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# Hypohalite Ion Catalysis of the Disproportionation of Chlorine Dioxide

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The disproportionation of chlorine dioxide in basic solution to give $ClO_2^-$ and $ClO_3^-$ is catalyzed by $OBr^-$ and $OCl^-$. The reactions have a first-order dependence in both $[ClO_2]$ and $[OX^-]$ (X = Br, Cl) when the $ClO_2^-$ concentrations are low. However, the reactions become second-order in $[ClO_2]$ with the addition of excess $ClO_2^-$, and the observed rates become inversely proportional to $[ClO_2^-]$. In the proposed mechanisms, electron transfer from $OX^-$ to $ClO_2$ ($k_1^{OBr^-} = 2.05 \pm 0.03$ $M^{-1}$ $s^{-1}$ for $OBr^-/ClO_2$ and $k_1^{OCl^-} = 0.91 \pm 0.04$ $M^{-1}$ $s^{-1}$ for $OCl^-/ClO_2$) occurs in the first step to give OX and $ClO_2^-$. This reversible step ($k_1^{OBr^-}/k_{-1}^{OBr} = 1.3 \times 10^{-7}$ for $OBr^-/ClO_2$, $k_1^{OCl^-}/k_{-1}^{OCl} = 5.1 \times 10^{-10}$ for $OCl^-/ClO_2$) accounts for the observed suppression by $ClO_2^-$. The second step is the reaction between two free radicals (XO and $ClO_2$) to form $XOClO_2$. These rate constants are $k_2^{OBr} = 1.0 \times 10^8$ $M^{-1}$ $s^{-1}$ for $OBr/ClO_2$ and $k_2^{OCl} = 7 \times 10^9$ $M^{-1}$ $s^{-1}$ for $OCl/ClO_2$. The $XOClO_2$ adduct hydrolyzes rapidly in the basic solution to give $ClO_3^-$ and to regenerate $OX^-$. The activation parameters for the first step are $\Delta H_1^{\ddagger} = 55 \pm 1$ kJ $mol^{-1}$, $\Delta S_1^{\ddagger} = -49 \pm 2$ J $mol^{-1}$ $K^{-1}$ for the $OBr^-/ClO_2$ reaction and $\Delta H_1^{\ddagger} = 61 \pm 3$ kJ $mol^{-1}$, $\Delta S_1^{\ddagger} = -43 \pm 2$ J $mol^{-1}$ $K^{-1}$ for the $OCl^-/ClO_2$ reaction.

## Introduction

It has long been known[1−6] that chlorine dioxide disproportionates in basic solutions to give $ClO_2^-$ and $ClO_3^-$. Recent work has shown that oxygen is also a product of the decomposition at low $ClO_2$ concentrations.[7] The disproportionation reaction is catalyzed by hypochlorite ion[8] and by bromite ion,[9] and the present work shows that hypobromite ion also catalyzes $ClO_2$ disproportionation. We also show that excess $ClO_2^-$ suppresses the rates of both the $OBr^-$ and the $OCl^-$ reactions. Hence, a new mechanism is needed for hypohalite catalysis that takes the $ClO_2^-$ suppression into account.

## Experimental Section

**Reagents.** All solutions were made with distilled, deionized water. Chlorine dioxide stock solution was prepared as described previously[10,11] and was protected from light and stored at 5 °C. The $ClO_2$ stock solution was standardized spectrophotometrically on the basis of the molar absorptivity of $ClO_2$, $\epsilon = 1230$ $M^{-1}$ $cm^{-1}$ at 359 nm.[11] Working solutions of NaOCl were prepared from a stock solution obtained by slowly bubbling $Cl_2(g)$ into a well-stirred solution of NaOH (∼0.3 M) maintained at 0−4 °C. Concentrations of the NaOCl solutions were determined spectrophotometrically at 292 nm ($\epsilon = 362$ $M^{-1}cm^{-1}$).[11] Sodium chlorite was purified and recrystallized as described previously,[9] and stock solutions were standardized spectrophotometrically ($\epsilon = 154.0$ $M^{-1}$ $cm^{-1}$ at 260 nm).[11] The ionic strength ($\mu$) was adjusted with $NaClO_4$ that was recrystallized from water, redissolved, and standardized gravimetrically. Solutions of phosphate and carbonate buffer were prepared from the reagent-grade salts. For kinetic measurements, the pH was buffered by mixing stock solutions of 1.0 M $Na_2HPO_4$ and $NaH_2PO_4$ ($pK_a = 6.26$)[11] or 1.0 M $NaHCO_3$ ($pK_a = 9.48$)[11] and $Na_2CO_3$ to yield the desired pH upon 10-fold dilution.

**Preparation of NaOBr Solutions.** We discovered in the process of this work that trace levels of $BrO_2^-$ in $HOBr/OBr^-$ solutions can affect the observed rate of catalytic disproportionation of $ClO_2$. This is due to electron-transfer reactions in which $BrO_2^-$ and $ClO_2$ give $BrO_2$ and $ClO_2^-$.[9] Precautions were taken to minimize the formation of $BrO_2^-$ in our preparation of $OBr^-$ solutions. Solutions of $HOBr/OBr^-$ disproportionate to $BrO_2^-$ and $Br^-$ with a rate that depends on $[HOBr]_T^2$, where $[HOBr]_T = [OBr^-] + [HOBr]$;

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however, $OBr^-$ is much slower to react than HOBr[12] ($pK_a$ of HOBr $= 8.59$ at 25.0 °C, $\mu = 1.0$ M).[12] Therefore, hypobromite was prepared by adding small amounts of $Br_2$(l) very slowly to a vigorously stirred 0.3 M NaOH solution. Bromide ion was removed with freshly precipitated AgOH in a method similar to that of Noszticzius et al.[13] in which 50 mL of 0.1 M $AgNO_3$ and 10 mL of 1 M NaOH were mixed in a 200 mL flask. After the AgOH precipitate was freed from its colloid fraction by 4−5 decantations with 0.1 M NaOH, 25 mL of the $OBr^-$ stock was added and shaken with the precipitate. After filtration, the clear light-yellow NaOBr solution was analyzed spectrophotometrically at 329 nm on the basis of its molar absorptivity of 332 $M^{-1}$ $cm^{-1}$.[14] The $OBr^-$ stock solution (~0.1 M) was prepared daily and kept in 0.1 M NaOH. The $OBr^-$ reactant solutions were diluted prior to the reaction. In the presence of 0.1 M $OH^-$, the $[Ag^+]$ in the $OBr^-$ stock solution would be $2 \times 10^{-7}$ M. In our kinetic studies, $1.45 \times 10^{-2}$ M or less of $OBr^-$ was used, which is a 7-fold dilution of the $OBr^-$ stock. Accordingly, $2.8 \times 10^{-8}$ M or less $Ag^+$ would be present in the reactant solution. Additional tests of ($OBr^- + Br^-$) solutions (without a AgOH treatment) gave the same kinetic results as solutions that were treated with AgOH. Ion chromatographic (IC) analysis was used to measure the $BrO_2^-$ content in the $OBr^-$ solution. In this analysis, excess of $(NH_4)_2SO_4$ solid was added into the $OBr^-$ sample solution at $p[H^+] = 9.5$ in order to remove $OBr^-$/HOBr, which reacts with the column packing. $BrO_2^-$ does not react with $NH_3/NH_4^+$.[15] The ion chromatographic results showed that the $[BrO_2^-]$ present in $OBr^-$ stock was only 0.07 mol % of the initial $[OBr^-]$. Interference from $BrO_2^-$ in the $OBr^-$ stock is negligible for kinetic studies in basic solutions. However, interference from the $BrO_2^-$ reaction becomes appreciable below $p[H^+]$ 7.7.

**Products and Stoichiometry.** Ion chromatography was used to identify and quantitatively determine the reaction products. Excess ethylenediamine was added to remove the $OBr^-$[16] before the product solutions were analyzed on the Dionex DX-500 IC. Detailed experimental procedures for the determination of the products by IC were described in earlier work.[9]

A Perkin-Elmer Lambda-9 UV−vis−NIR spectrophotometer used in conjunction with PECSS (Perkin-Elmer Computerized Spectroscopy Software) was used to acquire spectra for the reaction. Spectral scans were taken from 250 to 450 nm at 100 s intervals and after the reaction was complete.

**pH Measurement.** An Orion model 720 A digital pH meter equipped with a Corning combination electrode was used. The electrode was calibrated by titrations of standard $HClO_4$ with standard NaOH to correct the measured pH values to $-\log[H^+]$ ($=p[H^+]$) at 25.0 ± 0.1 °C and an ionic strength ($\mu$) adjusted to 1.0 M with $NaClO_4$.

**Kinetic Measurements.** Kinetic traces for slow reactions were acquired with the Perkin-Elmer Lambda-9 UV−vis−NIR spectrophotometer. The kinetics of the fast reactions were followed on an Applied PhotoPhysics SX.18 MV stopped-flow spectrophotometer (APPSF, optical path length = 0.962 cm). The molar absorptivities of $ClO_2$, $OCl^-$, and $ClO_2^-$ determined on the Lambda-9 UV−vis−NIR spectrophotometer[11] agreed with values measured on the APPSF. All reactions were run under pseudo-first-order conditions with $[HOBr]_T$ or $[HOCl]_T$ ($=[HOCl] + [OCl^-]$) in large excess over $[ClO_2]$. Reactions were maintained at an ionic strength of 1.0 M. The rates of the reactions were monitored at 359 or 380 nm for the disappearance of $ClO_2$. SigmaPlot 4.0[17] was used for the regression analysis.

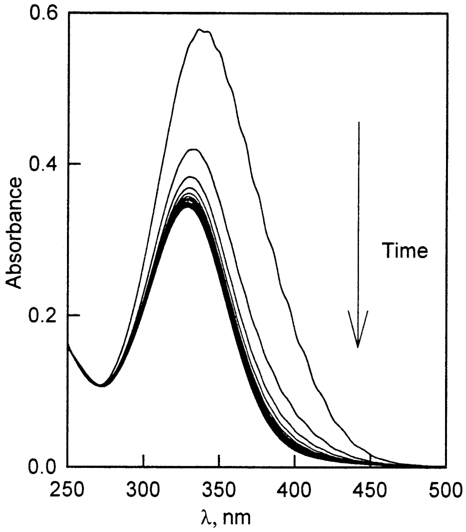

**Figure 1.** Spectral evidence of no $OBr^-$ loss in the catalyzed decay of $ClO_2$. Conditions: $[OBr^-]_T = 1.01$ mM, $[ClO_2]_i = 0.994$ mM, $[CO_3]_T = 0.10$ M, $p[H^+] = 11.6$, 25.0 °C, 1 cm cell, reaction time = 1.55 h, 100 s time interval per scan. Appreciable amounts of $ClO_2$ are already lost when the first scan was made because of a 3 min time interval between mixing and the first scan.

**Table 1.** Ion Chromatographic Determination of Products for the Reaction of $ClO_2$ with $OBr^-$ [a]

| $p[H^+]$ of reaction mixture | yield ratio[b] $[ClO_2^-]/[ClO_3^-]$ |
|---|---|
| 10.9 | 1.00 ± 0.04 |
| 11.4 | 1.00 ± 0.04 |

[a] Conditions: $[OBr^-]_i = [OBr^-]_f = 0.960$ mM, $[CO_3]_T = 0.10$ M, $[ClO_2]_i = 1.7$ mM, 25.0 °C. [b] Ethylenediamine was used to remove $OBr^-$ from the solution.

## Results and Discussion

### I. Reaction between $OBr^-$ and $ClO_2$.

**Stoichiometry.** When $OBr^-$ and $ClO_2$ solutions are mixed to give 1.0 mM concentrations of each at $p[H^+]$ 11.6, a significant absorbance drop at 359 nm is observed, and a final absorbance from 250 to 450 nm remains, in which the dominant absorbing species is $OBr^-$ (Figure 1). Ion chromatographic results show that $ClO_2^-$ and $ClO_3^-$ are the products of the reaction with a 1:1 stoichiometry (Table 1). After all the $ClO_2$ reacts, the remaining absorbance from 250 to 450 nm is in good agreement with the sum of the absorbance spectra of the added $OBr^-$ and the $ClO_2^-$ generated from the reaction where $[ClO_2^-] = {}^1/_2[ClO_2]_i$ and no $OBr^-$ is lost. The rate of the depletion of $ClO_2$ increases with the increase of $[OBr^-]$ added. It is apparent that the disproportionation of $ClO_2$ is catalyzed by $OBr^-$ (eq 1).

$$2ClO_2 + 2OH^- \xrightarrow{OBr^-} ClO_2^- + ClO_3^- + H_2O \qquad (1)$$

**Kinetics.** Without initial addition of excess $ClO_2^-$, the rates of loss of $ClO_2$ with added $OBr^-$ show a first-order

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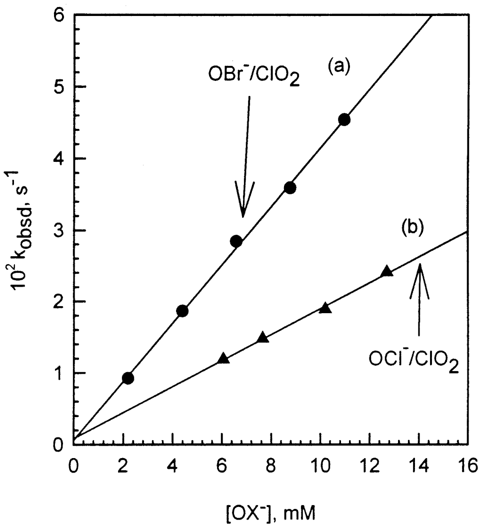

**Figure 2.** Dependence of the observed first-order rate constant on $[OX^-]$ for the reaction of $OX^-$ with $ClO_2$. (a) Conditions for the $OBr^-/ClO_2$ reaction: $[CO_3]_T = 0.10$ M, $\mu = 1.0$ M, $[ClO_2]_i = 0.41$ mM, no added $[ClO_2^-]_i$, $p[H^+] = 9.9-10.0$, 25.0 °C. Slope = $(4.09 \pm 0.09)$ $M^{-1}\,s^{-1}$; intercept = $(6 \pm 7) \times 10^{-4}$ $s^{-1}$. (b) Conditions for the $OCl^-/ClO_2$ reaction: $[CO_3]_T = 0.10$ M, $\mu = 1.0$ M, $[ClO_2]_i = 0.1$ mM, no added $[ClO_2^-]_i$, $p[H^+] = 10.6$, 25.0 °C. Slope = $(1.81 \pm 0.07)$ $M^{-1}\,s^{-1}$; intercept = $(8 \pm 6) \times 10^{-4}$ $s^{-1}$.

**Table 2.** No Effect of Carbonate Buffer or Bromide Ion on the Hypohalite Catalysis of $ClO_2$ Disproportionation[a]

| $OBr^-/ClO_2$ reaction | | $OCl^-/ClO_2$ reaction | |
|---|---|---|---|
| $[CO_3]_T$, M | $k_{obsd}/[OBr^-]$, $M^{-1}\,s^{-1}$ [b] | $[CO_3]_T$, M | $k_{obsd}/[OCl^-]$, $M^{-1}\,s^{-1}$ [g] |
| 0.00 | 4.20[c] | 0.05 | 1.83 |
| 0.05 | 4.15[d] | 0.30 | 1.85 |
| 0.30 | 4.28[e] | | |

| $[CO_3]_T$, M | added $[Br^-]$, M | $k_{obsd}^{2nd}$, $M^{-1}\,s^{-1}$ [f] |
|---|---|---|
| 0.05 | 0.0 | 33.2 |
| 0.10 | 0.0 | 32.2 |
| 0.10 | 0.05 | 31.3 |

[a] Conditions: 25.0 °C, $\mu = 1.0$ M. [b] $[ClO_2^-]_i = 0$ M. The $k_{obsd}/[OBr^-]$ values refer to eq 9. [c] Conditions: $[HOBr]_T = 14.3$ mM, $[ClO_2]_i = 0.22$ mM, $p[H^+] = 8.73$. [d] Conditions: $[HOBr]_T = 5.32$ mM, $[ClO_2]_i = 0.26$ mM, $p[H^+] = 9.87$. [e] Conditions: $[HOBr]_T = 5.32$ mM, $[ClO_2]_i = 0.26$ mM, $p[H^+] = 10.14$. [f] $[ClO_2^-]_i = 12.3$ mM, $[HOBr]_T = 13.32$ mM, $[ClO_2]_i = 0.12$ mM, $p[H^+] = 11.0-10.9$. The $k_{obsd}^{2nd}$ values refer to eq 11. [g] Conditions: $[HOCl]_T = 2.62$ mM, $[ClO_2]_i = 0.10$ mM, $p[H^+] = 9.87-10.13$.

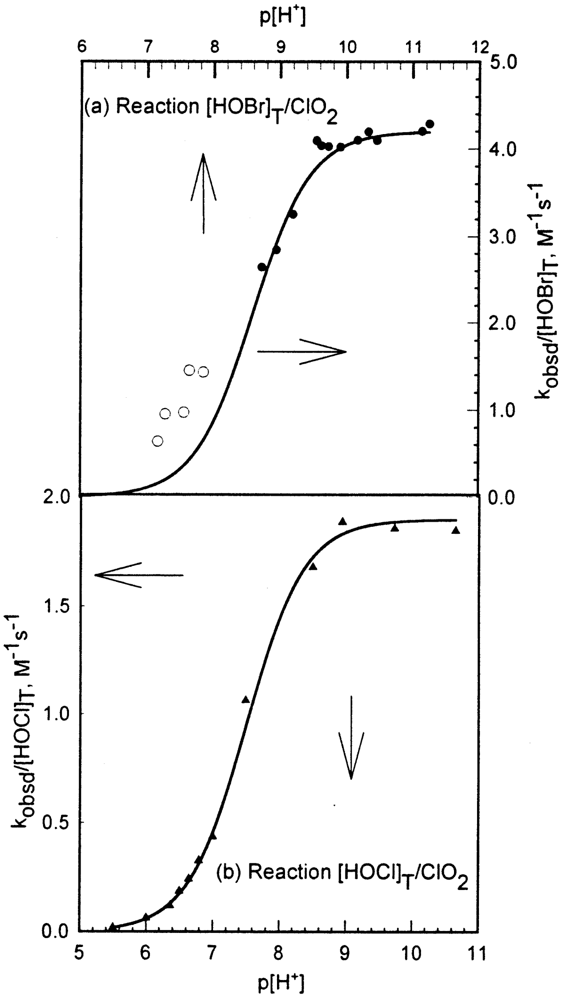

**Figure 3.** Dependence of $k_{obsd}/[HOX]_T$ on $p[H^+]$ for the catalytic reactions of $OBr^-$ and $OCl^-$ in $ClO_2$ disproportionation. The open circles (○) in Figure 3a are from measured rate constants under conditions where $BrO_2^-$ interference is expected. $pK_a^{HOBr} = 8.59$[12] and $pK_a^{HOCl} = 7.47$[27] were used for the calculations. Conditions: $[HPO_4]_T = 0.10$ M at $p[H^+] < 8$, $[CO_3]_T = 0.10$ M at $p[H^+] > 8.5$, $[ClO_2]_i = 0.1-0.01$ mM, $\mu = 1.0$ M, 25.0 °C.

dependence upon the concentration of chlorine dioxide (eq 2). The observed first-order rate constants ($k_{obsd}$) have a first-order dependence in $[OBr^-]$ (Figure 2a).

$$-d[ClO_2]/dt = k_{obsd}[ClO_2] \tag{2}$$

Our studies show that the reaction has no dependence on the concentration of carbonate buffer (Table 2) or on hydroxide ion concentration from $p[H^+]$ 10.0 to 11.2 ($pK_W = 13.6$).[18] As additional tests, we also prepared $OBr^-$ stock by bubbling $Br_2$ vapor into a well-stirred NaOH solution. Contamination of $BrO_2^-$ should be minimized by this method because locally high concentrations of $Br_2$ are avoided and the pH value should be uniform throughout the solution. The $k_{obsd}/[OBr^-]$ data (the points at $p[H^+]$ 11.14, 8.73, 8.95 in Figure 3a) obtained by using this $OBr^-$ stock solution are consistent with our other data. Additional evidence supports the conclusion that $BrO_2^-$ contamination does not interfere with data at higher pH. Because the $BrO_2^-/ClO_2$ reaction[9] is greatly accelerated by $[CO_3^{2-}]$ while the $OBr^-/ClO_2$ reaction has no $[CO_3^{2-}]$ dependence, appreciable amounts of $BrO_2^-$ present in the $OBr^-$ stock solution will cause a significant difference in the overall rates when $CO_3^{2-}$ is present compared to when it is absent. Our experiments show that, when excess $HOBr/OBr^-$ was used to buffer the reaction at $p[H^+]$ 8.73 (no carbonate buffer was added), the $k_{obsd}/[OBr^-]$ value (shown in Table 2 and Figure 3a) is in good agreement with the $k_{obsd}/[OBr^-]$ values for the reactions buffered with carbonate.

**Interference from Bromite Ion below $p[H^+]$ 8.5.** Prior to our efforts to minimize $BrO_2^-$ concentrations in the preparation of $OBr^-$ solutions, we experienced difficulty in obtaining reproducible rate constants for the $OBr^-$ reaction with $ClO_2$. After the preparation of $OBr^-$ solution with only

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**Table 3.** Calculations for the Interference from [$BrO_2^-$] When It Is 0.1% $[HOBr]_T$

| $p[H^+]$ | $[HOBr]_T$[a] (mM) | $[ClO_2]_i$[b] (mM) | $\Sigma k^{Nu}[Nu]$[c] ($M^{-1}\,s^{-1}$) | $r_{OBr^-}$[d] ($M\,s^{-1}$) | $r_{BrO_2^-}$[d] ($M\,s^{-1}$) | $r_{BrO_2^-}/r_{OBr^-}$ |
|---|---|---|---|---|---|---|
| 11.25[e] | 14.5 | 0.248 | $1.56 \times 10^7$ | $7.66 \times 10^{-6}$ | $6.34 \times 10^{-8}$ | 0.008 |
| 10.17[e] | 14.5 | 0.248 | $1.29 \times 10^7$ | $7.66 \times 10^{-6}$ | $5.70 \times 10^{-8}$ | 0.007 |
| 9.55[e] | 14.5 | 0.248 | $8.51 \times 10^6$ | $6.91 \times 10^{-6}$ | $4.38 \times 10^{-8}$ | 0.006 |
| 8.95[e] | 14.3 | 0.22 | $1.11 \times 10^6$ | $2.82 \times 10^{-6}$ | $1.13 \times 10^{-8}$ | 0.003 |
| 7.64[f] | 2.37 | 0.10 |  | $4.27 \times 10^{-9}$ | $7.20 \times 10^{-10}$ | 0.2 |
| 6.41[f] | 2.72 | 0.10 |  | $3.80 \times 10^{-9}$ | $9.80 \times 10^{-9}$ | 2.6 |

[a] $[HOBr]_T$ is the concentration used in the kinetic study. [b] $[ClO_2]_i$ is the initial concentration of $ClO_2$. [c] $\Sigma k^{Nu}[Nu] = k^{H_2O} \times 55.5 + k^{OH}[OH^-] + k^{CO_3}[CO_3^{2-}]$. At $p[H^+] < 7.64$, $[ClO_2^-] = 0$, the $\Sigma k^{Nu}[Nu]$ term does not contribute to the rate. [d] $r_{OBr^-}$ and $r_{BrO_2^-}$ are the $OBr^-$ and $BrO_2^-$ reaction rates at the first half-life of the $ClO_2$ decay. [e] $[CO_3]_T = 0.10$ M. [f] $[HPO_4]_T = 0.10$ M.

0.07% $BrO_2^-$ content, reproducibility was no longer a problem above $p[H^+]$ 8.5. However, there are several reasons why $BrO_2^-$ interference still occurs at lower pH. First, the disproportionation of HOBr to give $BrO_2^-$ and $Br^-$ is 3 orders of magnitude faster at pH 5−8 than it is at pH 11.[12] Therefore, at low pH, the concentration of $BrO_2^-$ increases during the time of the reaction. Second, HOBr is a poor catalyst (or a noncatalyst) of $ClO_2$ disproportionation, and longer reaction times are needed to observe the reaction at $p[H^+]$ values below 8.5 where more HOBr is present. This, in turn, allows more $BrO_2^-$ to form. Third, HOBr reacts rapidly with $ClO_2^-$ at pH 5−8 to generate $ClO_3^-$ and $Br^-$.[11] The removal of $ClO_2^-$ accelerates the $BrO_2^-$ catalysis of $ClO_2$ disproportionation.[9] Higher concentrations of $ClO_2^-$ are needed to suppress the $OBr^-$ catalysis. Because the $pK_a$ of $HBrO_2$ is 3.59,[19] its formation is not significant in the pH range of this study. However, low pH increases the rate of $BrO_2^-$ formation because of general-acid assistance from $H_2PO_4^-$. The combination of all these factors is complex.[9,11,12] Table 3 shows that, from our measured rate constants, the effect of 0.1% $BrO_2^-$ in $[HOBr]_T$ would be negligible for the $OBr^-/ClO_2$ studies at pH 8.95 or higher but would be significant at $p[H^+]$ 7.6 and lower (the details for the calculation are shown in the Supporting Information). Figure 3a shows that the pH dependence of the $OBr^-/ClO_2$ reaction from $p[H^+]$ 8.73 to 11.23 (●) fits the assumption that HOBr does not react (eq 3). The open circles (○) in Figure 3a are from measured rate constants under conditions where $BrO_2^-$ interference is expected. These are not included in the fit.

$$\frac{k_{obsd}}{[HOBr]_T} = k^{OBr^-}\frac{K_a^{HOBr}}{K_a^{HOBr} + [H^+]} \tag{3}$$

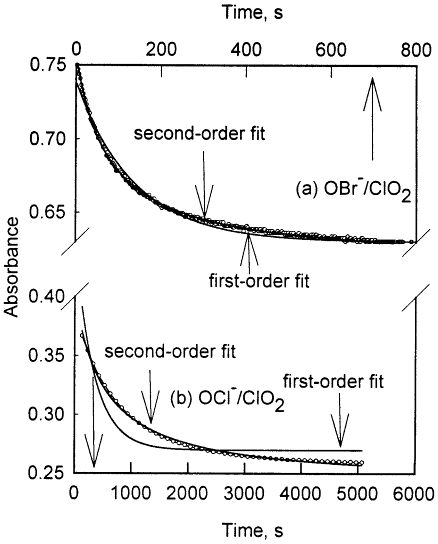

**Figure 4.** Kinetic traces of the $OX^-$ reactions with $ClO_2$ in excess $[ClO_2^-]$. (a) Conditions for the $OBr^-/ClO_2$ reaction: $[OBr^-] = 17.02$ mM, $[CO_3]_T = 0.10$ M, $[ClO_2]_i = 0.20$ mM, $[ClO_2^-] = 15.71$ mM, $p[H^+] = 10.50$, $\mu = 1.0$ M, 25.0 °C, $\lambda = 390$ nm, cell path = 0.962 cm. (b) Conditions for the $OCl^-/ClO_2$ reaction: $[OCl^-] = 18.77$ mM, $[CO_3]_T = 0.10$ M, $[ClO_2]_i = 0.045$ mM, $[ClO_2^-] = 7.98$ mM, $p[H^+] = 10.30$, $\mu = 1.0$ M, 25.0 °C, $\lambda = 380$ nm, cell path = 1.0 cm.

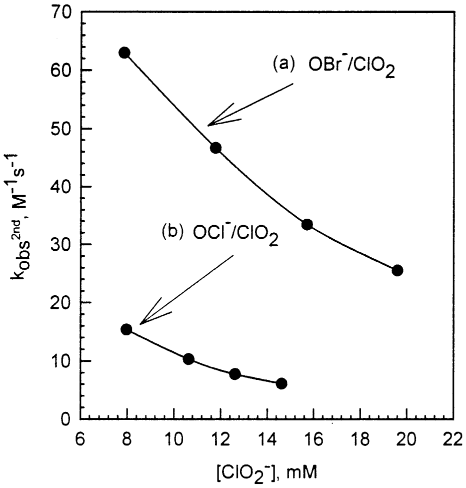

**Figure 5.** Suppression by $[ClO_2^-]$ of the second-order rate constant for the reaction of $OX^-$ with $ClO_2$. (a) Conditions for the $OBr^-/ClO_2$ reaction: $[OBr^-] = 17.02$ mM, $[CO_3]_T = 0.10$ M, $[ClO_2]_i = 0.20$ mM, $p[H^+] = 10.50$, $\mu = 1.0$ M, 25.0 °C, $\lambda = 390$ nm. (b) Conditions for the $OCl^-/ClO_2$ reaction: $[OCl^-] = 18.77$ mM, $[CO_3]_T = 0.10$ M, $[ClO_2]_i = 0.045$ mM, $p[H^+] = 10.30$, $\mu = 1.0$ M, 25.0 °C, $\lambda = 380$ nm. Regression fit: $k_{obs}^{2nd} = 2K_1^{OX^-}k_2^{OX}[OX^-]/[ClO_2^-]$.

**Effect of Chlorite.** When excess $ClO_2^-$ is added to the $OBr^-/ClO_2$ mixture, the reaction order shifts from first-order to second-order dependence in $[ClO_2]$ (Figure 4a). The inhibitory effect of $ClO_2^-$ on the rate at $p[H^+]$ 10.5 is shown in Figure 5a. The observed second-order rate constant is inversely proportional to the excess $[ClO_2^-]$. It is known that HOBr reacts with $ClO_2^-$ to generate $ClO_2$ and $ClO_3^-$ and that the reaction is general-acid catalyzed.[11] At $p[H^+] = 10.5$, [HOBr] is approximately 1% of the $[HOBr]_T$, so the reaction between HOBr and $ClO_2^-$ under these conditions is much slower than the $OBr^-$ catalysis of $ClO_2$ disproportionation. We also find no dependence on $Br^-$ and carbonate concentrations in the presence of excess $ClO_2^-$ (Table 2). This is in marked contrast to the large effect of many nucleophile species (including $CO_3^{2-}$ and $Br^-$) on the kinetics of the reaction between $BrO_2^-$ and $ClO_2$ because of nucleophile assistance of the electron transfer between the intermediate species $BrO_2$ with $ClO_2$.[9]

**Mechanism.** The rate inhibition by $ClO_2^-$ is mechanistically significant and strongly suggests that an electron

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transfer occurs from $OBr^-$ to $ClO_2$. The proposed mechanism for the reaction is given in eqs 4−7, where BrO is a highly reactive radical.

$$\mathrm{ClO_2 + OBr^-} \underset{k_{-1}^{\mathrm{OBr}}}{\overset{k_1^{\mathrm{OBr-}}}{\rightleftarrows}} \mathrm{ClO_2^- + BrO} \quad K_1^{\mathrm{OBr^-}} \tag{4}$$

$$\mathrm{BrO + ClO_2} \xrightarrow{k_2^{\mathrm{OBr}}} \mathrm{BrOClO_2} \tag{5}$$

$$\mathrm{BrOClO_2 + OH^-} \xrightarrow{\mathrm{rapid}} \mathrm{OBr^- + HClO_3} \tag{6}$$

$$\mathrm{HClO_3 + OH^-} \xrightarrow{\mathrm{rapid}} \mathrm{ClO_3^- + H_2O} \tag{7}$$

It could react with $ClO_2^-$ to go back to the reactants or react with excess $ClO_2$ to form an adduct, $BrOClO_2$. The stabilities of various $BrClO_3$ species in the gas phase have been studied by ab initio methods.[20] Calculations show that formation of $BrClO_3$ by the reaction between BrO and $ClO_2$ is very favorable. The BrOCl(O)O conformation was found to be the most stable of the $BrClO_3$ isomers; it is 34.3 kJ mol $^{-1}$ more stable than (BrO + OClO).[20] This calculation by Francisco and Clark[20] supports the second step in our proposed mechanism. Water solvation will undoubtedly have a large effect on the stability and reactivity of the intermediates. However, gas phase calculations provide a useful model to evaluate the plausibility of the proposed intermediate. The $BrOClO_2$ adduct can then be attacked by $OH^-$ to give $OBr^-$ and $HOClO_2$ (eq 6), and chloric acid is rapidly converted to $ClO_3^-$ as a final product in basic solution (eq 7).

A steady-state approximation in regard to BrO gives the rate expression in eq 8, where the factor of 2 accounts for the stoichiometric ratio in eqs 4 and 5. Typically, the concentration of $ClO_2$ used in this study was low (<0.2 mM).

$$-\mathrm{d[ClO_2]/d}t = \frac{2k_1^{\mathrm{OBr^-}}\, k_2^{\mathrm{OBr}}[\mathrm{OBr^-}][\mathrm{ClO_2}]^2}{k_{-1}^{\mathrm{OBr}}[\mathrm{ClO_2^-}] + k_2^{\mathrm{OBr}}[\mathrm{ClO_2}]} \tag{8}$$

When no initial $ClO_2^-$ was added, the $[ClO_2^-]$ generated from the disproportionation of $ClO_2$ was low, and the reverse step ($k_{-1}^{\mathrm{OBr}}$) in eq 4 could be neglected. Under this condition ($[ClO_2]/[ClO_2^-] \gg k_{-1}^{\mathrm{OBr}}/k_2^{\mathrm{OBr}}$), the rate expression in eq 8 simplifies to eq 9. To meet the required condition, the data for the first 75% of the reaction were used to determine the observed first-order rate constants.

$$-\mathrm{d[ClO_2]/d}t = 2k_1^{\mathrm{OBr^-}}[\mathrm{OBr^-}][\mathrm{ClO_2}] = k_{\mathrm{obsd}}[\mathrm{ClO_2}] \tag{9}$$

From the slope of the $k_{\mathrm{obsd}}$ versus $[OBr^-]$ plot in Figure 2a, $k_1^{\mathrm{OBr^-}}$ is determined as 2.05 ± 0.03 $M^{-1}$ $s^{-1}$. Reduction potential values for $OBr/OBr^-$ and $ClO_2/ClO_2^-$ are reported to be 1.34 and 0.934 V, respectively.[21] These potentials lead to a value of $1.3 \times 10^{-7}$ for the equilibrium constant $K_1^{\mathrm{OBr^-}}$ ($=k_1^{\mathrm{OBr^-}}/k_{-1}^{\mathrm{OBr}}$) for the first step (eq 4). From the $K_1^{\mathrm{OBr^-}}$ and $k_1^{\mathrm{OBr^-}}$ values, $k_{-1}^{\mathrm{OBr}}$ is estimated to be $1.6 \times 10^7$ $M^{-1}$ $s^{-1}$.

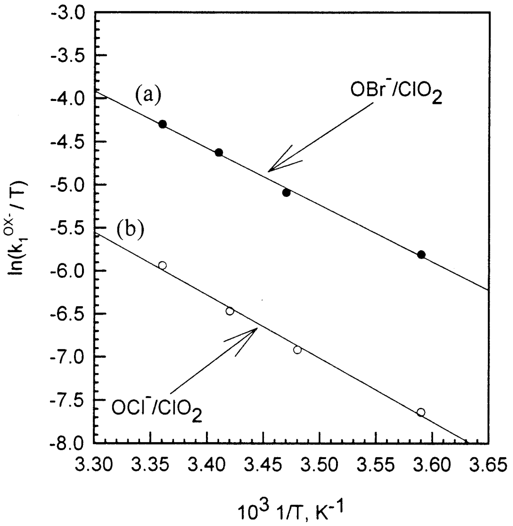

**Figure 6.** Eyring plots for the reaction of $OX^-/ClO_2$. Conditions for the $OBr^-/ClO_2$ reaction: $[HOBr]_T = 0.58$ mM, $[ClO_2^-] = 0.0$ M, $[ClO_2]_i = 0.010$ mM, $[CO_3]_T = 0.10$ M, $\mu = 1.0$ M, $p[H^+] = 10.70$. Slope $= -(6.6 \pm 0.3) \times 10^3$ K, intercept = 17.9 ± 0.9. Conditions for the $OCl^-/ClO_2$ reaction: $[HOCl]_T = 2.51$ mM, $[ClO_2^-]_i = 0.0$ M, $[ClO_2]_i = 0.10$ mM, $[CO_3]_T = 0.10$ M, $\mu = 1.0$ M, $p[H^+] = 10.60$. Slope $= -(7.2 \pm 0.4) \times 10^3$ K, intercept = 19 ± 1.

Because the $k_{-1}^{\mathrm{OBr}}$ value is large, the addition of excess $ClO_2^-$ could lead to the inequality, $k_{-1}^{\mathrm{OBr}}$ $[ClO_2^-] \gg k_2^{\mathrm{OBr}}[ClO_2]$, in the denominator in eq 8. Elimination of the $k_2^{\mathrm{OBr}}[ClO_2]$ term gives the rate expression in eq 10. Equations 10 and 11 are consistent with our experimental observations that the addition of excess $ClO_2^-$ causes the reaction to exhibit a second-order dependence in $[ClO_2]$ and that the reciprocal of the observed second-order rate constant is directly proportional to the excess $[ClO_2^-]$.

$$-\mathrm{d[ClO_2]/d}t = \frac{2K_1^{\mathrm{OBr^-}} k_2^{\mathrm{OBr}}[\mathrm{OBr^-}][\mathrm{ClO_2}]^2}{[\mathrm{ClO_2^-}]} \tag{10}$$

$$k_{\mathrm{obsd}}^{\mathrm{2nd}} = \frac{2K_1^{\mathrm{OBr^-}}\, k_2^{\mathrm{OBr}}[\mathrm{OBr^-}]}{[\mathrm{ClO_2^-}]} \tag{11}$$

The slope of the plot of $[OBr^-]/k_{\mathrm{obsd}}^{\mathrm{2nd}}$ versus $[ClO_2^-]$ (Supporting Information Figure 2) gives $1/(2K_1^{\mathrm{OBr^-}}\, k_2^{\mathrm{OBr}}) = (3.86 \pm 0.09) \times 10^{-2}$ $M^{-1}$ $s^{-1}$. This slope value and the $K_1^{\mathrm{OBr^-}}$ value allow $k_2^{\mathrm{OBr}}$ to be evaluated as $1.0 \times 10^8$ $M^{-1}$ $s^{-1}$.

**Activation Parameters Measurement.** The temperature dependence of the kinetics was determined over the temperature range from 5 to 25 °C at $p[H^+] = 10.70$ with $[HOBr]_T = 0.58$ mM, $[ClO_2]_i = 0.010$ mM, no added $ClO_2^-$, and $\mu = 1.0$ M. The activation enthalpy, $\Delta H_1^\ddagger = 55 \pm 1$ kJ $mol^{-1}$, and the activation entropy, $\Delta S_1^\ddagger = -49 \pm 2$ J $mol^{-1}$ $K^{-1}$, of the reaction are obtained from an Eyring Plot (Figure 6a). The activation parameters determined under this condition correspond to the electron-transfer step in eq 4. The positive $\Delta H_1^\ddagger$ and negative $\Delta S_1^\ddagger$ values correspond to the need to bring $OBr^-$ and $ClO_2$ together as well as their rearrangement prior to electron transfer to give OBr and $ClO_2^-$.

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**II. Reaction between $OCl^-$ and $ClO_2$.** An early study of the decomposition of $ClO_2$ in aqueous solution in the presence of HOCl was reported in 1959 by Flis and co-workers.[22] In a more recent investigation of the reaction by Csordás and co-workers,[8] a mechanism was proposed in which $ClO_2$ and $OCl^-$ form an adduct in a rate-determining step, followed by a rapid electron transfer from the adduct to the second $ClO_2$. Our results from a spectrophotometric study of the reaction stoichiometry agree with their conclusion that $OCl^-$ catalyzes the decomposition of $ClO_2$. We also observed a first-order dependence in both $[ClO_2]$ and $[OCl^-]$ (Figure 2b) when $ClO_2$ and $OCl^-$ reactant solutions were mixed. However, we found important evidence that Csordás et al. missed, in which addition of excess $ClO_2^-$ changes the reaction order from first-order to second-order dependence in $[ClO_2]$ (Figure 4b) and suppresses the rate (Figure 5b). These observations indicate that an electron transfer must occur from $OCl^-$ to $ClO_2$ in the first step, which therefore leads to a different mechanism from the one proposed by these authors. We find no buffer dependence for the reaction (Table 2). The mechanism we propose (eqs 12−15) is analogous to that for the reaction of $OBr^-$ with $ClO_2$ (eqs 4−7).

$$ClO_2 + OCl^- \underset{k_1^{OCl}}{\overset{k_1^{OCl^-}}{\rightleftarrows}} ClO_2^- + ClO \quad K_1^{OCl^-} \tag{12}$$

$$ClO + ClO_2 \xrightarrow{k_2^{OCl}} ClOClO_2 \tag{13}$$

$$ClOClO_2 + OH^- \xrightarrow{\text{rapid}} OCl^- + HClO_3 \tag{14}$$

$$HClO_3 + OH^- \xrightarrow{\text{rapid}} ClO_3^- + H_2O \tag{15}$$

Calculation of the stability of $Cl_2O_3$[23] shows that the formation of $ClOClO_2$ from the reaction in eq 13 would be favorable by 45.6 kJ $mol^{-1}$ in the gas phase.

Csordás et al.[8] excluded the possibility of an electron transfer between the reactants on the basis of the work by Fábián et al.[24] and Buxton et al.[25] However, the mechanism proposed for the ClO reaction with $ClO_2^-$ and $ClO_2$ by Fábián et al.[24] actually supports our proposed $k_{-1}^{OCl}$ and $k_2^{OCl}$ steps in eqs 12 and 13. When Buxton and Subhani[25] performed their pioneering pulse radiolysis study in 1972, it was erroneously thought that an OH-type radical was the primary product of the reaction between a hydrated electron and a halogen oxoanion. Later pulse radiolytic studies by Eriksen et al.[26] and Zuo et al.[27] detected and demonstrated that $ClO_2$ and $OCl^-$ are the products of the reaction between the solvated electron and $ClO_2^-$. Their interpretations were that the rate constant for the solvated electron reaction with $ClO_2^-$ was $2.5 \times 10^9$ $M^{-1}$ $s^{-1}$[26] and $4.4 \times 10^9$ $M^{-1}$ $s^{-1}$.[27] As will be shown, we find a value of $3.6 \times 10^9$ $M^{-1}$ $s^{-1}$ for the ClO reaction with $ClO_2^-$ to give $ClO_2$ and $OCl^-$ (eq 12, $k_{-1}^{OCl}$). This strongly suggests that ClO may be an intermediate in the reaction of $e(aq)^-$ with $ClO_2^-$, and the presence of excess $ClO_2^-$ causes the formation of $ClO_2$ and $OCl^-$. Hence, our results are in substantial agreement with those of Eriksen et al.[26] and Zuo et al.[27]

According to the mechanism in eqs 12−15, the rate expression for the reaction of $OCl^-$ and $ClO_2$ is given in eq 16.

$$-d[ClO_2]/dt = \frac{2k_1^{OCl^-}k_2^{OCl}[OCl^-][ClO_2]^2}{k_{-1}^{OCl}[ClO_2^-] + k_2^{OCl}[ClO_2]} \tag{16}$$

Equations 17 and 18 give the simplified rate expressions.

$$-d[ClO_2]/dt = 2k_1^{OCl^-}[OCl^-][ClO_2] \quad (\text{when } k_2^{OCl}[ClO_2] \gg k_{-1}^{OCl}[ClO_2^-]) \tag{17}$$

$$-d[ClO_2]/dt = \frac{2k_1^{OCl^-}k_2^{OCl}[OCl^-]}{k_{-1}^{OCl}[ClO_2^-]}[ClO_2]^2 \quad (\text{when } k_{-1}^{OCl}[ClO_2^-] \gg k_2^{OCl}[ClO_2]) \tag{18}$$

We followed the reaction for only 50% loss of $ClO_2$ in the $[OCl^-]$ dependence study to meet the requirement for eq 17 that $[ClO_2]/[ClO_2^-] \gg k_{-1}^{OCl}/k_2^{OCl}$. From the value of the slope in Figure 2b, $k_1^{OCl^-}$ is determined as $0.91 \pm 0.04$ $M^{-1}$ $s^{-1}$. By using the reported potential values,[21] $E°(OCl/OCl^-) = 1.50$ V, $E°(ClO_2/ClO_2^-) = 0.924$ V, the equilibrium constant $K_1^{OCl^-}$ for the electron-transfer step in eq 12 is calculated to be $2.55 \times 10^{-10}$. To have second-order dependence in $[ClO_2]$ (eq 18), concentrations of $ClO_2^-$ ranging from 7.98 to 14.63 mM were used in the $[ClO_2^-]$ dependence study to meet the required condition: $k_1^{OCl^-}[ClO_2^-] \gg k_2^{OCl}[ClO_2]$. However, at these high $[ClO_2^-]$, the kinetic traces deviate slightly from a second-order fit because of the interference of the $OCl^-/ClO_2^-$ reaction.[28] To avoid this problem, the rates were analyzed by an initial rate method with a five-point smoothing derivative program.[29,30] From the values of $K_1^{OCl^-}$, $k_1^{OCl^-}$, and the slope of the plot $[OCl^-]/k_{obsd}^{2nd}$ against $[ClO_2^-]$, the following values were obtained: $k_{-1}^{OCl} = 3.6 \times 10^9$ $M^{-1}$ $s^{-1}$, $k_{-1}^{OCl}/k_2^{OCl} = 0.260$, $k_2^{OCl} = 1.4 \times 10^{10}$ $M^{-1}$ $s^{-1}$. The resolved $k_2^{OCl}$ value exceeds the diffusion controlled rate constant value ($7 \times 10^9$ $M^{-1}$ $s^{-1}$), which is not reasonable. However, because the $k_2^{OCl}$ value is calculated indirectly from $E°(OCl/OCl^-)$ and $E°(ClO_2/ClO_2^-)$, and the $E°(OCl/OCl^-)$ value was estimated on the basis of some assumptions,[21] a small error in this value could cause a deviation of the $k_2^{OCl}$ value. If we set the $k_2^{OCl}$ to $7 \times 10^9$

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**Table 4.** Summary of Rate Constants and Activation Parameters for Hypohalite Ion Catalysis of the Disproportionation of Chlorine Dioxide[a]

| reaction | rate constant | value[b] ($M^{-1}$ $s^{-1}$) | $\Delta H^{\ddagger}$ (kJ $mol^{-1}$) | $\Delta S^{\ddagger}$ (J $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|---|
| $ClO_2 + OBr^- \underset{k_{-1}^{OBr}}{\overset{k_1^{OBr^-}}{\rightleftharpoons}} ClO_2^- + BrO$ | $k_1^{OBr^-}$ | 2.05(3) | 55(1) | −49(2) |
| | $k_{-1}^{OBr}$ | $1.6 \times 10^7$ | | |
| $BrO + ClO_2 \xrightarrow{k_2^{OBr}} BrOClO_2$ | $k_2^{OBr}$ | $1.0 \times 10^8$ | | |
| $ClO_2 + OCl^- \underset{k_{-1}^{OCl}}{\overset{k_1^{OCl^-}}{\rightleftharpoons}} ClO_2^- + OCl$ | $k_1^{OCl^-}$ | 0.91(4) | 61(3) | −43(2) |
| | $k_{-1}^{OCl}$ | $3.6 \times 10^9$ | | |
| $ClO + ClO_2 \xrightarrow{k_2^{OCl}} ClOClO_2$ | $k_2^{OCl}$ | $7 \times 10^9$ | | |

[a] Conditions: $\mu = 1.0$ M, $[CO_3]_T = 0.10$ M. [b] 25.0 °C

$M^{-1}$ $s^{-1}$, then $K_1^{OCl^-}$ and $E°(OCl + ClO_2 \rightarrow ClOClO_2)$ are calculated to be $5.11 \times 10^{-10}$ and −0.549 V, respectively. Correspondingly, $E°(OCl/OCl^-)$ equals 1.48 V assuming that the value of $E°(ClO_2/ClO_2^-)$ is accurate. The difference between this value and the reported value is 0.02 V, which is within the error of the literature value for $E°(OCl/OCl^-)$. On the basis of this argument, we consider the formation of $ClOClO_2$ in eq 13 to be diffusion controlled.

As shown in Figure 3b, the excellent fit of the pH dependence data to eq 19 indicates the lack of an HOCl ($pK_a^{HOCl} = 7.47$ at 25.0 °C , $\mu = 1.0$ M)[31] path. The level of $ClO_2^-$ generated from the disproportionation of $ClO_2$ is too low to inhibit the reaction. In addition, the $HOCl/ClO_2^-$ reaction will convert $ClO_2^-$ to $ClO_3^-$ and $Cl^-$.[32]

$$\frac{k_{obsd}}{[HOCl]_T} = 2k_1^{OCl^-}\frac{K_a^{HOCl}}{K_a^{HOCl} + [H^+]} \qquad (19)$$

The activation parameters for the reaction were determined (Figure 6b) as the following: $\Delta H_1^{\ddagger} = 61 \pm 3$ kJ $mol^{-1}$, $\Delta S_1^{\ddagger} = -43 \pm 2$ J $mol^{-1}$ $K^{-1}$. These values are in good agreement with the results reported by Csordás et al.[8] The rate constants and the activation parameters obtained in the present study are summarized in Table 4.

**Conclusions.** The first step of the hypohalite ion catalysis of the disproportionation of $ClO_2$ is the reaction between $OX^-$ and $ClO_2$ via electron transfer to give OX and $ClO_2^-$. At 25.0 °C, $k_1^{OBr^-}/k_1^{OCl^-} = 2.3$, and $ClO_2^-$ suppresses the rate of both reactions. Subsequent steps between the XO and $ClO_2$ radicals to give $XOClO_2$ are extremely fast ($k_2^{OBr} = 1.0 \times 10^8$ $M^{-1}$ $s^{-1}$ and $k_2^{OCl} = 7 \times 10^9$ $M^{-1}$ $s^{-1}$), and the base hydrolysis of $XOClO_2$ to give $OX^-$ and $ClO_3^-$ is also fast. Catalysis of $ClO_2$ disproportionation by $BrO_2^-$ is also very effective,[9] and the rate constant for the first electron-transfer step between $BrO_2^-$ and $ClO_2$ is 36 $M^{-1}$ $s^{-1}$ (17 times larger than that of $OBr^-$).

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**Supporting Information Available:** Tables and figures with supplemental data and the details for the calculation for the data in Table 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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