Mechanism of Chlorine Dioxide and Chlorate Ion Formation from the Reaction of Hypobromous Acid and Chlorite Ion

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The rate of oxidation of ClO_2^- by HOBr is first-order in each reactant and is general-acid-assisted in the presence of phosphate or carbonate buffers. The products are ClO_2 and ClO_3^-, where the relative yield depends on the concentration ratio of ClO_2^-/OH^-. The kinetic dependence indicates the presence of a steady-state intermediate, $HOBrOClO^-$ (or $HOBrClO_2^-$), that undergoes general-acid-assisted reactions to generate a metastable intermediate, BrOClO (or $BrClO_2$). This intermediate reacts very rapidly by two competing pathways: in one path ClO_2^- reacts to form $2ClO_2$ and Br^-, and in the other path OH^- (or H_2O) reacts to form ClO_3^- and Br^-. Competition between these pathways determines the yield of ClO_2 but does not affect the rate of loss of HOBr. The reactions are followed by the formation of ClO_2 in the presence of excess ClO_2^-. The rate expression for the loss of HOBr is $k_1[ClO_2^-][HOBr]\sum(k_{HA}[HA])/(k_{-1} + \sum(k_{HA}[HA]))$, where k_1 (for the formation of the intermediate) is 97 M^{-1} s^{-1} and k_{HA}/k_{-1} (M^{-1}) values, which depend on the acid (HA) strength, are 3.1×10^5 for H_3O^+, 8.3 for $H_2PO_4^-$, and 0.064 for HCO_3^- (25.0 °C, $\mu = 1.0$ M). Reactions between HOBr and ClO_2^- are much faster than those between HOCl and ClO_2^-.

Introduction

Intermediates of $XClO_2$ (where X = Cl, Br, or I) have been proposed as transient species in chlorite ion reactions with molecular chlorine, bromine, or iodine, as well as with hypohalous acids (HOX, where X = Cl or Br).[1−16] Taube and Dodgen[1] were the first investigators to propose a metastable intermediate, Cl_2O_2, in the reactions of ClO_2^- with Cl_2 or HOCl. Their tracer experiments with radioactive chlorine gave unlabeled ClO_2 and ClO_3^- as products along with labeled Cl^-. They concluded that the main pathway to products involved an intermediate in which the chlorine atoms were distinct from one another. An unsymmetrical intermediate ($Cl-Cl^{-O}_{-O}$ or Cl−O−Cl−O) was proposed with the mechanistic steps in eqs 1−4.

$$Cl_2^* + ClO_2^- \rightarrow Cl^*ClO_2 + Cl^{*-} \tag{1}$$

$$H^+ + HOCl^* + ClO_2^- \rightarrow Cl^*ClO_2 + H_2O \tag{2}$$

$$2Cl^*ClO_2 \xrightarrow{\text{fast}} Cl_2^* + 2ClO_2 \tag{3}$$

$$Cl^*ClO_2 + H_2O \xrightarrow{\text{fast}} Cl^{*-} + ClO_3^- + 2H^+ \tag{4}$$

The metastable intermediate, Cl_2O_2, can decompose either by a second-order reaction (eq 3) to give chlorine dioxide or by a first-order reaction with water (eq 4) to yield the chlorate ion. Equations 3 and 4 are considered to be fast reactions, whereas the steps leading up to the formation of the metastable intermediate are regarded as rate-limiting. Studies by Gordon and co-workers[2−4,7] and by Peintler et al.[8] provide additional kinetic information about the reactions of ClO_2^- with HOCl over a range of pH and reactant ratios. High concentrations of phosphate or acetate buffer were used in these experiments, but kinetic effects of the buffer were not considered.

Valdes-Aguilera et al.[15] studied the reactions of bromine with ClO_2^- and $HClO_2$ in three buffer systems (HSO_4^-/SO_4^{2-}, $ClCH_2COOH/ClCH_2COO^-$, and CH_3COOH/CH_3COO^-) and reported that ClO_2 was the exclusive oxidation product (no ClO_3^- was found). They proposed $BrClO_2$ as an intermediate (eq 5) and, in contrast to the behavior of Cl_2O_2, they propose that the $BrClO_2$ reaction with ClO_2^- (eq 6) is the rate-determining step.

$$Br_2 + ClO_2^- \rightleftarrows BrClO_2 + Br^- \tag{5}$$

$$BrClO_2 + ClO_2^- \rightarrow 2ClO_2 + Br^- \tag{6}$$

A complex pH dependence was observed, but kinetic effects of the buffers were not considered. They also indicated that HOBr was much less reactive than Br_2 in its reactions with ClO_2^-.

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In wastewater treatment, chlorine is a widely used disinfectant.[17] Chlorine hydrolysis (eq 7) is relatively rapid with a hydrolysis rate constant of 22.3 s^{-1} at 25.0 °C.[18]

$$Cl_2(aq) + H_2O \rightleftarrows HOCl + H^+ + Cl^- \qquad (7)$$

A typical range of bromide ion concentrations in groundwater is 0.01−3 mg/L.[19] Chlorine reacts extremely rapidly with Br^- (the rate constant is 7.7×10^9 M^{-1} s^{-1}) to give BrCl(aq), which hydrolyzes rapidly ($k > 10^5$ s^{-1}) to give HOBr.[20] The reaction between HOCl and Br^- also is proposed to proceed through BrCl, followed by rapid hydrolysis to HOBr. The rate constant for the overall reaction (eq 8) is 1.55×10^3 M^{-1} s^{-1}.[21]

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad (8)$$

Mixtures of HOCl and HOBr can react to generate chlorate ion (eq 9) or bromate ion (eq 10).[22]

$$3HOCl \xrightarrow{HOBr} ClO_3^- + 3H^+ + 2Cl^- \qquad (9)$$

$$2HOCl + HOBr \rightarrow BrO_3^- + 2Cl^- + 3H^+ \qquad (10)$$

Bromate ion is a carcinogen and nephrotoxin.[23−28] The Environmental Protection Agency has proposed that the maximum contaminant level (MCL) in drinking water should be less than 0.01 mg/L, with a maximum contaminant level goal (MCLG) of no detectable BrO_3^-.[19] Data on the health effects associated with exposure to ClO_3^- are not complete, so chlorate ion will not be regulated as part of the Disinfectants and Disinfection Byproduct Proposed Rule.[19] However, it is a candidate for future regulation. On the other hand, the proposed MCL for chlorite ion (ClO_2^-) is 1.0 mg/L. Reactions between mixtures of HOCl and HOBr initially produce chlorite ion and bromide ion (eq 11).[22]

$$HOCl + HOBr \rightarrow ClO_2^- + 2H^+ Br^- \qquad (11)$$

If HOCl is in higher concentration than HOBr (which is typically the case in water chlorination), the Br^- generated is rapidly converted back to HOBr (eq 8). As a consequence, the next stage in the halogen redox process is the reaction between HOBr and ClO_2^-. The present work addresses the kinetics and mechanism of this reaction.

Experimental Section

Reagents. Solutions were made with deionized, distilled water. Working solutions of NaOCl (ClO_3^--free) were prepared from a stock solution obtained by slowly bubbling $Cl_2(g)$ through stirred solutions of NaOH (~0.1 M) maintained at 0−4 °C. The NaOCl solutions were standardized spectrophotometrically. The molar absorptivity for NaOCl was determined by two methods. Iodometric titrimetric methods gave $\epsilon_{292} = 362 \pm 2$ M^{-1} cm^{-1}.[29] In a second method, a solution of $NaNO_2$ was added in excess to the NaOCl, and the mixture was adjusted to pH 5 with acetic acid. After complete reaction, the solution was diluted and analyzed for NO_3^- by capillary electrophoresis (CE) methods. The $[NO_3^-]$ determined was used to calculate the $[OCl^-]$. This gave 362 ± 5 M^{-1} cm^{-1} as the molar absorptivity for OCl^- at 292 nm, in agreement with the iodometric method.

Commercially available $NaClO_2$ was recrystallized by using a procedure modified from previous reports.[30] The carbonate content of the commercial solid (measured by CE) was removed by precipitation with a solution of $BaCl_2$. (Some $Ba(ClO_2)_2$ coprecipitated.) The remaining supernatant liquid was collected and cooled in an ice bath. The $NaClO_2$ was recrystallized in the temperature range from −5 to −15 °C, collected by vacuum filtration, and washed with 100% acetone. A final recrystallization step was performed on the solid from a 75:25 acetone/water mixture. The solid was washed, and argon gas was used to evaporate residual acetone from the final product. The $NaClO_2$ was stored over P_2O_5 in vacuo and kept in the dark. The purity was determined by standard iodometric titrimetry, and the product was confirmed to be free of other anionic impurities by capillary electrophoresis. The purified $NaClO_2$ has a molar absorptivity of $\epsilon = 154.0 \pm 0.7$ M^{-1} cm^{-1} at 260 nm. Sodium chlorite solutions were prepared from the recrystallized solid (99.98%).

Chlorine dioxide was synthesized by a process described in a review paper by Masschelein.[31] Acetic anhydride was added to a solution of $NaClO_2$, and argon gas was used to strip off ClO_2 from the main reaction tower. A second tower contained a 5% solution of $NaClO_2$ and served as a scrubber to remove any possible Cl_2 that may have formed in the process. The ClO_2 was trapped in a third gas collection tower which contained H_2O at 0−4 °C. Solutions of ClO_2 were freshly diluted prior to use. Small amounts of *n*-pentane were added to the solutions to cover the surface and retard the evaporation of ClO_2, as recommended by Lengyel and co-workers.[32] The molar absorptivity was found to be 1230 ± 10 M^{-1} cm^{-1} at 359 nm by using standard iodometric titrimetry.

Solutions of BrO_3^- and ClO_3^- were prepared from their respective sodium salts obtained from Aldrich. Reagent purity was confirmed by standard iodometric (for BrO_3^-) and Ce^{4+}/Fe^{2+} (for ClO_3^-) titrations.

Solutions of bromide-free HOBr were made by the reaction of HOCl with Br^- in a 1:1 mole ratio. An aliquot of this solution was made basic, and the solution was standardized spectrophotometrically based on the molar absorptivity of NaOBr, $\epsilon = 332$ M^{-1} cm^{-1} at 329 nm.[33] Under reaction

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conditions where an impurity of BrO_2^- (4−5%) was problematic in our analyses, an alternate preparation of HOBr was used where liquid Br_2 was added to cold solutions of NaOH. This solution was relatively free of BrO_2^- (less than 0.01 μM). The Br^- generated by this alternate preparation was removed by reaction with AgOH.[34]

A 1.0 M NaOH solution was prepared by diluting a saturated NaOH solution into He-sparged water. It was stored in polypropylene bottles under Ascarite II to protect from CO_2 absorption and standardized titrimetrically against primary standard KHP to a phenolphthalein end point. Stock $HClO_4$ solutions were standardized with a NaOH solution. These solutions were used for pH adjustments where necessary. Phosphate buffer solutions were prepared from NaH_2PO_4 and Na_2HPO_4. Carbonate buffer solutions were prepared from $NaHCO_3$ and NaOH. The ionic strength (μ) for all experiments, except for those where capillary electrophoresis was involved, was controlled with analytical reagent grade $NaClO_4$ that was recrystallized from water, redissolved, and standardized gravimetrically.

Methodology and Instrumentation. An Orion model 720A digital pH meter equipped with a Corning combination electrode (model 2513) was used in all pH measurements. The electrode was calibrated through titrations of standard $HClO_4$ with standard NaOH to correct the measured pH values to p[H^+] at 25.0 ± 0.1 °C and μ = 1.0 M. Analysis of the titration data by the method of Gran[35] was followed by a linear regression of measured pH and p[H^+] values. We use p[H^+] = −log [H^+] because values are expressed in molarities rather than in activities (pH = −log a_H).

A Hewlett-Packard ³ᴰCapillary Electrophoresis System equipped with a negative power supply, a variable-wavelength UV detector, and Hewlett-Packard extended light path capillaries (i.d. = 75 μm, L_{eff} = 72 cm, L_{tot} = 80.5 cm) was used for the product identification of anions. The capillary was contained in a Peltier temperature-controlled cartridge maintained at 15.0 ± 0.1 °C. A pressure sample injection mode was used. Data acquisition was performed with the HP ³ᴰCE Chemstation and software. The run buffer consisted of 0.10 M boric acid and 5.0 mM sodium borate at pH 8.0. Naphthalenedisulfonic acid (disodium salt from Kodak) (NDS) was incorporated into the buffer for the indirect detection of anions. Diethylenetriamine (Aldrich) was added to the buffer to reverse the electroosmotic flow to allow for the detection of the anions in the samples. As the separated ions migrate past the detector window, they are measured as negative peaks relative to the high baseline of the NDS. By reversing the signal and the reference wavelengths on the diode array detector of the Hewlett-Packard ³ᴰCapillary Electrophoresis System, a positive signal was obtained.

Hypochlorite stock solutions were tested for chlorate ion after treatment of an aliquot of the hypochlorite solution with analytical reagent grade (neat liquid) ethylenediamine.[36−39] This solution was subsequently injected onto the CE system to obtain any signal due to ClO_3^-. Ethylenediamine was used in 25-fold excess relative to the original hypochlorite concentration to form *N*-chloroethylenediamine that does not interfere with the analysis of ClO_3^- by CE. There also was no interference from the excess ethylenediamine, as it is a water-soluble compound that is present as a cation under the conditions of the separation.

Chlorate ion recovery from the reaction between HOBr and excess ClO_2^- was determined by CE. Prior to the analysis, the sample solution was placed into a gas collection tower and degassed with He to remove any dissolved ClO_2.

Spectrophotometric measurements of the reaction between HOBr and ClO_2^- were performed on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer used in conjunction with PECSS (Perkin-Elmer computerized spectroscopy software). Faster rates of reaction were followed with either an Applied PhotoPhysics stopped-flow spectrophotometer interfaced to a Acorn RISC PC using kinetic software (v 4.25) or with a Dionex-Durrum model D-110 stopped-flow instrument interfaced to a Zenith 151 CPU with a Metrabyte DASH-16 A/D interface card. All reactions were run under pseudo-first-order conditions with ClO_2^- in large excess relative to the initial [HOBr]. The rates of the reaction were monitored at 359 nm for the appearance of ClO_2. Reactions were followed for at least 4−5 half-lives. Reactions were thermostated at 25.0 ± 0.2 °C and were maintained at an ionic strength (μ) of 1.0 M. The rate constants reported are the results obtained from an average of 5−10 traces. The observed pseudo-first-order rate constant is defined by eq 12, where $[HOBr]_T$ = [HOBr] + [OBr^-].

$$\frac{-d[HOBr]_T}{dt} = k_{obsd}[HOBr]_T \tag{12}$$

The integrated form in terms of the observed chlorine dioxide is given by eq 13. The fraction of HOBr that is converted to ClO_2 varies with the reaction conditions, but these terms cancel out in eq 13.

$$\ln\left(\frac{[ClO_2]_\infty}{[ClO_2]_\infty - [ClO_2]_t}\right) = k_{obsd}t \tag{13}$$

Results and Discussion

Products. The chlorine dioxide formed from the reaction between HOBr and excess ClO_2^- is used to monitor the kinetics. Table 1 gives the yield of ClO_2 in terms of the fraction ClO_2

Table 1. Observed Rate Constants and Fraction of ClO_2 Produced from HOBr Reaction with Excess ClO_2^- [a]

[ClO_2^-], M	p[H^+]	k_{obsd}, s^{-1}	fraction ClO_2
0.001 344	6.68	0.0281(6)	0.178
0.001 973	6.67	0.042(3)	0.258
0.002 653	6.68	0.0582(4)	0.345
0.003 294	6.66	0.075(2)	0.359
0.003 759	6.68	0.0850(8)	0.395
0.004 604	6.66	0.106(5)	0.441
0.005 313	6.68	0.121(5)	0.450
0.006 578	6.66	0.162(5)	0.499
0.007 877	6.67	0.21(2)	0.542
0.010 51	6.66	0.22(1)	0.646
0.021 00	6.67	0.49(1)	0.746
0.031 50	6.67	0.74(1)	0.812
0.041 91	6.67	0.97(1)	0.876

[a] Conditions: [Br(I)] = 0.0525 mM, 0.10 M $[PO_4]_T$, μ = 1.0 M $NaClO_4$, 25.0 °C. The numbers in parentheses are standard deviations. The fraction of ClO_2 is defined as the concentration of ClO_2 found divided by twice the $[HOBr]_i$.

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Table 2. Chlorate Ion Found from the HOBr and ClO_2^- Reaction as Determined by CE[a]

p[H^+]	[ClO_3^-] found, M	ClO_3^- recovered,[b] (%)
6.10	8.2×10^{-5}	54
6.56	9.3×10^{-5}	61
7.06	1.0×10^{-4}	66
7.51	1.2×10^{-4}	79

[a] Reaction conditions: [ClO_2^-] = 3.761 mM, $[HOBr]_o$ = 0.151 mM, 0.02 M phosphate buffer (total), and 25.0 °C. [b] Percent is relative to $[HOBr]_o$.

produced ($f = [ClO_2]_{found}/2[HOBr]_i$) based on the stoichiometry in eq 14. The other product is ClO_3^- (eq 15).

$$HOBr + 2ClO_2^- \rightarrow 2ClO_2 + Br^- + OH^- \qquad (14)$$

$$HOBr + ClO_2^- \rightarrow ClO_3^- + Br^- + H^+ \qquad (15)$$

The yield of ClO_2 increases with increase of ClO_2^- concentration and with acidity. In the presence of excess ClO_2^-, the ClO_2 product is relatively stable and does not decay over the time intervals of the measurements. The relative yields of ClO_2 and ClO_3^- depend on competing kinetic pathways, but we will show that this occurs after the rate-determining steps. Therefore, one or more intermediate species must be present. Chlorate ion was confirmed as a reaction product by capillary ion electrophoresis measurements. The ClO_3^- yield increases with p[H^+], as shown in Table 2.

Kinetics. The observed first-order rate constant is directly proportional to the concentration of excess chlorite ion (Figure 1). Despite the fact that two ClO_2^- are needed per HOBr for ClO_2 formation (eq 14), and despite large variations in the yield of ClO_2 as conditions change, the reaction is always first order in [ClO_2^-]. The k_{obsd} values increase with increased concentrations of [H^+], [$H_2PO_4^-$], and [HCO_3^-]. A mechanism is needed that accounts for this acid assistance, the first-order dependence in both [HOBr] and [ClO_2^-], and the relative yields of ClO_2 and ClO_3^-.

Proposed Mechanism. In the proposed mechanism (eqs 16–18), a weak complex is formed between HOBr and ClO_2^-.

$$HOBr + ClO_2^- \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} HOBrOClO^- \qquad (16)$$

$$HA + HOBrOClO^- \xrightarrow{k_{HA}} BrOClO + H_2O\ A^- \qquad (17)$$

$$BrOClO \begin{cases} + ClO_2^- \xrightarrow[\text{fast}]{k_3} 2ClO_2 + Br^- \\ + OH^- \xrightarrow[\text{fast}]{k_4} ClO_3^- + Br^- + H^+ \end{cases} \qquad (18)$$

This requires an expansion of the number of valence electrons around the bromine atom from 8 to 10, in a manner similar to the bonding in Br_3^- or in $HOBrI^-$.[33] The intermediate given in eq 16 indicates O–Br–O bonding in $HOBrOClO^-$, but O–Br–Cl bonding is also possible, which would correspond to a $HOBrClO_2^-$ intermediate. Intermediates of this type have been proposed by Gordon et al.[3] for the reactions of HOCl with ClO_2^-, where HO–Cl–ClO_2^- precedes the formation of Cl–ClO_2. In our mechanism, $HOBrOClO^-$ is a steady-state intermediate that undergoes general-acid-assisted reactions to eliminate water and form BrOClO (or $BrClO_2$) as a metastable intermediate. We propose that BrOClO is extremely reactive. It can react rapidly with another ClO_2^- to give $2ClO_2$ and Br^-, or, alternatively, it can react rapidly with OH^- or H_2O to give ClO_3^- and Br^-. The ratio of products depends on the ratio of $k_3[ClO_2^-]/k_4[OH^-]$, but neither k_3 nor k_4 is in the rate expression because these reactions occur after the rate-determining formation of BrOClO. With $HOBrOClO^-$ as a steady-state species, the rate expression for the loss of HOBr is given by eq 19, where HA is any acid.

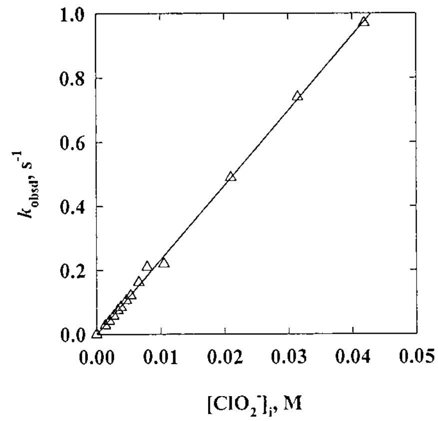

Figure 1. Chlorite ion dependence of the observed first-order rate constant for the reaction of HOBr with excess [ClO_2^-]. Conditions: $[HOBr]_o$ = 0.0525 mM, p[H^+] 6.67 ± 0.01, in 0.1 M $[PO_4]_T$, μ = 1.0 M ($NaClO_4$), 25.0 °C. The second-order rate constant determined from the slope is 23 M^{-1} s^{-1}.

$$\frac{-d[HOBr]_T}{dt} = \frac{k_1[ClO_2^-][HOBr](\sum(k_{HA}[HA]))}{k_{-1} + \sum(k_{HA}[HA])} \qquad (19)$$

In our studies, HA is H_3O^+, $H_2PO_4^-$, HCO_3^-, or H_2O. The expression for k_{obsd} (eq 20) has a first-order dependence in [ClO_2^-], does not depend on the k_3 or k_4 rate constants, but is highly dependent on the concentrations of acidic buffer species in accord with our observations.

$$k_{obsd} = \frac{k_1[ClO_2^-]\sum(k_{HA}[HA])\left[\frac{[H^+]}{[H^+] + K_a^{HOBr}}\right]}{k_{-1} + \sum(k_{HA}[HA])} \qquad (20)$$

In the proposed mechanism, OBr^- is not a reactive species. The value of pK_a^{HOBr} is 8.59 under our conditions,[40] so correction for the $[HOBr]/[HOBr]_T$ ratio is needed at higher pH. Equation 20 includes this correction.

The yield of ClO_2 (eq 21) depends on the competition between the BrOClO reaction with ClO_2^- and its reaction with H_2O or OH^- (eq 18).

$$f = ClO_2 \text{ fraction} = \frac{2k_3[ClO_2^-]}{k_4^{H_2O} + k_4^{OH}[OH^-] + 2k_3[ClO_2^-]} \qquad (21)$$

Figure 2 shows the dependence of the ClO_2 yield on the ClO_2^- concentration at p[H^+] = 6.67 ± 0.01. Figure 3 shows the p[H^+] dependence of the ClO_2 yield when the ClO_2^- concentration is constant (3.761 mM). These data give values for $k_4^{H_2O}/k_3 = 1.84(\pm0.04) \times 10^{-4}$ M and $k_4^{OH}/k_3 = 6.83(\pm0.05) \times 10^3$. The ratio of $k_4^{OH}/k_4^{H_2O}$ is 3.71×10^7 M^{-1}, so the OH^-

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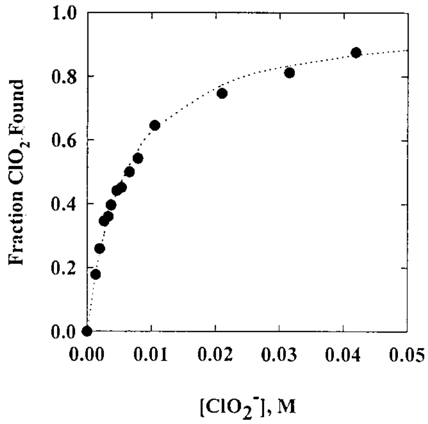


Figure 2. Yield of ClO_2 vs excess $[ClO_2^-]$. The fraction of ClO_2 is defined as the concentration of ClO_2 found divided by twice the initial [HOBr]. The dotted line is the least-squares fit obtained from eq 21. Conditions: $[HOBr]_o = 0.0525$ mM, p[H$^+$] 6.67 ± 0.01, 0.10 M $[PO_4]_T$, $\mu = 1.0$ M ($NaClO_4$), 25.0 °C.

path dominates above p[H$^+$] 7. In contrast to the strong buffer dependence found for the rate constants in eq 17, the yield of ClO_2 is not affected by changes in HPO_4^{2-} or CO_3^{2-} concentrations.

Acid and Buffer Dependence upon k_{obsd}. The dependence of k_{obsd} from p[H$^+$] 5.00 to 9.01 in 0.10 M phosphate or carbonate buffer can be accounted for in terms of the reaction mechanism (eqs 16−18) and eq 20. Because $HOBrOClO^-$ is a steady-state intermediate, we can evaluate the ratio of k_{HA}/k_{-1} rate constant, but not the individual rate constants for its acid-assisted conversion to BrOClO. The resulting expressions for k_{obsd} in phosphate buffer is given by eq 22 and in carbonate buffer by eq 23.

$$k_{obsd} = \frac{k_1\left(\frac{k_H[H^+]}{k_{-1}} + \frac{k_{H_2PO_4}}{k_{-1}}[H_2PO_4^-]\right)[ClO_2^-]\left[\frac{[H^+]}{[H^+] + K_a^{HOBr}}\right]}{1 + \frac{k_H[H^+]}{k_{-1}} + \frac{k_{H_2PO_4}}{k_{-1}}[H_2PO_4^-]} \tag{22}$$

$$k_{obsd} = \frac{k_1\left(\frac{k_{H_2O}}{k_{-1}} + \frac{k_H[H^+]}{k_{-1}} + \frac{k_{HCO_3}}{k_{-1}}[HCO_3^-]\right)[ClO_2^-]\left[\frac{[H^+]}{[H^+] + K_a^{HOBr}}\right]}{1 + \frac{k_{H_2O}}{k_{-1}} + \frac{k_H[H^+]}{k_{-1}} + \frac{k_{HCO_3}}{k_{-1}}[HCO_3^-]} \tag{23}$$

The k_{H_2O}/k_{-1} term is negligible for the phosphate buffer region and, therefore, is not given in eq 22. The correction term for the OBr^- concentration is small for most of the phosphate data but becomes appreciable for the carbonate data. The dependence of k_{obsd} on the $[H_2PO_4^-]$ concentration at p[H$^+$] 5.92 and 6.42 is given in Figure 4. The $[HCO_3^-]$ dependence is shown in Figure 5, and the p[H$^+$] dependence is given in Figure 6. All these data were used together in a least-squares fit of the rate constants that gave $k_1 = 97(6)$ M^{-1} s^{-1}, $k_H/k_{-1} = 3.1(5) \times 10^5$ M^{-1}, $k_{H_2PO_4}/k_{-1} = 8.3(6)$ M^{-1}, and $k_{HCO_3}/k_{-1} = 0.064(4)$ M^{-1}. It was not possible to obtain a reliable value for k_{H_2O}/k_{-1} because the contribution of this term to the reaction rate is very small. However, the intercept in Figure 5 and the values for k_H/k_{-1} at

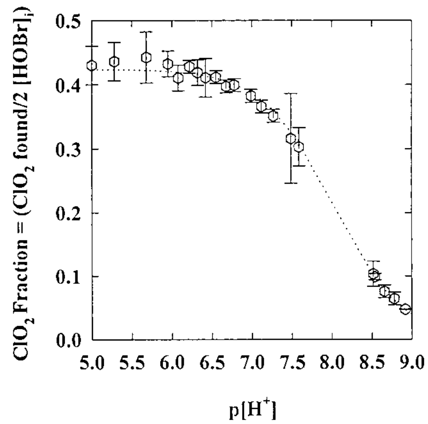


Figure 3. Yield of ClO_2 as a function of p[H$^+$]. Conditions: $[ClO_2^-]_i = 3.761$ mM, $[HOBr]_o = 0.0525$ mM, 0.10 M $[PO_4]_T$, $\mu = 1.0$ M ($NaClO_4$). The dotted line is the least-squares fit based on eq 21.

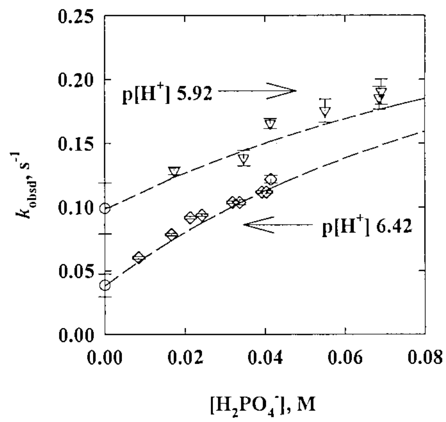


Figure 4. Effect of $H_2PO_4^-$ concentration on the observed first-order rate constant. Conditions: $[ClO_2^-] = 3.761$ mM, $[HOBr]_o = 0.0525$ mM, p[H$^+$] 5.91−5.92, or 6.39−6.45 in 0.10 M $[PO_4]_T$, $\mu = 1.0$ M ($NaClO_4$). The dashed line is the nonlinear least-squares fit based on eq 22. The y-intercepts (○) are the calculated rate constants for the term without phosphate.

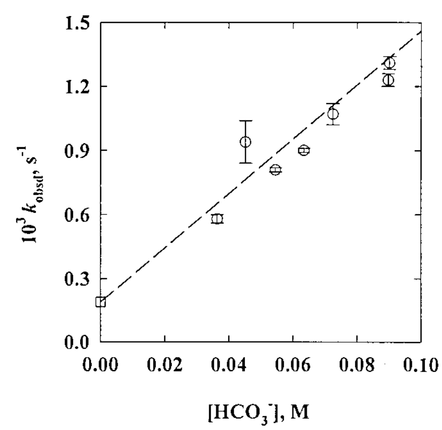


Figure 5. Effect of the HCO_3^- concentration on the observed first-order rate constant. Conditions: $[ClO_2^-] = 3.761$ mM, $[HOBr]_o = 0.0525$ mM, p[H$^+$] 8.49−8.52 in 0.10 M $[CO_3]_T$, $\mu = 1.0$ M ($NaClO_4$). The dashed line is the least-squares fit based on eq 23. The y-intercept (□) is the calcuated rate constant based on the k_H/k_{-1} term.

p[H$^+$] 8.51 ± 0.02 permit us to estimate that k_{H_2O}/k_{-1} is approximately 2×10^{-4}. The dashed line in Figures 4 and 5 show the fit of eqs 22 and 23 to these rate constants. Three calculated lines are given in Figure 6 in order to show the contributions of each acid as the pH changes. The dashed line for the phosphate-buffered reactions is obtained from eq 22.

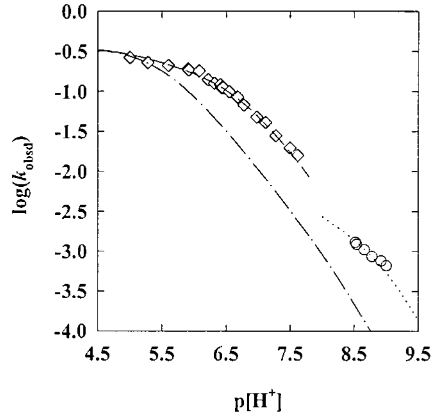
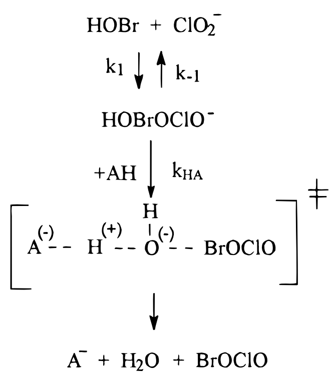


Figure 6. Dependence on the observed first-order rate constant as a function of solution p[H$^+$]. Conditions: $[HOBr]_o = 0.0525$ mM, $[ClO_2^-] = 3.761$ mM, in 0.10 M total buffer (◇, phosphate or ○, carbonate), $\mu = 1.0$ M ($NaClO_4$), 25.0 °C. The calculated nonlinear least-squares fits based on eq 22 with (- - - H^+ and $H_2PO_4^-$) and (•••) H^+, H_2O, and HCO_3^- based on eq 23, and for H^+ and H_2O terms only (–•–).

Scheme 1. Proposed General-Acid-Assisted Path To Generate BrOClO (or $BrClO_2$)



The dotted line for the carbonate buffered reactions is obtained from eq 23. The dashed–dot line shows the contribution of H_3O^+ and H_2O if $H_2PO_4^-$ and HCO_3^- are not present.

Brønsted–Pedersen Relationship. The buffer dependence upon k_{obsd} is a result of general-acid assistance by HA in the transfer of a proton combined with H_2O–Br bond cleavage in the step leading to BrOClO formation (eq 17 and Scheme 1). The ratio of rate constants (k_{HA}/k_{-1}) that we resolved from the p[H$^+$] and buffer dependence studies show a Brønsted relationship (eq 24),[41]

$$\log\left(\frac{k_{HA}}{k_{-1}p}\right) = \log G_a + \alpha \log(K_a q/p) \tag{24}$$

where p is the number of equivalent proton sites on the acid form of the buffer, HA, q is the number of equivalent basic sites on the conjugate base, A^-, G_A is the Brønsted proportionality constant, and α is the Brønsted coefficient. The α value can range from 0 to 1 and reflects the degree of proton transfer in the transition state. Table 3 summarizes the values for k_{HA}/k_{-1} and K_a^{HA} for each acid, HA. The k_{H_2O}/k_{-1} value is divided by the molarity of water (55.5 M) to convert it to the same units as the other acids. Figure 7 is a Brønsted plot with a slope (α) of 0.59 ± 0.1 based on the H_3O^+, $H_2PO_4^-$, and HCO_3^- data points. Rate constants for the acid-catalyzed decomposition of the complex, $HOBrOClO^-$, increase with increasing acid strength.

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

Table 3. Summary of Rate and Equilibrium Constants[a]

$k_1 = 96 \pm 6$ M^{-1} s^{-1}, p$K_a^{HOBr} = 8.59$[b]
$k_4^{H_2O}/k_3 = (1.84 \pm 0.04) \times 10^{-4}$ M
$k_4^{OH}/k_3 = (6.83 \pm 0.05) \times 10^3$

HA	pK_aHA	k_{HA}/k_{-1}, M^{-1}
H_3O^+	−1.72[c]	(3.1 ± 0.5) × 10^5
$H_2PO_4^-$	6.26[d]	8.3 (±0.6)
HCO_3^-	9.48[d]	0.064 (±0.004)
H_2O	15.74[e]	∼3.5 × 10^{-6}[f]

[a] Conditions: $\mu = 1.0$ M ($NaClO_4$), 25.0 °C, pK_w = 13.60. [b] reference 40. [c] −log(55.5). [d] Determined for reaction conditions. [e] The value is from −log(K_w/55.5). [f] Value calculated from ($k_{HA}^{H_2O}/k_{-1}$)/55.5.

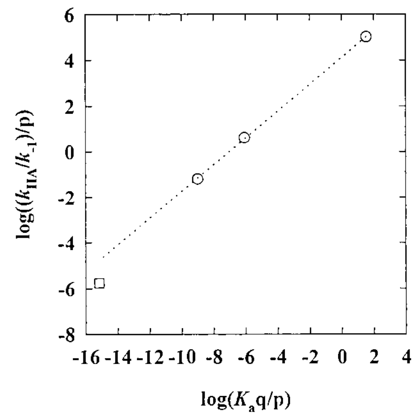


Figure 7. Brønsted plot for general-acid assistance of the reaction between the steady-state intermediate, $HOBrOClO^-$, and HA, where K_a is the ionization constant of HA. The slope of the line (α) equals 0.59 ± 0.01 (eq 24).

$XClO_2$ Intermediates. Taube and Dodgen[1] addressed the connectivity of the intermediate Cl_2O_2. Their results showed that Cl_2O_2 was not symmetrical (i.e., it is neither Cl–O–O–Cl nor O–Cl–Cl–O) but could be either Y-shaped (Cl–Cl$^{-O}_{-O}$) or chain-like (Cl–O–Cl–O). Although many authors imply Y-shaped structures for Cl_2O_2 and $BrClO_2$, the connectivity is not known in aqueous solution. We have written the metastable intermediate as Br–O–Cl–O because of some related studies between HOCl and BrO_2^-.[42] However, the present work cannot distinguish between Br–O–Cl–O and Br–Cl$^{-O}_{-O}$. On the other hand, chloryl chloride (Cl-ClO_2) has been prepared in both noble gas matrixes and in the gas phase, and evidence was found for a Y-shaped intermediate.[43] Photolysis of matrix-isolated $ClClO_2$ resulted in the isomers ClOClO and ClOOCl. In the gas phase, $ClClO_2$ decomposes into ClO_2 and Cl_2. At room temperature and a partial pressure of 1 mbar, the half-life of $ClClO_2$ is 1 min.[43] The isomer, ClOClO, has been prepared in noble gas matrixes by Jacobs and co-workers.[44] Molecules of ClOClO, BrOClO, and IOClO have been isolated and characterized in argon matrixes.[45] These molecules have been found to rearrange to $XClO_2$ (X = Cl, Br, or I) upon exposure to visible radiation, but $ClClO_2$ and $BrClO_2$ can be isomerized back to the chain form by near-UV radiation.[45]

(42) Perrone, T. F.; Margerum, D. W. To be submitted for publication.
(43) Muller, H. S. P.; Willner, H. *Inorg. Chem.* **1992**, *31*, 2527–2534.
(44) Jacobs, J.; Kronberg, M.; Muller, H. S. P.; Willner, H. *J. Am. Chem. Soc.* **1994**, *116*, 1106–1114.
(45) Johnsson, K.; Engdahl, A.; Kolm, J.; Nieminen, J.; Nelander, B. *J. Phys. Chem.* **1995**, *99*, 3902–3904.

Recently, Guha and Francisco[46] have calculated geometries, vibrational spectra, and relative energies of BrOClO, $BrClO_2$, $ClBrO_2$, ClOBrO, and other $XBrO_2$ isomers in the gas phase. These calculations show that $BrClO_2$ is more stable than BrOClO by only 3.7 kcal mol^{-1}. Solvation effects are not known, and in aqueous solution the relative energies of these two forms could shift significantly. The above studies show that either BrOClO or $BrClO_2$ is a reasonable intermediate for the proposed mechanism.

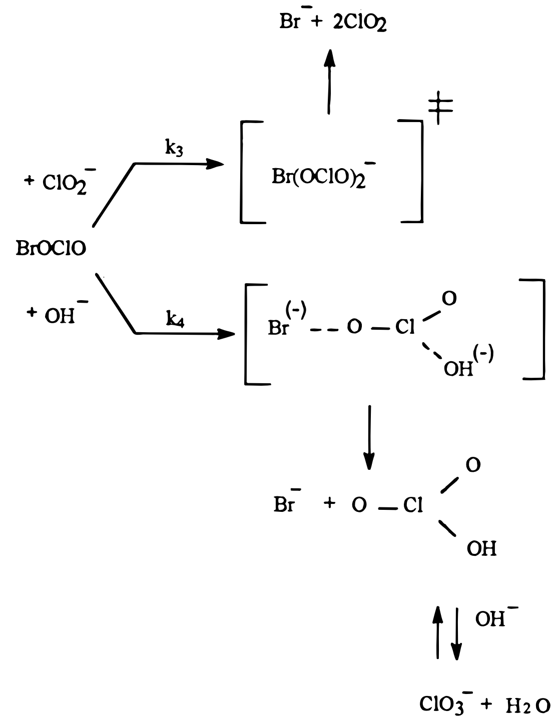
Reaction Pathways. The general-acid-assisted dependence that we have observed and assigned to eq 17 in the mechanism requires that proton transfer occur during the process of generating BrOClO (or $BrClO_2$). If proton transfer occurred in a prior equilibrium to convert $HOBrOClO^-$ to $H_2OBrOClO$ before the rate-determining step, the reaction rate would depend only on the H^+ concentration, as opposed to the experimental dependence on general acid (HA) concentrations. Therefore, we suggest the transition state shown in Scheme 1, where the oxygen−bromine bond breaks as proton transfer occurs. The Brønsted value of 0.59 indicates that a significant degree of proton transfer occurs in the transition state, leading to BrOClO (or $BrClO_2$) formation.

Scheme 2 shows the proposed pathways for the conversion of BrOClO to products. Under our conditions, the reactions of BrOClO with ClO_2^- and with OH^- occur after the rate-determining step. Hence, k_3 and k_4 do not contribute to the k_{obsd} values, but the ratios of $k_3[ClO_2^-]/(k_4^{H_2O} + k_4^{OH}[OH^-])$ determine the yields of ClO_2 compared to ClO_3^-. As seen in Scheme 2, OH^- attack (k_4 path) at the chlorine atom of BrOClO will lead to the elimination of Br^- and the formation of ClO_3^-.

Valdez-Aguilera et al.[15] studied the Br_2 reaction with ClO_2^- and reported a $BrClO_2$ intermediate that reacts rapidly with ClO_2^- with a rate constant of 2.94×10^3 M^{-1} s^{-1}. This value meets our requirement that $k_3[ClO_2^-]$ is much larger than $k_3\sum k_{HA}[HA]/(1 + \sum k_{HA}[HA])$. A self-exchange rate constant for ClO_2/ClO_2^- has been evaluated[47] to be 3.3×10^4 M^{-1} s^{-1}. It seems unlikely that the less favorable electron-transfer reaction would occur rapidly between $BrClO_2$ and ClO_2^- to give ClO_2 and $BrClO_2^-$ (followed by breakup of $BrClO_2^-$ to Br^- and ClO_2). We propose a $Br(OClO)_2$- intermediate that dissociates into $Br^- + 2ClO_2$. The intermediate might be formed by ClO_2^- attack on chlorine in BrOClO, leading to Br^- elimination and two ClO_2 molecules. Alternatively, ClO_2^- attack on bromine in BrOClO could give a $(OClOBrOClO)^-$ intermediate that breaks up to form $ClO_2 + Br^- + ClO_2$.

(46) Guha, S.; Francisco, J. S. *J. Phys. Chem. A* **1997**, *101*, 5347−5359.
(47) Awad, H. H.; Stanbury, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 3636−3642.

Scheme 2. Proposed Reactions of BrOClO To Give ClO_2 and ClO_3^-



The observed rate constants[7,8] for ClO_2 formation in the reactions of HOCl with ClO_2^- appear to be 1−2 orders of magnitude smaller than those for HOBr with ClO_2^- under similar conditions. The buffer dependencies for the HOCl reactions have not been resolved, so it is difficult to make exact comparisons.

Acknowledgment. This work was supported by Environmental Protection Agency Grant 821245 and by National Science Foundation Grant CHE-96-22683.

Supporting Information Available: Listings of kinetic data and yield of ClO_2 (5 pages). Ordering information is given on any current masthead page.

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