Kinetics of Hypobromous Acid Disproportionation

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The kinetics of aqueous hypobromous acid disproportionation are measured at 25.0 °C from p[H$^+$] 0.2 to 10.2. The reactions are second order in HOBr with a maximum rate at pH 3−8. The rate of disproportionation decreases significantly above pH 8 as OBr$^-$ forms. Another suppression observed below pH 3 is attributed to the reversibility of initial steps in the decomposition. The rate expression is given by $-d[\mathrm{Br(I)}]/dt = n\{(c/(c + [\mathrm{H}^+])k_{1a} + k_{\mathrm{B}}[\mathrm{B}])[\mathrm{HOBr}]^2 + k_{1b}[\mathrm{OBr}^-]^2\}$, where $k_{1a} = 2 \times 10^{-3}$ M^{-1} s^{-1}, k_{B}[B] is a general-base-assisted pathway, $k_{1b} = 6 \times 10^{-7}$ M^{-1} s^{-1}, *n* is a stoichiometric factor that ranges from 2 to 5, and *c* is a ratio of rate constants that is equal to 0.03 M. Decomposition is catalyzed by HPO_4^{2-} ($k_{\mathrm{B}} = 0.05$ M^{-2} s^{-1}) and by CO_3^{2-} ($k_{\mathrm{B}} = 0.33$ M^{-2} s^{-1}). Above pH 8, the first observable product is BrO_2^- (initially $n = 2$). Below pH 4, $n = 5$ due to Br_2 and BrO_3^- formation. From pH 4 to 7, *n* varies from 5 to 3. A detailed mechanism is presented.

Introduction

Hypobromous acid (HOBr) forms in water disinfection processes during chlorine or ozone treatment of water which contains bromide ion. Concentrations of bromide ion in ground water are typically in the range of <0.01−3 mg/L.[1] Bromate ion, a carcinogen and neurotoxin, is a disproportionation product of HOBr, so it is desirable to minimize formation of bromate to within the Environmental Protection Agency's maximum contaminant level (MCL) of 0.010 mg/L.[2] The atmospheric chemistry of HOBr is also significant due to its proposed role in the loss of tropospheric ozone in the Arctic region.[3]

In neutral or weakly alkaline solution, some authors report decomposition of HOBr as a third- or mixed-order process,[4−6] while others report a second-order process with the mechanism shown in eqs 1−3 (where Br(I) refers to HOBr or OBr$^-$ and Br(III) represents BrO_2^- or $HBrO_2$).[7−9] This disagreement may be due to varying conditions used in different studies.[10] Additional complications may include inadequate titration methods to distinguish Br(I), BrO_2^-, and BrO_3^-[11,12] or use of an inaccurate pK_a value for HOBr.[7] Metal contamination of reagents may be another source of error.[13]

$$\mathrm{Br(I)} + \mathrm{Br(I)} \xrightarrow{k_1} \mathrm{Br(III)} + \mathrm{Br}^- + n\mathrm{H}+ \qquad (1)$$

$$\mathrm{Br(I)} + \mathrm{Br(III)} \xrightarrow{k_2} \mathrm{BrO_3}^- + \mathrm{Br}^- + n\mathrm{H}^+ \qquad (2)$$

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

Literature values for k_1 and k_2 are shown in Table 1.[14−19] The reaction involving [Br(III)] in eq 2 is generally regarded as being faster than that of eq 1. Reported activation energies for eq 1 are 58 ± 3 kJ/mol in 1 M H_2SO_4[15] and 81.2 kJ/mol[11] and 95 ± 2 kJ/mol[20] in base. At higher pH, hypobromous acid dissociates to hypobromite ion with a pK_a of 8.8 at 25.0 °C and an ionic strength (μ) of 0.50 M.[21] Equation 4 has also been shown as a minor pathway in base, but its contribution is negligible in metal-free solutions protected from light.[10,22]

$$2\mathrm{OBr}^- \rightarrow \mathrm{O_2} + 2\mathrm{Br}^- \qquad (4)$$

The rate of HOBr disproportionation at high pH is suppressed due to deprotonation of HOBr. Chapin reports that Br(I) is least stable at pH 7.3 and most stable at pH 13.4.[4] Hamano and Nakamori also show a similar trend.[12] Kulkarni and Nabar[23] and Gottardi and Bock[24] monitored HOBr disproportionation at pH 6−10 and observed that the fastest decomposition occurred around pH 7.6. However, without detailed buffer conditions for their work at pH < 7.5, it is not clear whether the trend is due to pH or to decreasing buffer assistance. Furthermore, they did not address comproportionation of Br$^-$ and HOBr to form Br_2.

Only Chapin[4] and Skrabal[25] mention catalysis by buffers. Hypochlorite decomposition is reported to be accelerated by acetate, borate, carbonate, and, to a lesser extent, phosphate buffer.[4] Fábián et al. observe a small phosphate and carbonate

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Table 1. Literature Values for the Rate Constants at 25 °C of Eqs 1 and 2

pH	medium/buffer^a	10^3k_1, M^{-1} s^{-1}	10^3k_2, M^{-1} s^{-1}	ref
−0.2	1.67 M $HClO_4$	0.023^b		14
−0.02	1.0 M H_2SO_4	0.031^{b,c}	3200	15
6.9	0.10 M phosphate	0.24		16
7.5	borate	2.4^d		12
7.9	0.4 M total borate	1.3		8
8.2	0.4 M total borate		225	8
8.5	borate	1.6^d		12
8.6	0.05 M total borate	0.47		17
8.84	borate	0.83^e	18	7
9.2	0.4 M total borate		9.8	8
9.5	borate	1.1^d		12
10.0	borate	0.025^d		12
10.4	carbonate	0.060		16
12	NaOH	0.00036^d		12
12.8	NaOH	0.00026^e	0.0036	18
13.1	NaOH	0.00032		19
13.5	NaOH	0.00104^f		11
13.9	NaOH	0.00113^f		11

^{a} Buffer concentration not specified in some instances. ^{b} Authors indicate $k_{app} = 5k_1$. ^{c} 20 °C. ^{d} Obtained from second-order integrated fit of authors' Br(I) decay data. ^{e} Authors indicate $k_{app} = 2k_1$. ^{f} Authors indicate $k_{app} = 3k_1$.

effect in the decomposition of HOCl.[26] No buffer dependencies for HOBr decomposition are reported in the literature. Most authors did not attempt a mechanistic explanation of how Br(I) is oxidized to Br(III) and Br(V).

Engel et al. proposed the general rate expression (eq 5) with $k_1 = 8.3 \times 10^{-4}$ M^{-1} s^{-1} and $k_2 = 0.018 \pm 0.003$ M^{-1} s^{-1} at pH 8.84 and 25 °C.[7] We propose a more detailed expression

$$\frac{-\mathrm{d}[\mathrm{Br(I)}]}{\mathrm{d}t} = 2k_1[\mathrm{Br(I)}]^2 + \mathrm{k}_2[\mathrm{Br(I)}][\mathrm{Br(III)}] \qquad (5)$$

for the k_1 term reflecting a buffer-assisted second-order pathway for the reaction between HOBr and HOBr. A rate expression to encompass the pH range 0−14 is discussed, and a detailed mechanism and buffer dependence study is presented.

Experimental Section

Reagents. Distilled, doubly-deionized water was used for all solutions. All experiments were carried out at 25.0 ± 0.4 °C and ionic strength (μ) = 0.50 M (adjusted with $NaClO_4$) unless otherwise indicated. Perchloric acid (70%) was purged with argon or helium before use to remove volatile oxidizing impurities. Solutions of phosphate and carbonate buffer were prepared from the reagent-grade salts. Absorbance measurements at 225 nm showed no evidence for the presence of I^- (ϵ = 14 380 M^{-1} cm^{-1}) in these buffer solutions. At 25.0 °C and μ = 0.5 M, the pK_a values are 6.46[27] for $H_2PO_4^-$ and 9.70[27,28] for HCO_3^- and pK_w = 13.61.[29]

All Br(I) and Cl(I) solutions were handled under low actinic lights. Hypobromous acid solutions for studies in carbonate buffer were prepared by adding liquid Br_2 to buffer solutions. For studies at pH < 2, the bromide ion in the hypobromite solutions was reduced to $<5 \times 10^{-4}$ M by reaction with AgOH in a method similar to that of Noszticzius et al.[30] Subsequent mixing with excess acid produced HOBr(aq) solutions with sufficiently low bromide-ion content to monitor HOBr(aq) and low levels of Br_2(aq) simultaneously. For studies in phosphate buffer, solutions of OCl^- and Br^- were mixed in equimolar concentrations to yield bromide-free HOBr.[31] Hypochlorite solutions were prepared by bubbling Cl_2(g) into NaOH(aq).

Instrumentation and Methods. A Perkin-Elmer Lambda 9 UV−vis−NIR spectrophotometer was used to obtain spectrophotometric data as a function of time. Cells (b = 1.00 or 2.00 cm) were thermostated for all disproportionation studies. An Orion model SA 720 pH meter and an Orion combination pH electrode were used to measure pH values. These pH values were converted to p[H$^+$] at 25.0 °C and μ = 0.50 M based on electrode calibration by titration of standardized $HClO_4$ with NaOH.

For studies in phosphate buffer, the loss of HOBr was followed photometrically at 260 nm (ϵ = 95 M^{-1} cm^{-1}).[32,33] The cell was quickly capped with minimal headspace so that volatilization of HOBr was negligible. As Br^- accumulates over time, small amounts of Br_2 (ϵ_{260} = 63 M^{-1} cm^{-1})[34] and Br_3^- (ϵ_{260} = 37 200 M^{-1} cm^{-1})[34] form in accord with eqs 6[35] and 7,[34] where $K_{com} = 1.6 \times 10^8$ M^{-2} and K_{Br} = 16.8 M^{-1} at 25 °C and μ = 0.5 M. The total absorbance contribution at 260 nm

$$\mathrm{HOBr} + \mathrm{Br}^- + \mathrm{H}^+ \overset{K_{com}}{\rightleftharpoons} \mathrm{Br}_2 + \mathrm{H}_2\mathrm{O} \qquad (6)$$

$$\mathrm{Br}_2 + \mathrm{Br}^- \overset{K_{Br}}{\rightleftharpoons} \mathrm{Br}_3^- \qquad (7)$$

from Br_2, Br_3^-, and BrO_3^- (ϵ = 6 M^{-1} cm^{-1})[36] was subtracted for experiments at pH < 6.5; this adjustment is less than a 10% correction from pH 5.9 to 6.5. Rate constants were determined using the method of initial rates based on eq 8. Typical runs in phosphate buffer followed

$$\frac{-\mathrm{d}[\mathrm{Br(I)}]}{\mathrm{d}t} = k_{app}[\mathrm{Br(I)}]^2 \qquad (8)$$

6−7% decomposition of 1.3 mM HOBr solutions inside a 2.00-cm cell.

For studies at pH < 2, HOBr loss was monitored at 310 nm (ϵ = 39 M^{-1} cm^{-1});[32,33] the absorbance contribution of Br_2 (ϵ = 8 M^{-1} cm^{-1})[34] formation was subtracted when calculating the observed rate constant. For studies at pH 7.4−10.2, distribution of [HOBr] and [OBr^-] can be resolved using eqs 9 and 10 (where b is the cell path) given the p[H$^+$]

$$[\mathrm{OBr}^-] = \frac{A_{329} - b\epsilon_{\mathrm{HOBr}}[\mathrm{HOBr}]}{b\epsilon_{\mathrm{OBr}}} \qquad (9)$$

$$[\mathrm{HOBr}] = \frac{A_{329}}{b[\epsilon_{\mathrm{OBr}}(10^{\mathrm{p[H^+]} - \mathrm{p}K_a}) + \epsilon_{\mathrm{HOBr}}]} \qquad (10)$$

and the absorbance at 329 nm (A_{329}), where OBr^- has its absorbance maximum (ϵ = 332 M^{-1} cm^{-1})[21] and HOBr (ϵ = 33 M^{-1} cm^{-1})[32,33] absorbs much less. Equation 8 is used to determine k_{app} by initial rates. Reactions were monitored for 3−13% loss of $[\mathrm{HOBr}]_T$, where $[\mathrm{HOBr}]_T$ = [HOBr] + [OBr^-].

Results and Discussion

Stoichiometric Considerations. We must relate k_1 to the experimental rate constant k_{app}, which combines k_1, k_2, and stoichiometric factors. The reaction stoichiometry, n, is expressed in terms of $-(1/n)\mathrm{d}[\mathrm{Br(I)}]/\mathrm{d}t$ because n varies according to the conditions. Equation 3 describes the stoichiometry for complete disproportionation of Br(I) above pH 6.5 (if the solution is initially bromide free).[7,11,13,18,20] However, the relative rates of eqs 1 and 2 must be considered during the early stages of decomposition. The k_2/k_1 ratio is reported to be ≥100 at both pH 0[15,37] and 8.2.[8] Therefore, the stoichiometry of eq 3 (n = 3) is valid even at the early stages of decomposition

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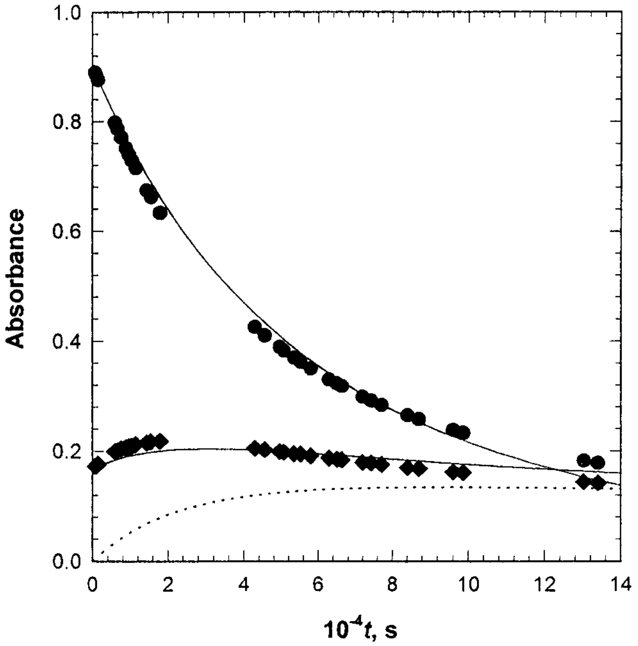

Figure 1. Experimental absorbance at 329 nm (●) and 257 nm (◆) fit to eq 5 (solid curves) for the loss of 4.05 mM [Br(I)] at p[H$^+$] 9.02, $b = 1.00$ cm, 25.4 °C, 0.30 M $[CO_3^{2-}]_T$, and $\mu = 0.46$ M, $2k_1 = 0.011$ M^{-1} s^{-1}, and $k_2 = 0.008$ M^{-1} s^{-1}. The dotted line shows the simulated absorbance contribution from BrO_2^- at 257 nm.

since eq 1 is clearly the rate-determining step. Hence, measured k_{app} values are equivalent to $3k_1$. The k_2/k_1 ratio decreases to 22 at pH 8.84[7] and to 14 at pH 12.8.[18] Consequently, eq 1 rather than eq 3 describes disappearance of HOBr for <10% loss of $[HOBr]_T$ if bromite is absent initially. Bromite ion builds to appreciable levels in these instances so that $n = 2$. Our kinetic analyses at pH 8.87−10.20 were carried out within this time frame, which results in $k_{app} = 2k_1$. Studies under basic conditions that follow much greater than 10% decomposition obey a stoichiometry that is closer to $3\Delta[HOBr]_T$:$1\Delta[BrO_3^-]$ since eq 2 takes place to a significant extent. Lister and McLeod[11] point out that a rate expression involving $3k_1$ is valid to within 3% at pH > 13 when analyzing data covering 10−40% decomposition of $[OBr^-]_i$. Depending on the magnitude of k_2/k_1, mixed stoichiometries (between 2 and 3) likely occur within the pH 8.0−8.8 region during the early stages of decomposition. However, we did not conduct studies in this pH range. In acidic conditions (pH < 4), bromine formation occurs and the overall stoichiometry is given by eq 11, where $K = 1 \times 10^{10}$ M^{-1} is calculated using standard electrode potentials.[38] Kshirsagar and Field[15] give eq 12 as the corresponding rate expression, which includes the generation of Br_2 (eq 6). In solutions of low Br^- ion or Br_2, the initial decay of

$$5HOBr \overset{K}{\rightleftharpoons} 2Br_2 + BrO_3^- + 2H_2O + H^+ \qquad (11)$$

$$\frac{-d[HOBr]}{dt} = \frac{5\, k_1\, k_2[HOBr]^3}{k_2[HOBr] + k_{-1}[Br_2]/(K_{com}[HOBr])} \qquad (12)$$

HOBr is given by the simplified rate expression in eq 13, where $n = 5$ and $k_{app} = 5k_1$.[15] Fractional stoichiometries between 3

$$\frac{-d[HOBr]}{dt} = 5k_1[HOBr]^2 \qquad (13)$$

and 5 are expected between pH 4.0 and 6.5 since both eqs 3 and 11 have significant contributions. In summary, the value of n varies from 5 (pH < 4) to 3 (pH > 6.5), but at pH > 8, $n = 2$ at the initial stages of decomposition.

Table 2. Rate Constants for HOBr Disproportionation in Buffer-Free Conditions[a]

p[H$^+$]	n	10^3k_1, M^{-1} s^{-1}
0.20	5.0	0.44[b,c]
1.05	5.0	0.43[b]
3.62	5.0	1.2
6.00	3.3	0.88[d]
5.88−7.01	3.0−3.4	1.0[e]
6.94	3.0	3.9[f]
7.39	3.0	3.7[b]
8.88	2.0	0.084[g]
9.40	2.0	1.0
9.42	2.0	1.2
9.52	2.0	0.024
9.53	2.0	0.042
10.12	2.0	0.0085[h]

[a] Conditions: [Br(I)] = 0.4−2.4 mM, $\mu = 0.50 \pm 0.02$ M, 25.0 °C. Rate constants, where $k_{app} = nk_1$, were determined at 260 nm by initial rates using eq 8. [b] Measured at 310 nm. [c] $\mu = 0.63$ M. [d] Obtained from the intercept of the $[HPO_4^{2-}]$ dependence data in Table 3 at p[H$^+$] = 6.00 ± 0.04. [e] Obtained from the intercept of the $[HPO_4^{2-}]$ data in Table 3 where $[PO_4]_T = 0.20$ M, p[H$^+$] = 5.88−7.01. [f] Obtained from the intercept of the $[PO_4]_T$ dependence data in Table 3 at p[H$^+$] = 6.94 ± 0.02. [g] Obtained from the intercept of the $[CO_3^{2-}]_T$ dependence data in Figure 3 at p[H$^+$] = 8.88. [h] Extrapolated from the $[CO_3^{2-}]_T$ dependence at p[H$^+$] = 10.12.

Order of Reaction. The loss of a 4.0 mM Br(I) solution was monitored at 329 and 257 nm over 37 h at 25.4 °C. The reaction was carried out at p[H$^+$] 9.02 in 0.30 M carbonate buffer with $\mu = 0.46$ M (Figure 1). Reaction progress was followed for over two half-lives. At 329 nm, the absorbance is largely (>90%) due to OBr^-, with the rest of the absorbance due to HOBr and BrO_2^- ($\epsilon = 85$ M^{-1} cm^{-1}).[39] The solid lines in Figure 1 show simulated absorbance data that produce a reasonable fit using eq 5 with $2k_1 = 0.011$ M^{-1} s^{-1} and $k_2 = 0.008$ M^{-1} s^{-1}. Therefore, we find second-order and not third-order behavior at p[H$^+$] 9.02. All the initial rate studies used dilute Br(I) (0.4−2.4 mM) to assure second-order kinetics.

In the same experiment, the absorbance at 257 nm is due primarily to a combination of HOBr ($\epsilon = 94$ M^{-1} cm^{-1})[32,33] and BrO_2^- ($\epsilon = 210$ M^{-1} cm^{-1}).[39] An increase in signal is observed over the first 5 h of the reaction, indicating a buildup of bromite ion. The dotted line in Figure 1 shows the simulated absorbance contribution due to BrO_2^- at 257 nm. Formation of an appreciable amount of BrO_2^- was also observed by Engel et al. at pH 8.84.[7] However, our ratio of k_2/k_1 is 1.5 in 0.30 M carbonate buffer compared to Engel's ratio of 22 in an unspecified amount of borate buffer.

HOBr Disproportionation in Acid. Decomposition of 2.3 mM HOBr(aq) solutions was monitored spectrophotometrically. Due to small but appreciable initial levels of Br_2, rate constants were obtained using eq 12 instead of eq 13. Experiments in 0.09 and 0.63 M $HClO_4$ (first two entries in Table 2) gave $k_{app} = 5k_1 = (2.2 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}. These rate constants are smaller than those at pH 3.6−7.4 (Table 2) but significantly larger than the previously reported values in 1.67 M $HClO_4$[14] and 1 M H_2SO_4.[15] These findings suggest an inverse dependence in [H$^+$]. Qualitatively, the rate of disproportionation decreases below pH 3 by a factor of $c/(c + [H^+])$, where $c = 0.03$ M. The decrease in rate is attributed to reversibility of the initial decomposition steps at high acid concentrations.

Phosphate Buffer Dependence. Decomposition of HOBr was studied from p[H$^+$] 5.9 to 7.0 in constant 0.20 M $[PO_4]_T$

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Table 3. Rate Constants for HOBr Disproportionation in Phosphate Buffer[a]

$p[H^+]$	$[PO_4^{2-}]_T$	n	10^3k_1, $M^{-1}\ s^{-1}$ [b]
6.93	0.10	3.05	6.2
6.96	0.15	3.05	7.5
6.92	0.20	3.05	8.6
5.96	0.05	3.36	1.8[c]
6.03	0.10	3.31	3.0[c]
6.03	0.25	3.31	6.3[c]
5.88	0.20	3.41	3.1
6.12	0.20	3.26	3.4
6.15	0.20	3.25	4.1
6.17	0.20	3.24	4.5
6.23	0.20	3.21	7.2
6.37	0.20	3.16	6.0
6.56	0.20	3.10	6.0
6.59	0.20	3.10	6.1
6.66	0.20	3.08	7.9
6.85	0.20	3.06	8.8
7.01	0.20	3.04	9.7
6.20	0.10	3.22	3.7
6.14	0.10	3.25	3.5

[a] Conditions: $[Br(I)] = 1.2-1.5$ mM, $\mu = 0.43-0.54$ M, 25.0 °C. [b] Rate constants were determined by initial rates using eq 8 and $k_1 = k_{app}/n$. [c] 26.1 ± 0.3 °C.

buffer, where $[PO_4]_T = [H_2PO_4^-] + [HPO_4^{2-}]$. No appreciable buildup of BrO_2^- is observed spectrophotometrically at pH 5.9–7.0, which confirms that k_2/k_1 is larger than at pH 9. The results (Table 3) show that it is the base form of phosphate (HPO_4^{2-}) that assists disproportionation. The data from $p[H^+]$ 5.88 to 7.01 at $[PO_4]_T = 0.20$ M correspond to $k_{1obsd} = k_1 + k_p[HPO_4^{2-}]$, where $k_1 = (1.0 \pm 0.8) \times 10^{-3}\ M^{-1}\ s^{-1}$ and $k_p = (5.3 \pm 0.7) \times 10^{-2}\ M^{-2}\ s^{-1}$. The k_1 term is the second-order rate constant for HOBr disproportionation extrapolated to zero buffer, while the k_p term is the third-order rate constant for base assistance by HPO_4^{2-}. Two additional, three-point dependencies in $[PO_4]_T$ (first six entries in Table 3) were collected at $p[H^+]$ 6.00 ± 0.04 ($k_1 = (8.8 \pm 0.9) \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_p = 0.080 \pm 0.009\ M^{-2}\ s^{-1}$) and $p[H^+] = 6.94 \pm 0.02$ ($k_1 = (3.9 \pm 0.3) \times 10^{-3}\ M^{-1}\ s^{-1}$, $k_p = 0.030 \pm 0.003\ M^{-2}\ s^{-1}$). The average value for k_p from the above data sets is $0.05 \pm 0.02\ M^{-2}\ s^{-1}$.

The above values for k_1 were combined with two additional points collected in the absence of buffer at $p[H^+]$ 3.62 and 7.39 (Table 2). Averaging these five data points gives a value of $k_1 = (2.3 \pm 1.7) \times 10^{-3}\ M^{-1}\ s^{-1}$; this is a maximum value of k_1 from pH 3 to 8. Experimental data from $p[H^+]$ 3.62 to 7.39 are shown by the dark circles in Figure 2, where scatter in the k_1 values is apparent. We show that phosphate buffer accelerates the rate, and hence, the k_1 values are obtained by extrapolation to zero buffer concentration. We found that the results for unbuffered solutions were very difficult to reproduce. Despite great care, we also found unaccountable scatter in the results as we varied pH. We used atomic absorption methods to test for iron and copper impurities in the reagents and found only trace levels (e.g., 0.4 ppm Fe and 0.06 ppm Cu in NaH_2PO_4, which is far below permissible levels for reagent grade). There are inherent errors in the use of initial rates (an approach which is necessary to minimize Br_2 and Br_3^- formation) and in the buffer extrapolations.

Bromide Dependence. A weak dependence in bromide ion had been observed previously by Engel et al.,[7] where k_{app} increased by a factor of 1.5 at pH 8.84 in borate buffer when $[Br^-]$ was raised from 19 to 87 mM. Chloride catalysis has also been observed at pH 8.60.[17] We also observe a weak bromide effect at $p[H^+] = 8.89$ in 0.10 or 0.15 M carbonate and $\mu = 0.50$ M. A factor of a 1.5 ± 0.3 increase in rate resulted from a 10-fold increase in $[Br^-]$ to 0.017 M. These observations confirm Engel's findings of a Br^- ion effect, although the effect in our study is weaker than that of Engel's. One possible explanation for this effect proposed by Engel is that a larger bromide ion concentration increases $[Br_2]$ (which is still quite small) by eq 6. This may provide additional decomposition pathways for [Br(I)], such as the hypothesized reaction between Br_2 and OBr^-.[7]

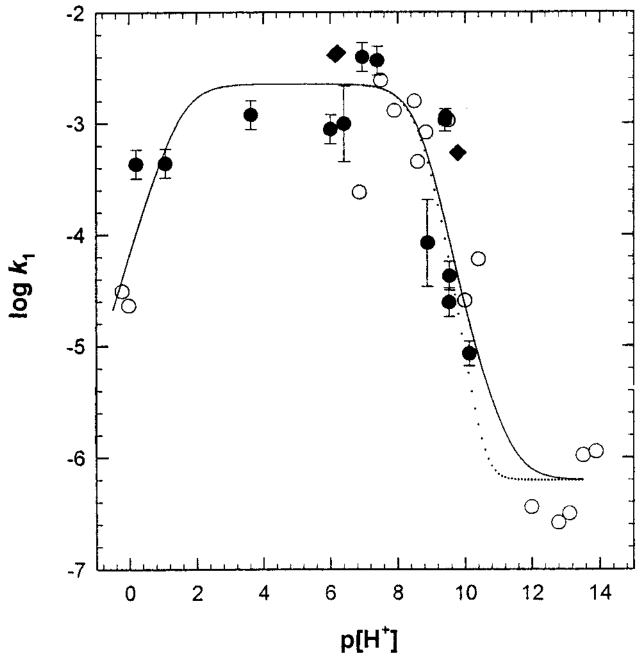

Figure 2. Summary of [Br(I)] disproportionation rate constants as a function of pH (● extrapolated to zero buffer or unbuffered, ◆ buffered), and literature values (○). The calculated fit (dotted line) without buffer shows the model $k_1 = c/(c + [H^+])k_{1a}[HOBr]^2 + k_{1b}[OBr^-]^2$, where $k_{1a} = 2 \times 10^{-3}\ M^{-1}\ s^{-1}$, $k_{1b} = 6 \times 10^{-7}\ M^{-1}\ s^{-1}$, $c = 0.03$ M, $k_1[HOBr]_T^2 = k_{1a}[HOBr]^2 + k_{1b}[OBr^-]^2$, and $k_{app} = nk_1$. The solid line represents the inclusion of a proposed hydroxide-assisted pathway $k_{OH}[OH^-][HOBr]^2$ which is equivalent to $k_{1ab} = 2.3 \times 10^{-4}\ M^{-1}\ s^{-1}$ for the reaction of OBr^- and HOBr.

Rate Expression for HOBr Disproportionation as a Function of pH. It remains to be determined whether disproportionation of [Br(I)] occurs only through reaction of HOBr + HOBr (eq 14) or also through HOBr + OBr^- (eq 15) or OBr^- + OBr^- (eq 16). Figure 2 shows our experimental values for k_1 (● for data extrapolated to zero buffer concentration or unbuffered, ◆ for reactions with 0.05–0.10 M buffer) as well as literature values without buffer correction (○). All k_{app} rate constants were converted to k_1 using the appropriate stoichiometric value (n). A value of k_{1a} (eq 14) of $(2.3 \pm 1.7) \times 10^{-3}\ M^{-1}\ s^{-1}$ was determined from our five data points (buffer free) from $p[H^+]$ 3.6 to 7.4 (Table 2). The dotted line in Figure 2 from pH 7 to 14 is obtained by using a pK_a value of 8.80 for HOBr and eq 17, where k_{1b} (eq 16) is evaluated as $(6 \pm 4) \times 10^{-7}\ M^{-1}\ s^{-1}$ from literature values at pH 12–14.[11,12,18,19] A value for the k_{1ab} (eq 15) term was estimated to be $2.3 \times 10^{-4}\ M^{-1}\ s^{-1}$ from an extrapolation of general-base-assisted rate constants (to be discussed). The solid line plotted in Figure 2 shows this predicted contribution from pH 10 to 12.

$$HOBr + HOBr \xrightarrow{k_{1a}} BrO_2^- + Br^- + 2H^+ \qquad (14)$$

$$HOBr + OBr^- \xrightarrow{k_{1ab}} BrO_2^- + Br^- + H^+ \qquad (15)$$

$$OBr^- + OBr^- \xrightarrow{k_{1b}} BrO_2^- + Br^- \qquad (16)$$

$$k_1[HOBr]_T^2 = k_{1a}[HOBr]^2 + k_{1b}[OBr^-]^2 \qquad (17)$$

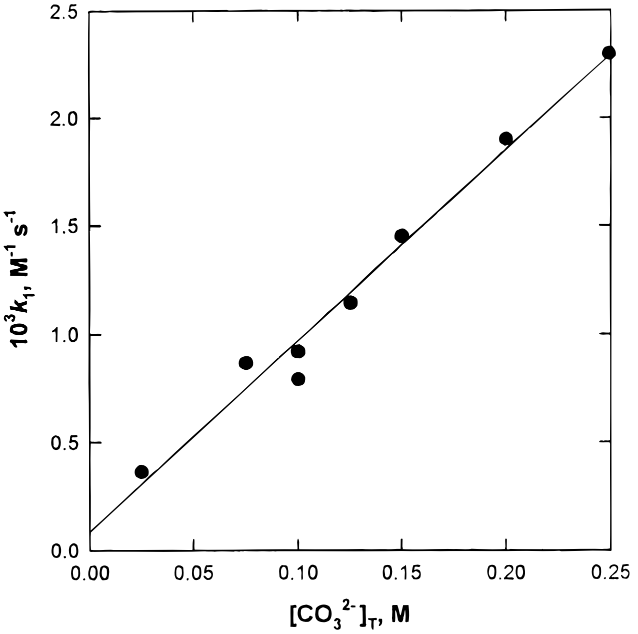

Figure 3. Carbonate buffer dependence of Br(I) disproportionation for [Br(I)] = 0.6−2.4 mM, $p[H^+] = 8.88 \pm 0.02$, 25.0 °C, $\mu = 0.50$ M.

Hypobromite decomposition has been previously studied and reported to obey second-order kinetics in the absence of metals.[4,11,13,20,40] While we did not carry out experiments at $p[H^+] > 10.2$, some authors report an increase in k_{app} above pH 13.5.[4,11,13,20] At $[OH^-] = 0.3-5$ M, Perlmutter-Hayman and Stein report assistance by $[OH^-]$ and with increasing size of the alkali metal cation associated with the hydroxide.[20] Our plot in Figure 2 does not include these effects.

Carbonate Buffer Dependence. A carbonate buffer dependence was performed by varying $[CO_3^{2-}]_T$ (= $[HCO_3^-]$ + $[CO_3^{2-}]$) from 0.025 to 0.25 M at $p[H^+]$ 8.89 ± 0.02 at 25 °C, $[Br(I)] = [Br^-] = 1.4-2.0$ mM, and $\mu = 0.50$ M. A strong first-order dependence in carbonate was observed (Figure 3) with k_x (in terms of $[CO_3^{2-}]_T[HOBr]^2{}_T$) = $(8.8 \pm 0.5) \times 10^{-3}$ M^{-2} s^{-1}. The intercept in Figure 3 also provides an estimate of the rate of disproportionation in the absence of buffer. A value of $k_1 = (8.4 \pm 7.6) \times 10^{-5}$ M^{-1} s^{-1} was determined by this method. Additional runs at $p[H^+]$ 9.40−9.53 in the absence of buffer are shown in Table 2, where k_1 ranges $(2.4-120) \times 10^{-5}$ M^{-1} s^{-1}. However, the lack of buffer raises the experimental uncertainty due to increased difficulty in accurately measuring pH in addition to a small decrease in pH while decomposition is in progress.

Rate Expression for Carbonate Dependence. A complete rate expression for HOBr disproportionation requires modification of eq 17 to include the appropriate buffer term. At pH > 9 it remains to be determined which form of carbonate (HCO_3^- or CO_3^{2-}) reacts and with which $[Br(I)]^2$ term the buffer assists. A pH dependence from pH 9.0 to 10.5 in constant $[CO_3^{2-}]_T$ buffer is complicated by the fact that HOBr disproportionation is already affected significantly by pH in this region. Nevertheless, the difference in pK_a values of HOBr and HCO_3^- permits distinction of the proper rate expression. Values for the third-order rate constant, k_C or k_C', for each possible buffer pathway are selected such that the equality in eq 18 is maintained, where $k_x = 0.009$ M^{-2} s^{-1} is experimentally determined at $p[H^+]$ 8.88 from the slope of Figure 3, and f_{HOBr} and f_{OBr} represent the fraction of $[HOBr]_T$ that is in the form of HOBr and OBr^-, respectively.

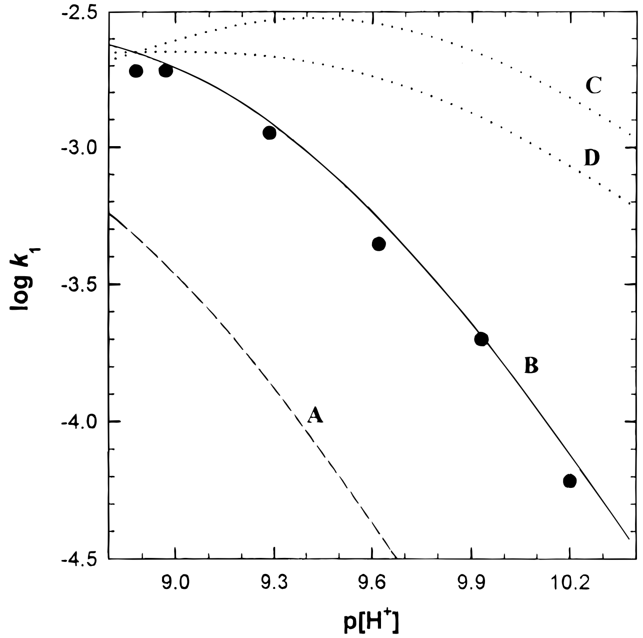

Figure 4. Data in 0.20 M carbonate buffer plotted with possible buffer rate expressions with $k_{1a} = 2 \times 10^{-3}$ M^{-1} s^{-1} and $k_{1b} = 6 \times 10^{-7}$ M^{-1} s^{-1}. Tested rate expressions are given in the text.

$$(k_1 + k_x[CO_3^{2-}]_T) = (k_{1a} + k_C[CO_3^{2-}])f_{HOBr}^2 + (k_{1b} + k_C'[HCO_3^-])f_{OBr}^2 \quad (18)$$

Each k_C parameter (M^{-2} s^{-1}) is calculated as $k_C \leq 0.33$, and $k_C' \leq 0.034$ based on the slope of the line in Figure 3. However, the equality in eq 18 dictates that no more than one term can be at its maximum value. The magnitude of k_C or k_C' is less than its maximum value if both terms contribute or if the respective parameter is negligible. Figure 4 shows experimental data collected at $p[H^+]$ 8.88−10.20 in 0.20 M total carbonate buffer. The following cases show assignments for k_C and k_C' in tested rate expressions in Figure 4 based on eq 18. Curve A

A.	$k_C = 0$	$k_C' = 0$
B.	$k_C = 0.33$ M^{-2} s^{-1}	$k_C' = 0$
C.	$k_C = 0$	$k_C' = 0.034$ M^{-2} s^{-1}
D.	$k_C = 0.15$ M^{-2} s^{-1}	$k_C' = 0.018$ M^{-2} s^{-1}

represents k_{1a} in an unbuffered system. The other models predict how various terms increase k_{1a}. For expression D, where multiple buffer terms are tested, smaller k_C and k_C' parameters were selected to maintain the equality in eq 18. The value of k_{1b} is negligible in this pH range without buffer assistance, but k_{1a} is included in all models. The best fit is given by case B, where $k_C = 0.33$ M^{-2} s^{-1} and $k_C' = 0$. This is consistent with data in phosphate buffer, where the basic form of the buffer is the species that assists decomposition.

Boric acid/borate buffer systems behave differently because both OCl^- and OBr^- form complexes with $B(OH)_3$.[39] This complexation slows the rate of decomposition of Br(I) at pH 8.3.

General−Base Assistance. General-base-assisted rate constants follow the Brønsted−Pedersen relationship of eq 19,[41] where *p* is the number of equivalent protons in acid HB, *q* is the number of sites that can accept a proton in the conjugate

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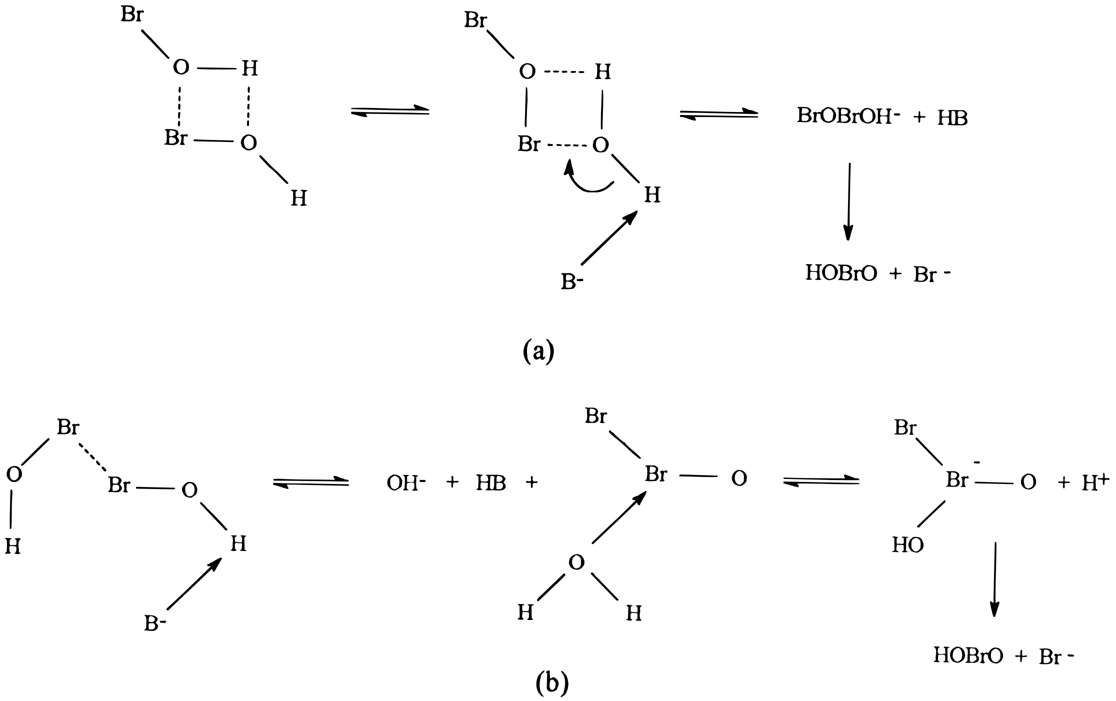
(40) Sakharov, A. A. *Uch. Zap. Petrozavodsk. Gos. Univ.* **1966** (Pub. 1967), *14*, 76−84.

(41) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 198.

Scheme 1



base B^-, G_B is a constant, and β is a measure of proton transfer in the transition state and ranges from 0 to 1. By applying the

$$\log(k_B/q) = \log G_B - \beta \log(K_a q/p) \qquad (19)$$

Brønsted−Pedersen relationship, the third-order buffer-assisted rate constants for carbonate and phosphate can be used to predict a value of $\beta = 0.3$ and $k_{OH} = 16\ M^{-2}\ s^{-1}$ in terms of $-d[HOBr]/dt = k_{OH}[OH^-]\ [HOBr]^2$. This rate expression is indistinguishable from $k_{1ab}[HOBr][OBr^-]$ based on eq 15. When this pathway is compared to that of k_1 in the absence of base assistance, we expect the hydroxide pathway to be comparable in magnitude from pH 9.8 to 11.3. While we did not directly determine the hydroxide rate constant, an estimated fit (solid line in Figure 2) represents the inclusion of this pathway. Given our reported error for k_p, uncertainty in the magnitude of the hydroxide pathway is likely. We were unable to detect an appreciable hydroxide pathway at $p[H^+] \leq 10.2$ in the presence of the more-dominant carbonate pathway. Inclusion of k_{1ab} into eq 18 requires that k_C and k_{OH} be reduced to $0.32\ M^{-2}\ s^{-1}$ and $15\ M^{-2}\ s^{-1}$ to maintain the equality based on the experimental slope in Figure 3.

Mechanistic Detail. A mechanism to explain the redox process during HOBr disproportionation must reflect second-order behavior in [HOBr], assistance from a general base, buildup of BrO_2^- at pH > 8, and suppression of the rate at pH < 3. Formation of a HOX dimer has been proposed as the first step in the decomposition of HOCl from pH 5 to 8.[26] A similar mechanism is proposed for HOBr at neutral pH (eqs 20−25). The ratio of either k_d/k_{-d} or k_{-d}/k_e must be small since no intermediates such as Br_2O are observed spectrophotometrically. Loss of a proton to form $Br_2O_2H^-$ (eq 21) is assisted by a general base (eq 22). Two kinetically indistinguishable pathways leading to BrO_2^- formation are suggested in Scheme 1. Pathway (a) corresponds to the mechanism proposed for HOCl[26] and proceeds through Br−O−Br, whereas pathway (b) passes through Br−Br−O. Elimination of Br^- produces $HBrO_2$ in eq 23, and ionization of $HBrO_2$ ($pK_a = 3.43$)[33] in eq 24 gives BrO_2^-, which reacts with HOBr as shown in eq 25.

$$2HOBr \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} Br_2O{\cdot}H_2O \qquad (20)$$

$$Br_2O{\cdot}H_2O \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} Br_2O_2H^- + H^+ \qquad (21)$$

$$B^- + Br_2O{\cdot}H_2O \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} Br_2O_2H^- + HB \qquad (22)$$

$$Br_2O_2H^- \xrightarrow{k_g} HBrO_2 + Br^- \qquad (23)$$

$$HBrO_2 \overset{K_a}{\rightleftharpoons} BrO_2^- + H^+ \qquad (24)$$

$$HOBr + BrO_2^- \xrightarrow{k_2} BrO_3^- + Br^- + H^+ \qquad (25)$$

Equations 20, 21, and 23 give the following rate expression (eq 26) when the steady-state approximation is applied to both $Br_2O{\cdot}H_2O$ and $Br_2O_2H^-$. The $k_{-d}k_{-e}[H^+]$ term in eq 26 becomes negligible at pH > 3 so that the maximum value of k_{1a} is given by eq 27. The reversibility of eq 21 is required to

$$-\frac{1}{n}\frac{d[HOBr]}{dt} = \frac{k_d k_e k_g}{k_e k_g + k_{-d}k_g + k_{-d}k_{-e}[H^+]}[HOBr]^2 \qquad (26)$$

$$k_{1a} = \frac{k_d k_e k_g}{k_e k_g + k_{-d}k_g} \qquad (27)$$

explain the experimental decrease in k_{1a} under highly acidic conditions. Below pH 3, the $k_{-d}k_{-e}[H^+]$ term in eq 26 becomes important and k_{1a} is reduced according to eq 28, where $c = (k_e k_g + k_{-d}k_g)/k_{-d}k_{-e} = 0.03$ M.

$$\frac{-d[HOBr]}{dt} = n\left(\frac{c}{c + [H^+]}\right)k_{1a}[HOBr]^2 \qquad (28)$$

Conclusion

Disproportionation of HOBr and OBr^- proceeds by a slow, second-order process in the absence of light and metals. The rate decreases significantly above pH 8 due to deprotonation of HOBr. Decomposition is accelerated by general bases. Equation 29 provides a complete model for HOBr disproportionation from pH 0 to 14, where n is the stoichiometric constant

Table 4. Equilibrium and Rate Constants[a]

	value	ref
HOBr	$pK_a = 8.8$	21
$HBrO_2$	$pK_a = 3.43$	33
$H_2PO_4^-$	$pK_a = 6.46$	27
HCO_3^-	$pK_a = 9.7$	27, 28
H_2O	$pK_w = 13.61$	29
k_{1a}	2×10^{-3} M^{-1} s^{-1}	*b*
k_{1b}	6×10^{-7} M^{-1} s^{-1}	*b*
$B = H_2PO_4^-$	$k_B = 0.05$ M^{-2} s^{-1}	*b*
$B = CO_3^{2-}$	$k_B = 0.32$ M^{-2} s^{-1}	*b*
$B = OH^-$[c]	$k_B = 15$ M^{-2} s^{-1}[c,d]	*b*
$c = (k_e k_g + k_{-d} k_g)/k_{-d} k_{-e}$	0.03 M	*b*

[a] 25.0 °C, $\mu = 0.5$ M. [b] This work. [c] Equivalent to $k_{1ab} = 2.5 \times 10^{-4}$ M^{-1} s^{-1}. [d] Calculated from eq 19.

and B represents a general base. The value for *n* falls in the

$$\frac{-d[Br(I)]}{dt} = n\left[\left(\frac{c}{c + [H^+]}k_{1a} + k_B[B]\right)[HOBr]^2 + k_{1b}[OBr^-]^2\right] + k_2[Br(I)][Br(III)] \quad (29)$$

range of 2−5 depending on pH and on the extent of the reaction. Table 4 presents a summary of equilibrium constants used and rate constants determined in this work. Acid suppression occurs below pH 3 and is represented by the $c/(c + [H^+])$ factor, where c is a ratio of rate constants that is equal to 0.03 M.

The above kinetic treatment can be used to predict the time needed for undesirable levels of BrO_3^- to be formed in water treatment systems. At pH 5−8 and 25 °C, if 1 mg/L of Br^- (a high level) were all converted to HOBr, it would require over 300 h for the HOBr disproportionation reaction to reach the maximum contamination level of BrO_3^- (MCL = 0.01 mg/L) set by the EPA. This computation assumes no catalysis from light, buffer, or HOCl. Bromate ion formation is very slow but not insignificant. However, HOBr is very reactive, and other reactions could diminish BrO_3^- formation.

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Supporting Information Available: Tables of molar absorptivities of bromine species, kinetics in carbonate buffer, and a figure for dependence of k_1 on $[HPO_4^{2-}]$ (3 pages). Ordering information is given on any current masthead page.

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