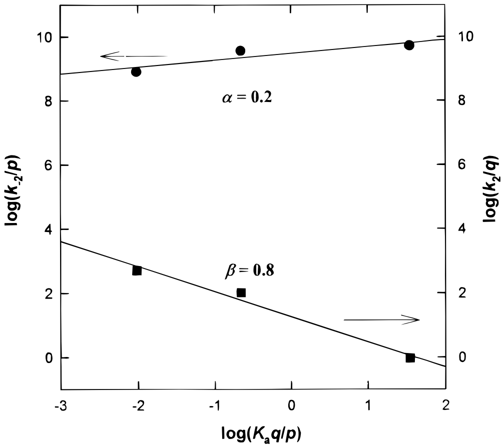


Figure 6. Brønsted−Pedersen plots. The left ordinate shows the general-acid-assisted reverse reaction of Br_2 hydrolysis. The α value determined from the slope is 0.2 ± 0.1. The right ordinate shows the general-base-assisted forward reaction of Br_2 hydrolysis. The β value determined from the slope is 0.8 ± 0.1.

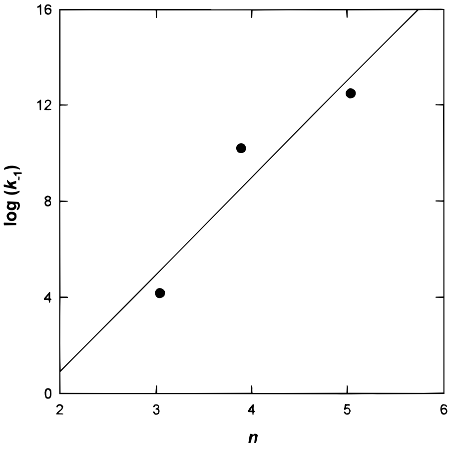


Figure 7. Correlation of the k_{-1} values for HA + HOX + X^- with the nucleophilicity (n) of X^- (Cl^-, Br^-, I^-).

Extrapolation of eq 18 in Figure 7 to include hydroxide ion would predict a value of $k_2 = 10^{13.7}$ M^{-1} s^{-1} (25.0 °C, μ = 0.50 M) for $A^- = OH^-$ in eq 3, on the basis of $\beta = 0.8$, $K_a = K_w/[H_2O] = 10^{-15.35}$, $q = 3$ for OH^-, $p = 2$ for H_2O, and pK_w = 13.61 at 25.0 °C in 0.50 M $NaClO_4$.[40,41] However, this value exceeds the diffusion limit. Even the direct reaction with OH^- (without the intervening H_2O molecule) would be expected to occur at the diffusion-controlled limit in water ($k_D = 10^{9.8}$ M^{-1}

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Table 5. Kinetic Parameters for the General-Acid-Assisted Reactions of Halogen Hydrolysis

reaction	α	n^a	k_{-1}, M^{-2} s^{-1}	ref
HA + HOCl + Cl^-	0.40 ± 0.05	3.04	1.5×10^4	31
HA + HOBr + Br^-	0.2 ± 0.1	3.89	1.6×10^{10}	this study
HA + HOI + I^-	0.21 ± 0.04^b	5.04	3.1×10^{12}	4, 45

[a] Nucleophilicity of halide ions. [b] Estimated from the linear relationships between α, n, and k_1.

s^{-1} at 25.0 °C).[42] Contribution from the OH^- pathway is negligible under our acidic conditions ($[H^+] > 7 \times 10^{-3}$ M).

Rate constants and α values for the general-acid-assisted reactions of HOX with different halide ions (X^-) are summarized in Table 5. Previous studies[31,43,44] have shown that the third-order rate constants for the reaction of H^+ + HOCl + X^- follow the Swain−Scott relationship (eq 20), where n is the nucleophilicity of X^- and s is the sensitivity of the reaction

$$\log\left(\frac{k}{k_0}\right) = sn \qquad (20)$$

site. The sensitivity factor is extremely large for the H^+ + HOCl + X^- reactions, where $s = 3.8$. As Table 5 and Figure 7 show, the third-order rate constants for H^+ + HOX + X^- also increase with the increasing nucleophilicity of X^-, and the sensitivity factor is still large ($s = 4$). We also showed that the k_{-1} values increase and α values decease linearly as the nucleophilicity of X^- increases.[31] This predicts the Brønsted α values for the reaction of H^+ + HOI + I^- to be 0.21 ± 0.04.

Table 5 shows that when the n values are large, the reactions are very favorable, and the degree of proton transfer from HA is small because there is less need for acid assistance. On the other hand, if the nucleophilicity is small, the reaction requires a larger degree of assistance by proton transfer as reflected by the larger α value for Cl^-. This is an interesting correlation between the role of general-acid assistance for proton transfer to oxygen and the role of nucleophilicity of X^- as it reacts with the adjacent halogen in HOX. We observed the same correlation in the study of H^+ + HOCl + X^-.[31]

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Supporting Information Available: A plot of experimental data using eqs 10 and 11 and tables of the data plotted in Figures 2−5 (3 pages). Ordering information is given on any current masthead page.

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