Inorganic Chemistry

Article

Kinetics and Mechanisms of Bromine Chloride Reactions with Bromite and Chlorite Ions

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Chloride ion catalyzes the reactions of HOBr with bromite and chlorite ions in phosphate buffer (p[H$^+$] 5 to 7). Bromine chloride is generated in situ in small equilibrium concentrations by the addition of excess Cl$^-$ to HOBr. In the BrCl/ClO$_2^-$ reaction, where ClO$_2^-$ is in excess, a first-order rate of formation of ClO$_2$ is observed that depends on the HOBr concentration. The rate dependencies on ClO$_2^-$, Cl$^-$, H$^+$, and buffer concentrations are determined. In the BrCl/BrO$_2^-$ reaction where BrCl is in pre-equilibrium with the excess species, HOBr, the loss of absorbance due to BrO$_2^-$ is followed. The dependencies on Cl$^-$, HOBr, H$^+$, and HPO$_4^{2-}$ concentrations are determined for the BrCl/BrO$_2^-$ reaction. In the proposed mechanisms, the BrCl/ClO$_2^-$ and BrCl/BrO$_2^-$ reactions proceed by Br$^+$ transfer to form steady-state levels of BrOClO and BrOBrO, respectively. The rate constant for the BrCl/ClO$_2^-$ reaction (k_2^{Cl}) is 5.2 × 10^6 M^{-1} s^{-1} and for the BrCl/BrO$_2^-$ reaction (k_2^{Br}) is 1.9 × 10^5 M^{-1} s^{-1}. In the BrCl/ClO$_2^-$ case, BrOClO reacts with ClO$_2^-$ to form two ClO$_2$ radicals and Br$^-$. However, the hydrolysis of BrOBrO in the BrCl/BrO$_2^-$ reaction leads to the formation of BrO$_3^-$ and Br$^-$.

Introduction

Bromine chloride, BrCl, is a very reactive species that is of relevance to several environmental and chemical areas. Tropospheric ozone depletion in the Arctic region at sunrise is dependent in part on BrCl.[1] Also, the formation of BrO$_3^-$, a known carcinogen, in bromide-containing water is attributed to BrCl reaction with hypochlorite ion.[2] Recently, studies of BrCl reactions have been conducted to gain a better understanding of its chemistry. These include its hydrolysis (eq 1)[3–5] and its reactions with N$_2$H$_5^+$,[6] HOCl,[2] HOBr,[2] *p*-xylene,[7] and ascorbic acid.[8]

$$HOBr + Cl^- + H^+ \rightleftharpoons BrCl + H_2O \qquad (1)$$
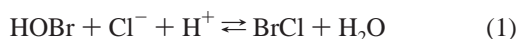
Many kinetic studies of chlorite reactions have been performed over the years;[9–13] however, only a few bromite

reactions have been examined because of the limited commercial availability of sodium bromite.[14–16] A recent bromite preparation and purification method[17] has permitted the investigation of several systems including BrO$_2^-$ reactions with O$_3$,[18] S(IV),[19] ClO$_2$,[17] HOCl,[20] and HOBr.[21]

In the present study the reactions of BrCl with ClO$_2^-$ and BrO$_2^-$ are investigated in the p[H$^+$] range of 5 to 7 by stopped-flow spectroscopy. We propose that both reactions proceed through BrOXO (X = Cl or Br) intermediates

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analogous to those formed in the chloride-free HOBr/XO$_2^-$ reactions.[21,22]

Experimental Section

Reagents. All solutions were prepared with doubly deionized distilled water. HOBr solutions were prepared by adding liquid Br$_2$ slowly to ice-chilled 0.2 M NaOH solution with rapid stirring. Bromide was removed from the NaOBr solution by mixing the stock with AgOH solution (freshly prepared by adding AgNO$_3$ to NaOH) and filtering out AgBr.[23] NaOBr solutions were stored in a refrigerator. Bromide-free NaCl was prepared by mixing distilled bromide-free HCl with saturated NaOH followed by gravimetric standardization.[5] NaClO$_2$ and NaBrO$_2$ were prepared and purified by methods described earlier.[17,22] The stock NaBrO$_2$ is 63.4% pure by weight with 7.0% NaBrO$_3$, 1.3% NaBr, 1.9% Na$_2$SO$_4$, 14.1% NaOH, and 12.2% H$_2$O. Analytical-reagent grade NaH$_2$PO$_4$ (pK_a = 6.26)[22] and Na$_2$HPO$_4$ were used without further purification. Ionic strength was adjusted to μ = 1.0 M with recrystallized NaClO$_4$.

pH Measurement. An Orion model 720A pH meter equipped with a Corning combination electrode was used for pH measurement. The electrode was calibrated with previously standardized HClO$_4$ and NaOH to correct pH to p[H$^+$], where p[H$^+$] = − log-[H$^+$] and pK_w is 13.60 (25.0 °C, 1.0 M NaClO$_4$).[24]

Spectrophotometry and Kinetics. A Perkin-Elmer Lambda 9 UV−vis−NIR spectrophotometer was used to standardize BrO$_2^-$ (ϵ_{295} = 115 M^{-1} cm^{-1}),[25] ClO$_2^-$ (ϵ_{260} = 154 M^{-1} cm^{-1}),[22] and OBr$^-$ (ϵ_{329} = 332 M^{-1} cm^{-1}).[26] An Applied PhotoPhysics SX18 MV stopped-flow spectrophotometer (APPSF, optical path length = 0.962 cm) equipped with a PD.1 photodiode array for simultaneous multiwavelength detection and a photomultiplier tube for single-wavelength detection was used in studying the kinetics of the reactions. The kinetics of the BrCl reaction with excess ClO$_2^-$ were followed at the λ_{max} of the product, ClO$_2$ (ϵ_{359} = 1230 M^{-1} cm^{-1}),[22] eqs 2−4. The term [HOBr]$_T$ equals the sum of [HOBr] and [OBr$^-$] in the absence of Cl$^-$. Upon the addition of chloride,

$$-\frac{d[HOBr]_T}{dt} = k_{obsd}^{Cl}[HOBr]_T \qquad (2)$$

$$-\frac{d[HOBr]_T}{dt} = k_I^{Cl}[ClO_2^-][HOBr]_T + k_{II}^{Cl}[ClO_2^-][BrCl] \qquad (3)$$

$$k_{obsd}^{Cl} = k_I^{Cl}[ClO_2^-] + \alpha k_{II}^{Cl}[ClO_2^-] \qquad (4)$$

low levels of the other nine species in Table 1 form, including the highly reactive BrCl. The α term is the BrCl concentration that forms relative to [HOBr]$_T$ (eq 5) as will be discussed in a later section. The BrCl/BrO$_2^-$ kinetics were studied by following the

$$\alpha = \frac{[BrCl]}{[HOBr]_T} \qquad (5)$$

loss of BrO$_2^-$ in the 240 to 245 nm region where [HOBr]$_T$ is present in large excess with respect to BrO$_2^-$ (eqs 6−8). SigmaPlot 8.0[27]

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Table 1. Equilibrium Constants for a System Containing HOBr, Br$^-$, Cl$^-$, and H^{+a}

reaction	equilibrium	constant values
BrCl + Cl$^-$ ⇌ BrCl$_2^-$	K_1^{BrCl}	3.8 M^{-1}
BrCl + H$_2$O ⇌ HOBr + Cl$^-$ + H$^+$	K_{h1}	1.3 × 10^{-4} M^2
Br$_2$ + H$_2$O ⇌ HOBr + Br$^-$ + H$^+$	K_{h2}	6.1 × 10^{-9} M^2
Cl$_2$ + H$_2$O ⇌ HOCl + Cl$^-$ + H$^+$	K_{h3}	1.04 × 10^{-3} M^2
BrCl + Cl$^-$ ⇌ Cl$_2$ + Br$^-$	K_8^{BrCl}	9.1 × 10^{-7}
Br$_2$ + Br$^-$ ⇌ Br$_3^-$	K_4^{Br2}	16.1 M^{-1}
Br$_2$ + Cl$^-$ ⇌ Br$_2$Cl$^-$	K_3^{Br2}	1.3 M^{-1}
HOBr + Cl$^-$ ⇌ HOCl + Br$^-$	K_7^{HOBr}	6.5 × 10^{-6}
Cl$_2$ + Cl$^-$ ⇌ Cl$_3^-$	K_5^{Cl2}	0.18 M^{-1}
HOBr ⇌ OBr$^-$ + H$^+$	pK_a^{HOBr}	8.59
HOCl ⇌ OCl$^-$ + H$^+$	pK_a^{HOCl}	7.47
BrCl + Br$^-$ ⇌ Br$_2$Cl$^-$	K_2^{BrCl}	1.8 × 10^4 M^{-1}
Cl$_2$ + Br$^-$ ⇌ BrCl$_2^-$	K_6^{Cl2}	4.2 × 10^6 M^{-1}
BrCl + H$_2$O ⇌ HOCl + Br$^-$ + H$^+$	K_{h4}	8.7 × 10^{-10} M^2
2BrCl ⇌ Br$_2$ + Cl$_2$	K_D^{BrCl}	7.6 × 10^{-3}

^{a} Reference 4 and references within. All equilibrium constants are at 25 °C and μ = 1.0 M.

was used for regression analysis, and MathCad 8[28] was used for complex algebraic treatments.

$$-\frac{d[HOBr]_T}{dt} = k_{obsd}^{Br}[BrO_2^-] \qquad (6)$$

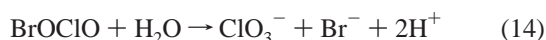$$-\frac{d[HOBr]_T}{dt} = k_I^{Br}[HOBr]_T[BrO_2^-] + k_{II}^{Br}[BrCl][BrO_2^-] \qquad (7)$$

$$k_{obsd}^{Br} = k_I^{Br}[HOBr]_T + \alpha k_{II}^{Br}[HOBr]_T \qquad (8)$$

Product Analysis. A Dionex DX-500 chromatograph was used to identify the products of the BrCl/BrO$_2^-$ reaction by a method similar to EPA 300.1.[29] Samples were injected via an autosampler (AS 40) through a 25 μL injection loop onto quaternary amine anion-exchange guard (AG9 HC) and separation (AS9 HC) columns. Analytes were eluted with 9 mM Na$_2$CO$_3$ at a flow rate of 1.0 mL/min. Gas-assisted suppressed-conductivity detection (ED 40), with an ASRS-Ultra suppressor in the self-regenerating mode and a current of 100 mA, was used to determine the analytes. Residual NaOBr was removed by the addition of Na$_2$SO$_3$ to each sample immediately prior to injection to prevent column damage.[30]

Results and Discussion

Chloride Catalysis of HOBr/ClO$_2^-$ Reaction via a BrCl Intermediate. The reaction of HOBr with ClO$_2^-$ is known to produce ClO$_2$ with an established stoichiometry (eq 9).[22] The reaction kinetics are on the stopped-flow time scale. Our

$$HOBr + 2ClO_2^- + H^+ \rightarrow 2ClO_2 + Br^- + H_2O \qquad (9)$$
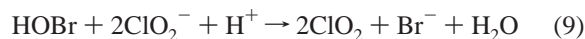
studies show a large increase in the reaction rate even with millimolar levels of Cl$^-$. We assign this acceleration to BrCl because we know it is a highly reactive species[2] and chloride is not. We also know that BrCl forms readily from HOBr and Cl$^-$ (eq 1).[3−5] The large chloride acceleration levels off when [Cl$^-$] is ∼0.1 M. This is consistent with a mechanism where BrCl and ClO$_2^-$ react to produce BrOClO as a steady-

(28) *MathCad 8 for Windows*; MathSoft: Cambridge, MA, 1998.
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state species (eqs 10 and 11). BrOClO as an intermediate has been proposed in an earlier study.[22] Furman and

$$BrCl + ClO_2^- \underset{k_{-2}^{Cl}}{\overset{k_2^{Cl}}{\rightleftharpoons}} BrOClO + Cl^- \qquad (10)$$

$$BrOClO + ClO_2^- \overset{k_3}{\longrightarrow} 2ClO_2 + Br^- \qquad (11)$$

Margerum have found that BrOClO can either hydrolyze or react with a chlorite ion as shown in eqs 12−14 and 11, respectively.

$$HOBr + ClO_2^- \rightleftharpoons HOBrOClO^- \qquad (12)$$

$$HOBrOClO^- + HA \rightarrow BrOClO + H_2O + A^- \qquad (13)$$

$$BrOClO + ClO_2^- \rightarrow 2ClO_2 + Br^- \qquad (11)$$

$$BrOClO + H_2O \rightarrow ClO_3^- + Br^- + 2H^+ \qquad (14)$$

In the current study, the rate of ClO_2 formation is followed at 359 nm upon the addition of Cl^- where ClO_2^- is in large excess over HOBr to give ClO_2 as the main product. Data collected with the photodiode array APPSF confirm that ClO_2 is a product of the reaction (Figure 1a). The large absorbance band at lower wavelengths is due to chlorite that is present in large excess, $\epsilon_{260} = 154$ M^{-1} cm^{-1}.[22] The ClO_2 formation follows first-order kinetics whether Cl^- is present or absent. However, the presence of chloride ion leads to a greater rate of ClO_2 formation (Figure 1b). Subtraction of the rate constant for the uncatalyzed HOBr/ClO_2^- reaction (k_{HOBr/ClO_2^-} = $k_I^{Cl}[ClO_2^-]$) from the observed rate constant (k_{obsd}^{Cl}) yields a rate constant that we attribute to the BrCl/ClO_2^- reaction ($k_{BrCl}^{Cl} = \alpha k_{II} [ClO_2^-]$) as shown in eqs 15 and 16.

$$\alpha k_{II}^{Cl} [ClO_2^-] = k_{obsd}^{Cl} - k_I^{Cl} [ClO_2^-] \qquad (15)$$

$$k_{BrCl}^{Cl} = k_{obsd}^{Cl} - k_{HOBr/ClO_2^-} \qquad (16)$$

Figure 2a shows the saturation kinetics exhibited at high $[Cl^-]$. An increase in ClO_2^- and H^+ concentrations (Figures 3 and 4a) also increases the k_{BrCl}^{Cl} values.

Small amounts of BrCl ($<10^{-7}$ M) build up when HOBr is mixed with Cl^- under our experimental conditions. The dependence of the rate on [BrCl] requires an accurate evaluation of the [BrCl] relative to the total concentration of hypobromous acid and hypobromite, [HOBr]$_T$, (eq 5). The involvement of BrCl in a complex set of equilibria,[4] Table 1, must be taken into account. We developed an equation (Supporting Information Appendix A) and used MathCad 8 to calculate the distribution of all of the species in the system based on the concentrations of total HOBr, Br$^-$, Cl$^-$, and H$^+$ and the known equilibrium constants. This algorithm is an expansion of one established by Liu.[30] Our equation accounts for the effect of the Br$^-$ formed on the distribution of the species shown in Table 1. Table 2 shows the levels of Cl$_2$, BrCl, and Br$_2$ that form as a function of chloride ion concentration under the conditions of the BrCl/ClO_2^- study. In the course of the reaction, Br$^-$ forms as a product (eqs
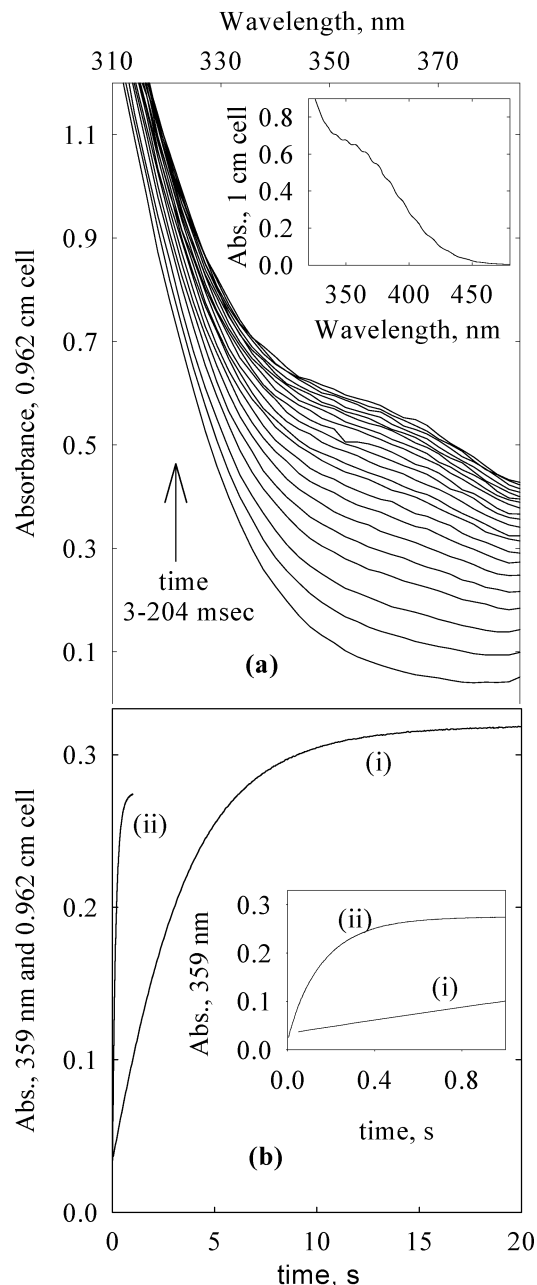
Figure 1. (a) APPSF photodiode array spectra of ClO_2 formation in the BrCl/ClO_2^- reaction: $[Cl^-] = 19.1$ mM, $[PO_4]_T = 5.0$ mM, $[HOBr]_T = 0.252$ mM, $[ClO_2^-] = 28.3$ mM, 25.0 °C, and $\mu = 1.0$ M. The inset shows the typical absorption spectrum of the ClO_2 product measured with a narrow band-pass spectrophotometer. The large absorbance at lower wavelength is due to the excess species ClO_2^-. (b) Kinetic traces for the first-order formation of ClO_2 in (i) 0.0 mM Cl^- and (ii) 0.192 M Cl^-: $[HOBr]_T = 0.114$ mM, $[ClO_2^-] = 25$ mM, $[PO_4]_T = 5$ mM, p$[H^+] = 6.68$, 25.0 °C, $\mu = 1.0$ M, and $\lambda = 359$ nm. (i) $k_{obsd}^{Cl} = 0.30$ s^{-1} and (ii) $k_{obsd}^{Cl} = 6.10$ s^{-1}.

11 and 14). We find that α is nearly constant throughout the reaction (Figure S1), which means that as [HOBr]$_T$ decreases the BrCl concentration decreases. Figure S1 presents [HOBr]$_T$ in descending order to reflect the consumption of HOBr during the course of the reaction.

The plot of k_{BrCl}^{Cl}/α versus $[Cl^-]$ (Figure 2b) shows that high $[Cl^-]$ suppresses the rate where k_{BrCl}^{Cl}/α is the rate constant for the BrCl/ClO_2^- reaction divided by the relative concentration of BrCl with respect to the total HOBr
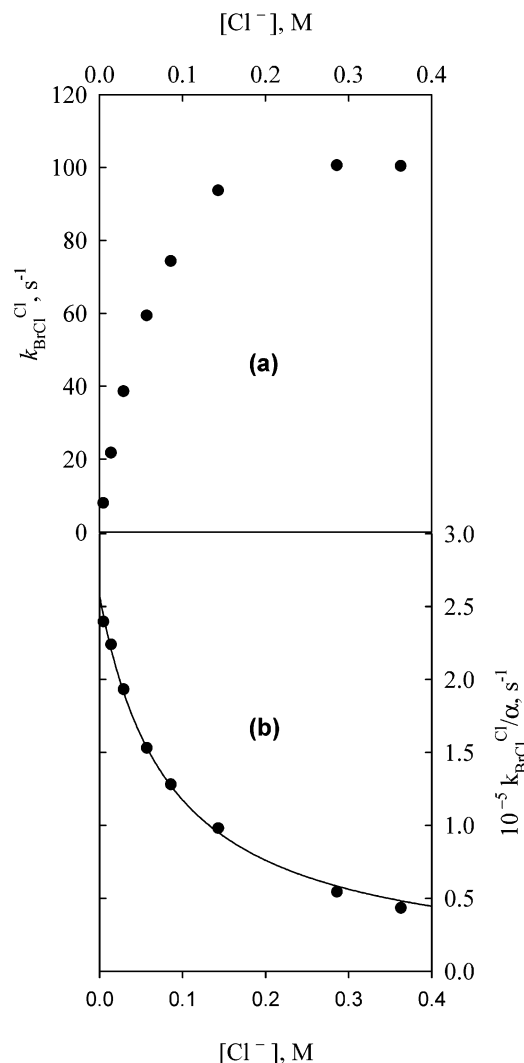
Figure 2. (a) Saturation behavior of the BrCl/ClO₂⁻ reaction upon the addition of Cl⁻. (b) Chloride ion suppression is observed after accounting for the relative concentration of BrCl (i.e., accounting for the α term). The solid line is a fit of the data to eq 20. Conditions: 49.25 mM ClO₂⁻, [HOBr]$_T$ = 0.295 mM, p[H⁺] = 6.04, [PO₄]$_T$ = 5.0 mM, 25.0 °C, μ = 1.0 M, and λ = 359 nm. k_2^{Cl} = 5.2(1) × 10⁶ M⁻¹ s⁻¹, k_{-2}^{Cl}/k_3 = 0.59(3).

Table 2. Concentration of Molecular Halogens in the Presence of Chloride Ion for BrCl/XO₂⁻ Reactions

Cl⁻, M	Cl₂, M	BrCl, M	Br₂, M	α = [BrCl]/[HOBr]$_T$
		BrCl/ClO₂⁻ Reaction^a		
1.0 × 10⁻³	1.21 × 10⁻¹²	2.01 × 10⁻⁹	5.81 × 10⁻⁸	7.04 × 10⁻⁶
5.0 × 10⁻³	1.35 × 10⁻¹¹	1.00 × 10⁻⁸	1.29 × 10⁻⁷	3.50 × 10⁻⁵
1.00 × 10⁻²	3.81 × 10⁻¹¹	1.99 × 10⁻⁸	1.81 × 10⁻⁷	6.96 × 10⁻⁵
3.00 × 10⁻²	1.96 × 10⁻¹⁰	5.9 × 10⁻⁸	3.07 × 10⁻⁷	2.06 × 10⁻⁴
5.00 × 10⁻²	4.21 × 10⁻¹⁰	9.75 × 10⁻⁸	3.91 × 10⁻⁷	3.41 × 10⁻⁴
		BrCl/BrO₂⁻ Reaction^b		
1.0 × 10⁻³	2.49 × 10⁻¹²	1.51 × 10⁻⁸	1.59 × 10⁻⁶	3.26 × 10⁻⁶
5.0 × 10⁻³	2.78 × 10⁻¹¹	7.55 × 10⁻⁸	3.55 × 10⁻⁶	1.63 × 10⁻⁵
1.00 × 10⁻²	7.87 × 10⁻¹¹	1.51 × 10⁻⁷	5.01 × 10⁻⁶	3.25 × 10⁻⁵
3.00 × 10⁻²	4.09 × 10⁻¹⁰	4.51 × 10⁻⁷	8.60 × 10⁻⁶	9.71 × 10⁻⁴
5.00 × 10⁻²	8.81 × 10⁻¹⁰	7.48 × 10⁻⁷	1.10 × 10⁻⁵	1.61 × 10⁻⁴

^{a} [HOBr]$_T$ = 0.28 mM, p[H⁺] = 6.04, μ = 1.0 M, and 25.0 °C.
^{b} [HOBr]$_T$ = 4.64 mM, p[H⁺] = 6.37, μ = 1.0 M, and 25.0 °C.

concentration. Also, k_{BrCl}^{Cl}/α versus [ClO₂⁻] yields a quadratic dependence in [ClO₂⁻] (Figure 3). After correction for the relative [BrCl], the rate constant for the BrCl/ClO₂⁻ reaction shows no dependence in H⁺ concentration (Figure
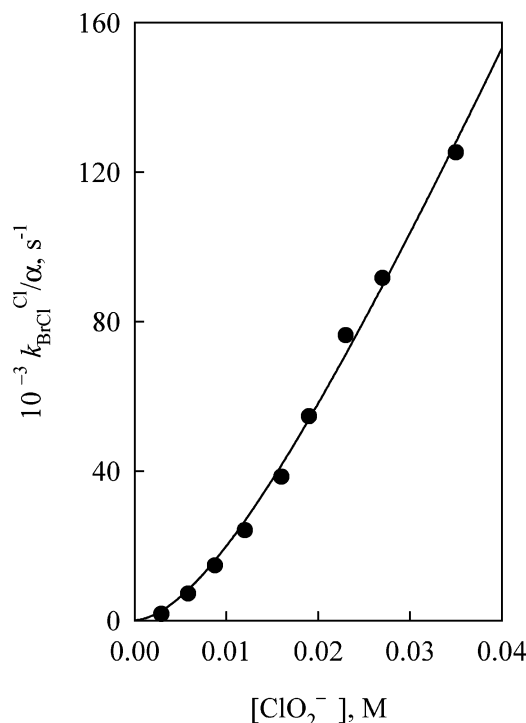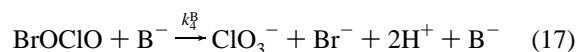

Figure 3. Greater than first-order dependence in [ClO₂⁻] for the rate constants of the BrCl/ClO₂⁻ reaction. The solid line is a fit of the data to eq 20. Conditions: [Cl⁻] = 37.6 mM, [HOBr]$_T$ = 0.305 mM, [PO₄]$_T$ = 5.0 mM, p[H⁺] = 6.01, 25.0 °C, and μ = 1.0 M.

4b). On the basis of these data, the mechanism in eqs 10, 11, and 17 is proposed. The term B⁻ in eq 17 represents all bases that catalyze BrOClO hydrolysis including H₂O, OH⁻,

$$BrCl + ClO_2^- \underset{k_{-2}^{Cl}}{\overset{k_2^{Cl}}{\rightleftharpoons}} BrOClO + Cl^- \quad (10)$$

$$BrOClO + ClO_2^- \xrightarrow{k_3} 2ClO_2 + Br^- \quad (11)$$

$$BrOClO + B^- \xrightarrow{k_4^B} ClO_3^- + Br^- + 2H^+ + B^- \quad (17)$$

and HPO₄²⁻. Treating BrOClO as a steady-state species leads to eq 18. The solid lines in Figures 2b and 3 show that the experimental data fit well to eq 18.

$$\frac{k_{BrCl}^{Cl}}{\alpha} = \frac{k_2^{Cl}[ClO_2^-]\left([ClO_2^-] + \dfrac{k_4^B[B]}{k_3}\right)}{\dfrac{k_{-2}}{k_3}[Cl^-] + [ClO_2^-] + \dfrac{k_4^B[B]}{k_3}} \quad (18)$$

On the basis of the dependence in [Cl⁻], the rate constants obtained are k_2^{Cl} = 5.2(1) × 10⁶ M⁻¹ s⁻¹ and k_{-2}^{Cl}/k_3 = 0.59-(3). Although Cl⁻ accelerates the HOBr/ClO₂⁻ reaction beacause of BrCl production, high levels of Cl⁻ suppress this acceleration (Figure 2b), as can be seen in eq 18. The results obtained for the [ClO₂⁻] dependence are in agreement with those in the [Cl⁻] plot. The yield of ClO₂ from the HOBr/ClO₂⁻ reaction is dependent on the concentration of the buffer (Figure 5). On the basis of the percent of ClO₂ formed and using eq 19, $k_4^{HPO_4}/k_3$ is 0.19 and $k_4^{H_2O}/k_3$ is 1 × 10⁻⁴ M. In the study of the BrCl/ClO₂⁻ reaction, low

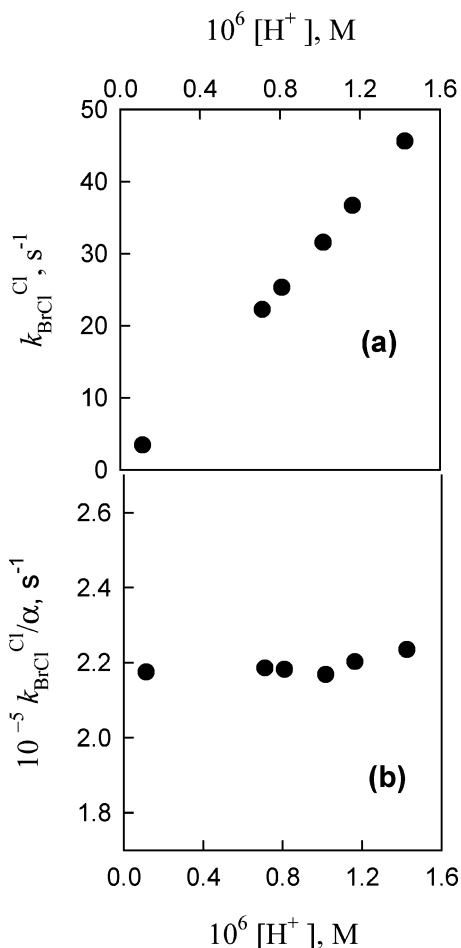**Figure 4.** (a) Increase of k_{BrCl}^{Cl} as a function of acid concentration. (b) Lack of acid effect on the $BrCl/ClO_2^-$ rate constants after accounting for the α term. Conditions: $[ClO_2^-] = 49.4$ mM , $[PO_4]_T = 5.0$ mM, $[HOBr]_T = 0.253$ mM, 19.1 mM Cl^-, 25.0 °C, $\mu = 1.0$ M, and at 359 nm.

concentrations of phosphate and a high concentration of ClO_2^- are used to make the reaction in eq 11 the dominant pathway (relative to eq 17) for BrOClO loss. Thus, eq 18 is reduced to eq 20, which is used to calculate the k_2^{Cl} and k_{-2}/k_3 values. This explains the lack of effect of acid (Figure 4b) and buffer (Figure S4) on the $BrCl/ClO_2^-$ reactions. In fact, the acid dependence in Figure 4a is due to the formation of BrCl (eq 1) and to shifts in the other equilibria in Table 1. Division of k_{-2}^{Cl}/k_3 by the k_4^B/k_3 values obtained in Figure 5 gives relative rate constants for the reaction of BrOClO with Cl^- compared to the base-catalyzed hydrolysis reactions with values of $k_{-2}^{Cl}/k_4^{H_2O} = 5.9(3) \times 10^3$ M^{-1} and $k_{-2}^{Cl}/k_4^{HPO_4} = 3.1(2)$.

$$\% \text{ yield } ClO_2 = \frac{100(2k_3[ClO_2^-])}{2k_3[ClO_2^-] + k_4^{HPO_4}[HPO_4^{2-}] + k_4^{H_2O}} \quad (19)$$

$$\frac{k_{BrCl}^{Cl}}{\alpha} = \frac{k_2^{Cl}[ClO_2^-]^2}{\dfrac{k_{-2}}{k_3}[Cl^-] + [ClO_2^-]} \quad (20)$$

Chloride Catalysis of $HOBr/BrO_2^-$ Reaction via a BrCl Intermediate. The reaction of HOBr with BrO_2^- is known
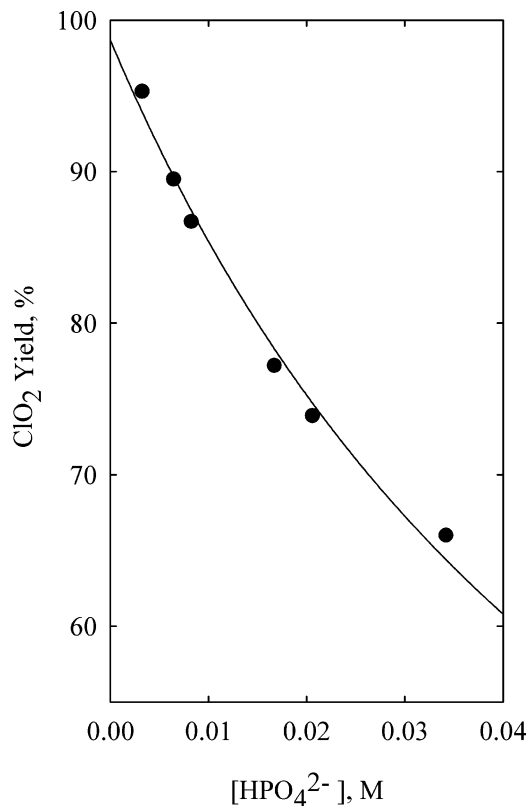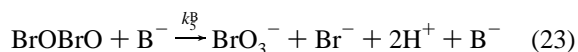
Figure 5. Dependence of ClO_2 yield on $[HPO_4^{2-}]$ for the $HOBr/ClO_2^-$ reaction: $[HOBr]_T = 0.102$ mM, $[ClO_2^-] = 6.00$ mM, $p[H^+] = 6.24$, 25.0 °C, $\mu = 1.0$ M, and $\lambda = 359$ nm. $k_4^{HPO_4}/k_3 = 0.19$, $k_4^{H_2O}/k_3 = 1.0 \times 10^{-4}$ M. The solid line is a fit of the data to eq 19.

to produce BrO_3^- with an established stoichiometry (eq 21).[21] The reaction kinetics are slower than the kinetics of the analogous $HOBr/ClO_2^-$ reaction but are still on the stopped-

$$HOBr + BrO_2^- \rightarrow BrO_3^- + Br^- + H^+ \quad (21)$$
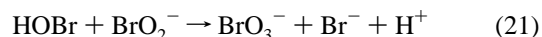
flow time scale. The present study confirms the rate of the $HOBr/BrO_2^-$ reaction but also shows that chloride ion increases the rate. We attribute this acceleration to the $BrCl/BrO_2^-$ reaction. As in the $HOBr/ClO_2^-$ case, the acceleration levels off at ~0.1 M Cl^-. A mechanism consistent with these findings is proposed in eqs 22 and 23 where BrOBrO is a

$$BrCl + BrO_2^- \underset{k_{-2}^{Br}}{\overset{k_2^{Br}}{\rightleftharpoons}} BrOBrO + Cl^- \quad (22)$$

$$BrOBrO + B^- \xrightarrow{k_3^B} BrO_3^- + Br^- + 2H^+ + B^- \quad (23)$$

steady-state species. BrOBrO is a species similar to the BrOClO proposed in the $HOBr/ClO_2^-$ reaction. The reaction in eq 23 is base catalyzed ($B^- = HPO_4^{2-}$ or H_2O), as will be discussed later. Products analysis shows that the concentration of BrO_3^- formed is not affected by the presence of chloride ion.

In the present study, we confirm the rate of the $HOBr/BrO_2^-$ reaction in the absence of Cl^- and determine its rate in the presence of Cl^- by following the loss of BrO_2^-. To minimize its self-decomposition, BrO_2^- is used as the limiting species. Figure 6a shows data collected with the
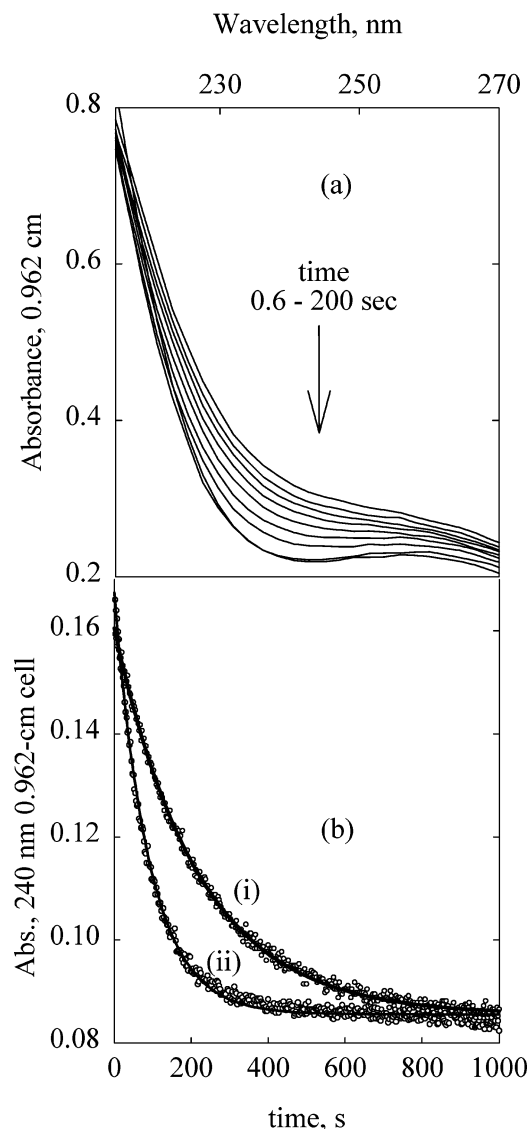
Figure 6. (a) APPSF photodiode array spectra of BrO_2^- loss in the BrCl/BrO_2^- reaction: $[HOBr]_T = 2.52$ mM, $[Cl^-] = 15.3$ mM , $[PO_4]_T = 80$ mM, $p[H^+] = 6.28$, $[BrO_2^-] = 70\ \mu M$, 25.0 °C, and $\mu = 1.0$ M. (b) Kinetic traces for the first-order decay of BrO_2^- in (i) 0.0 mM Cl^- and (ii) 20 mM Cl^-: $[HOBr]_T = 0.724$ mM, $[BrO_2^-] = 70\ \mu M$, $p[H^+] = 5.95$, $[PO_4]_T = 80$ mM, 25.0 °C, $\mu = 1.0$ M, and $\lambda = 240$ nm. (i) $k_{obsd}^{Br} = 4.61(3) \times 10^{-3}$ s^{-1} and (ii) $k_{obsd}^{Br} = 1.16(1) \times 10^{-2}$ s^{-1}.

photodiode array for the loss of bromite absorption. This loss follows first-order kinetics (Figure 6b). A step similar to that in eq 11 is not included in the mechanism because a simple first-order dependence in BrO_2^- is observed. In a behavior similar to the HOBr/ClO_2^- reaction, we find that Cl^- increases the rate of BrO_2^- loss. Subtraction of the rate constant for the HOBr/BrO_2^- reaction ($k_{HOBr/BrO_2^-} = k_I^{Br}[HOBr]_T$) from the observed rate constant (k_{obsd}^{Br}) yields a rate constant that we attribute to the BrCl/BrO_2^- reaction ($k_{BrCl}^{Br} = \alpha k_{II}^{Br}[HOBr]_T$) as shown in eqs 24 and 25. The BrCl levels are low under the conditions of this study, [BrCl] < 10^{-6} M.

$$\alpha k_{II}^{Br}[HOBr]_T = k_{obsd}^{Br} - k_I^{Br}[HOBr]_T \qquad (24)$$

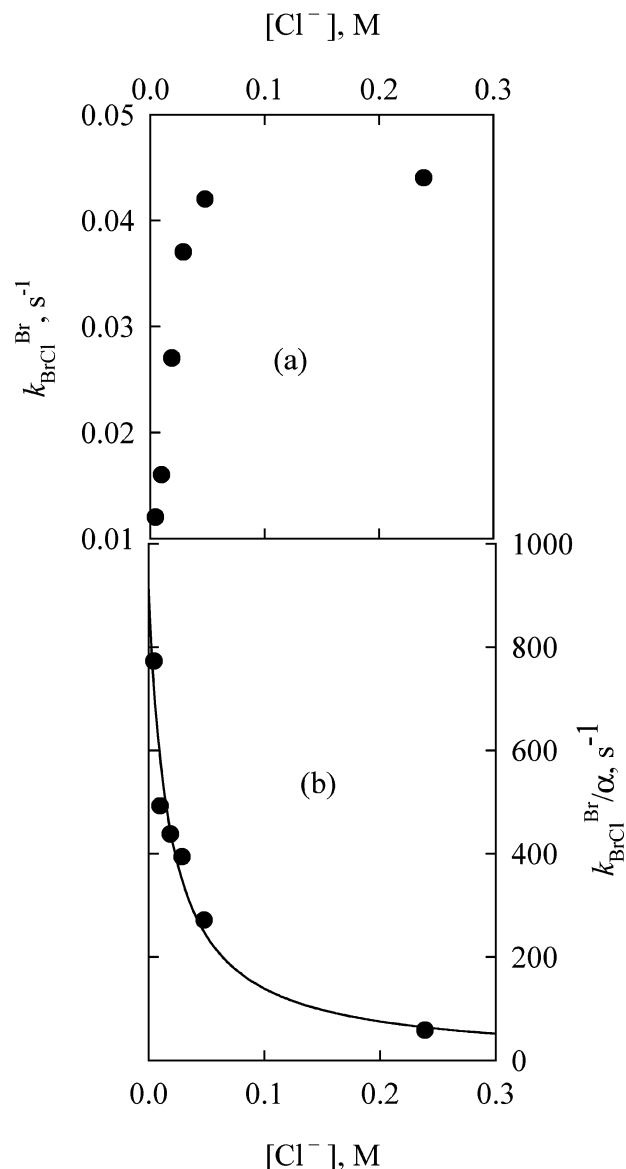$$k_{BrCl}^{Br} = k_{obsd}^{Br} - k_{HOBr/BrO_2^-} \qquad (25)$$

Figure 7. (a) Saturation behavior of the BrCl/BrO_2^- reaction upon the addition of Cl^-. (b) Chloride ion suppression is observed after accounting for the relative concentration of BrCl (i.e., accounting for the α term). The solid line is a fit of the data to eq 26. Conditions: $[HOBr]_T = 4.87$ mM, $p[H^+] = 6.37$, $[PO_4]_T = 80$ mM, $[BrO_2^-] = 0.1$ mM, 25.0 °C, $\mu = 1.0$ M, and $\lambda = 245$ nm. $k_2^{Br} = 1.9(2) \times 10^5$ M^{-1} s^{-1}, $k_{-2}^{Br}/k_5^{HPO_4} = 2.6(6)$.

Table 2 shows the concentrations of Cl_2, BrCl, and Br_2 that are present under these conditions. A $[Cl^-]$ dependence study shows that the increase in k_{BrCl}^{Br} with $[Cl^-]$ also exhibits saturation behavior (Figure 7a). A $[Cl^-]$ suppression trend is observed when the relative concentration of BrCl, α, is taken into account (Figure 7b). The term α that was defined in eq 5 is used. The purpose of this term is to define [BrCl] in terms of total HOBr concentration. An increase of $[HOBr]_T$, which is present in large excess over BrO_2^-, also increases the k_{BrCl}^{Br}/α value (Figure 8). In addition, the results indicate that the BrCl/BrO_2^- reaction is base-catalyzed (Figures 9a and 9b). Ion chromatographic data show that BrO_3^- is a product of this reaction (Figure S10).

When BrOBrO is treated as a steady-state species, eqs 26−28 are obtained. Equation 26 shows the dependence of k_{BrCl}^{Br}
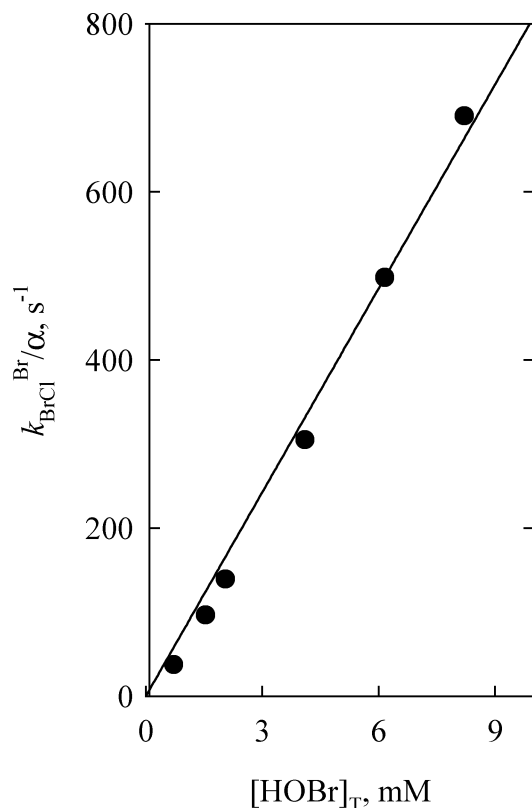
Figure 8. Linear dependence k_{BrCl}^{Br} on $[HOBr]_T$. Conditions: $[BrO_2^-]$ = 70 μM, p[H$^+$] = 5.91, [Cl$^-$] = 20 mM, $[PO_4]_T$ = 80 mM, 25.0 °C, μ = 1.0 M, and λ = 240 nm.

on Cl$^-$ and total hypobromous acid concentrations. The rearrangements of eq 26 to the forms in 27 and 28 show the dependence in H$^+$ and HPO$_4^{2-}$ concentrations. The solid line

$$\frac{k_{BrCl}^{Br}}{\alpha} = \frac{k_2^{Br}[HOBr]_T}{1 + \frac{k_{-2}^{Br}[Cl^-]}{k_5^B[B]}} \quad (26)$$

$$\frac{k_{BrCl}^{Br}}{\alpha} = \frac{\left(\frac{k_5^{HPO_4}[PO_4]_T}{k_{-2}^{Br}[Cl^-](1 + [H^+]/K_a^{HPO_4})}\right)k_2^{Br}[HOBr]_T}{\frac{k_5^{HPO_4}[PO_4]_T}{k_{-2}^{Br}[Cl^-](1 + [H^+]/K_a^{HPO_4})} + 1} \quad (27)$$

$$\frac{k_{BrCl}^{Br}}{\alpha} = \frac{\left(\frac{k_5^{HPO_4}[HPO_4^{2-}]}{k_{-2}^{Br}[Cl^-]}\right)k_2^{Br}[HOBr]_T}{\frac{k_5^{HPO_4}[HPO_4^{2-}]}{k_{-2}^{Br}[Cl^-]} + 1} \quad (28)$$

in Figure 7b shows the fit of the data to eq 26, which yields k_2^{Br} = 1.9(2) × 10^5 M^{-1} s^{-1} and k_{-2}^{Br}/k_5^B = 60(20) M^{-1}. Similarly, experimental data in Figure 8 fit to eq 26 as $[HOBr]_T$ is increased. A linear fit of the data in Figure 8 gives a slope of 8.1(2) × 10^4 M^{-1} s^{-1}. We find the reaction in eq 23 to be catalyzed by the basic form of phosphate, HPO$_4^{2-}$, and the data in Figures 9a and 9b fit the rate expressions in eq 27 and 28 (solid lines). From the
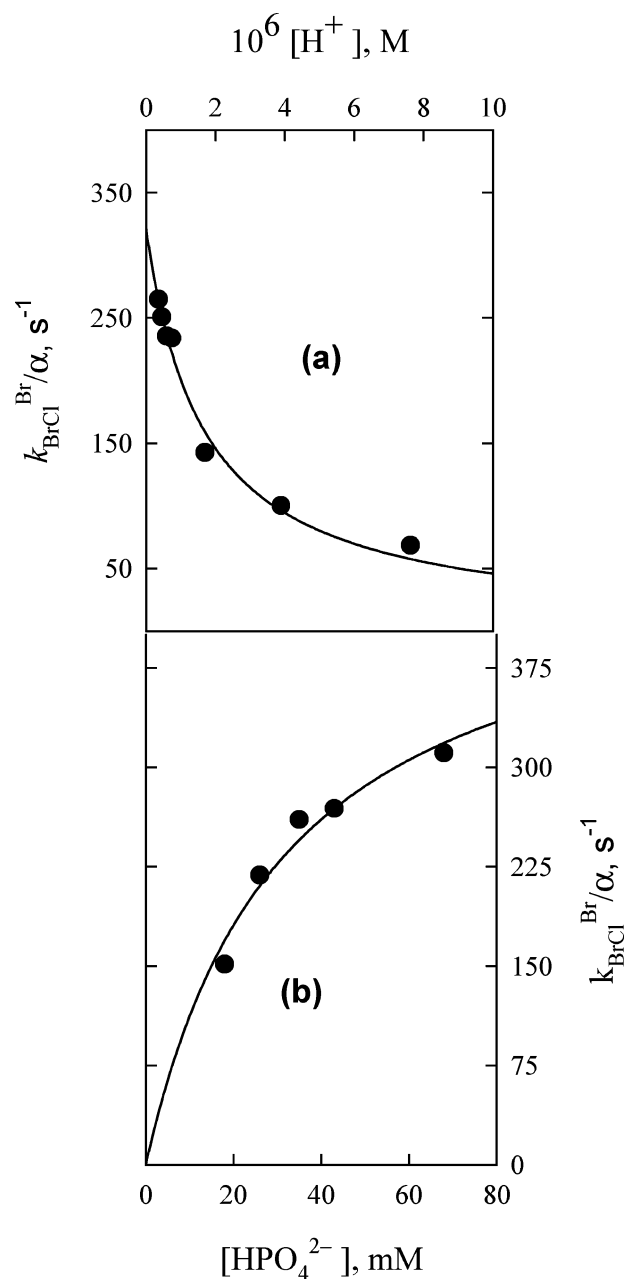
Figure 9. (a) Acid suppression of the BrCl/BrO$_2^-$ reaction. Conditions: $[HOBr]_T$ = 2.87 mM, [Cl$^-$] = 15.3 mM, $[BrO_2^-]$ = 0.1 mM, $[PO_4]_T$ = 80 mM, 25.0 °C, μ = 1.0 M, and λ = 245 nm. The solid line is a fit of the data to eq 27. (b) The rate of the BrCl/BrO$_2^-$ reaction is accelerated by the basic form of phosphate buffer. $[HOBr]_T$ = 2.78 mM, p[H$^+$] = 5.99(2), [Cl$^-$] = 15.3 mM, $[BrO_2^-]$ = 0.1 mM, 25.0 °C, μ = 1.0 M, and λ = 245 nm. The solid line is a fit of the data to eq 28.

dependence in $[HOBr]_T$, [H$^+$], [HPO$_4^{2-}$], and k_2^{Br} = 1.9(2) × 10^5 M^{-1} s^{-1}, the value of $k_{-2}^{Br}/k_5^{HPO_4}$ is 2.6(6).

**Comparison of BrCl/Bromite and BrCl/Chlorite Reactions.** We propose that reactions of both BrCl/ClO$_2^-$ and BrCl/BrO$_2^-$ proceed by Br$^+$ transfer mechanisms to form BrOXO and Cl$^-$ (eqs 10 and 22). The BrCl/ClO$_2^-$ reaction is 27.4 times faster than the BrCl/BrO$_2^-$ reaction. This kinetic behavior is attributed to the relative stabilities of BrOClO versus BrOBrO. Gas-phase calculations by Guha and Francisco[31] show that BrOClO is thermodynamically favored over

(31) Guha, S.; Francisco, J. S. *J. Phys. Chem. A* **1997**, *101*, 5347−5359.

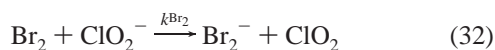**Table 3.** Summary of Constants for BrCl/BrO$_2^-$ and BrCl/ClO$_2^-$ Reactions

constants	values
k_2^{Cl}	$5.2(1) \times 10^6 \, M^{-1} \, s^{-1}$
$k_4^{HPO_4}/k_3$	0.19
$k_4^{H_2O}/k_3$	$1.0 \times 10^{-4} \, M$
k_{-2}^{Cl}/k_3	0.59(3)
$k_{-2}^{Cl}/k_4^{HPO_4}$	3.1(2)
$k_{-2}^{Cl}/k_4^{H_2O}$	$5.9(3) \times 10^3 \, M^{-1}$
k_2^{Br}	$1.9(2) \times 10^5 \, M^{-1} \, s^{-1}$
$k_{-2}^{Br}/k_5^{HPO_4}$	2.6(6)
$k_{-2}^{Br}/k_5^{H_2O}$	negligible

BrOBrO. Table 3 summarizes all the constants obtained for the BrCl/BrO$_2^-$ and BrCl/ClO$_2^-$ reactions. The BrCl/XO$_2^-$ reactions proceed by a different mechanism than the O$_3$/XO$_2^-$ reactions.[18] However, both BrCl and O$_3$ react with ClO$_2^-$ at a greater rate than with BrO$_2^-$. Nicoson et al. attributed the greater rate of electron transfer in O$_3$/ClO$_2^-$, relative to that in O$_3$/BrO$_2^-$, to the stability of the initial product, ClO$_2$ (eqs 29 and 30).[18] In the current study, the stability of BrOClO

$$O_3 + ClO_2^- \rightarrow ClO_2 + O_3^- \qquad (29)$$

$$O_3 + BrO_2^- \rightarrow BrO_2 + O_3^- \qquad (30)$$
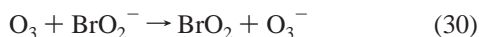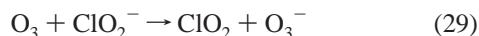
over BrOBrO leads to a larger rate constant for the BrCl/ClO$_2^-$ case. The suppression by Cl$^-$ in the overall reactions (Figures 2b and 7b) provides evidence that Br$^+$ transfer rather than electron transfer is the process by which BrCl/XO$_2^-$ reactions proceed.

Comparison of Molecular Halogen Reactions. There is a need to establish whether Br$_2$ and Cl$_2$, which are present at low levels along with BrCl, contribute to the observed reaction rate under our experimental conditions. The rate constants for ClO$_2^-$ reactions with Cl$_2$ and Br$_2$ have been reported.[32,33] The concentrations of Br$_2$ and Cl$_2$ present in the BrCl/ClO$_2^-$ system are calculated using our algorithm as detailed in Table 1 and Supporting Information Appendix A. Nicoson and Margerum[32] reported a $k^{Cl_2} = 5.7(2) \times 10^5$ M^{-1} s^{-1} for Cl$_2$/ClO$_2$ (eq 31), whereas Tóth and Fábián[33] reported $k^{Br_2} = 1.3(2) \times 10^3$ M^{-1} s^{-1} for the Br$_2$/ClO$_2^-$ reaction (eq 32). By use of the molecular halogen concentra-

$$Cl_2 + ClO_2^- \xrightarrow{k^{Cl_2}} ClOClO + Cl^- \qquad (31)$$

$$Br_2 + ClO_2^- \xrightarrow{k^{Br_2}} Br_2^- + ClO_2 \qquad (32)$$

tions in Table 2 and the rate constants for X$_2$/ClO$_2^-$ reactions, we find that the effects of Br$_2$ and Cl$_2$ on the BrCl/ClO$_2^-$ reaction are negligible.

We can compare the reactivity of molecular halogens with ClO$_2^-$ on the basis of the electrophilicity scale described by Jia et al.[6] In that study Jia et al. found that the rate of N$_2$H$_5^+$/ XY (X = Br or Cl; Y = I, Br, or Cl) was dependent on the energetics of both the new N−X bond formation and the

Y$^-$ loss. The Lewis acid strength has a less important contribution on the rate. The rate constants for X$_2$/ClO$_2^-$ are in agreement with the electrophilicity scale where BrCl(8.9) > Cl$_2$(8.2) > Br$_2$(7.3). However, the fact that electron transfer is the dominant pathway for Br$_2$ implies that if a Br$^+$ transfer mechanism existed for Br$_2$/ClO$_2^-$ it must be negligible with a rate constant much smaller than $k^{Br_2} = 1.3 \times 10^3$ M^{-1} s^{-1}.

The BrCl/BrO$_2^-$ reaction is also compared to the Cl$_2$/BrO$_2^-$ and Br$_2$/BrO$_2^-$ systems (eqs 33 and 34). Similar to the ClO$_2^-$ case, we find that the reactions in eq 33 ($k^{Cl/Br} = 8.7 \times 10^5$ M^{-1} s^{-1})[20] and in eq 34 ($k^{Br/Br} = 58.4$ M^{-1} s^{-1})[32]

$$Cl_2 + BrO_2^- \xrightarrow{k^{Cl/Br}} BrOClO + Cl^- \qquad (33)$$

$$Br_2 + BrO_2^- \xrightarrow{k^{Br/Br}} BrOBrO + Br^- \qquad (34)$$

have negligible effects on the BrCl/BrO$_2^-$ study. When comparing the reactions of BrO$_2^-$ with Cl$_2$, BrCl, and Br$_2$, a trend similar to that of X$_2$/ClO$_2^-$ is not observed. The order of Cl$_2$ and BrCl is reversed. We attribute this inconsistency to the greater stability of the interhalogen intermediate, BrOClO, in the Cl$_2$/BrO$_2^-$ reaction over BrOBrO for the BrCl/BrO$_2^-$ and Br$_2$/BrO$_2^-$ reactions, respectively. This is in agreement with what has been discussed in an earlier section regarding the difference in the rate of the BrCl reactions with bromite and chlorite ions.

Characteristics of XOXO Molecules. Several authors have proposed the presence of ClOClO[31,34] and BrOClO[31,33,35] as intermediates in the gas phase and in solution. In the current study we propose BrOClO as an intermediate in the BrCl/ClO$_2^-$ reaction. We also introduce BrOBrO as the analogous intermediate for the BrCl/BrO$_2^-$ reaction. These are proposed as steady-state intermediates as opposed to previous studies in which the intermediates were kinetically metastable species that reacted very rapidly to give products.[22,32,36] The distinction of the BrOClO and BrOBrO species as steady-state intermediates in this case is a result of an appreciable reverse path (k_{-2}) that is in competition with the forward path (k_3 and k_5) to give products. In other systems[22,32,36] BrOClO and BrOBrO were reactive intermediates that were not restricted to the steady-state approximation because the reverse path was not appreciable compared to the forward path. Yet these intermediates were required to give the observed reaction products.

As the evidence in the HOCl/BrO$_2^-$ study indicates,[20] BrOClO has a chainlike structure. We also favor the chainlike structure for BrOBrO rather than a Y-shaped form. On the basis of the electrophile/nucleophile argument, it is more likely for the more electronegative O atoms of BrO$_2^-$, the nucleophile, to attack the electrophilic bromine of BrCl to displace Cl$^-$. Such interaction would form a chainlike structure analogous to that of the BrOClO intermediate.

(32) Nicoson, J. S.; Margerum, D. W. *Inorg. Chem.* **2002**, *41*, 342−347.
(33) Tóth, Z.; Fábián, I. *Inorg. Chem.* **2000**, *39*, 4608−4614.
(34) Taube, H.; Dodgen, H. *J. Am. Chem. Soc.* **1949**, *71*, 3330−3336.
(35) Schmitz, G.; Rooze, H. *Can. J. Chem.* **1987**, *65*, 497−501.
(36) Jia, Z.; Margerum, D. W.; Francisco, J. S. *Inorg. Chem.* **2000**, *39*, 2614−2620.

Conclusions

This work shows that chloride ion catalyzes $HOBr/XO_2^-$ reactions. The catalysis is proposed to proceed through a BrCl intermediate. Although BrCl is present in small concentrations in the systems, it has a significant effect on the rates of the studied reactions. The results are in agreement with previous reports that discuss the role of BrCl as a reactive species in ozone depletion and in drinking water disinfection.[1,2] The findings in this study also serve as a cautionary reminder that researchers should not use NaCl to control ionic strength. High levels of chloride can lead to the formation of the highly reactive BrCl if the system includes bromine-containing species.

Supporting Information Available: Supplemental kinetic and stoichiometric data and an algorithm for [BrCl] calculation. This material is available free of charge via the Internet at http://pubs. acs.org.

IC048982M