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Oxidation of Chlorine(III) by Hypobromous Acid: Kinetics and Mechanism

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The kinetics and mechanism of the chlorine(III)–HOBr reaction were studied by the stopped-flow method under acidic conditions, pH 1.0–3.0, in 1.0 M $NaClO_4$ and at 25.0 °C. The overall redox process occurs in two consecutive steps via the formation of the $BrClO_2$ intermediate. The electron transfer reactions are coupled with bromine hydrolysis, the formation of the tribromide ion, and the protolytic equilibrium of chlorine(III). On the basis of simultaneous evaluation of the kinetic traces, the following rate constants were obtained for the redox steps: $HClO_2 + HOBr \rightleftharpoons BrClO_2 + H_2O$, $k_3 = (3.34 \pm 0.02) \times 10^4\ M^{-1}\ s^{-1}$, $k_{-3} = (3.5 \pm 1.3) \times 10^3\ s^{-1}$; $BrClO_2 + ClO_2^- \rightleftharpoons 2ClO_2 + Br^-$, $k_4 = (2.9 \pm 1.0) \times 10^7\ M^{-1}\ s^{-1}$. The second step was practically irreversible under the conditions applied, and the value of k_{-4} could not be determined. The equilibrium constant for the formation of $BrClO_2$, $K_3 = 9.5\ M^{-1}$, was calculated from the kinetic results, and it was confirmed that this species is a very powerful oxidant. The redox potential was also estimated for the $BrClO_2 + e^- = Br^- + ClO_2$ reaction: $\epsilon_0 \sim 1.70$ V.

Introduction

Noncomplementary redox reactions between halogen and oxyhalogen species often exhibit complex kinetic patterns which can be understood in terms of multistep kinetic models. The corresponding mechanisms are centered on the formation and subsequent reactions of reactive intermediates such as X_2O_2 (X = halogen) and related compounds.[1−20] The prototype of these species, Cl_2O_2, was first postulated in the chlorite ion−chlorine reaction by Taube and Dodgen in 1949.[1] While the significance of such intermediates has been corroborated in numerous studies, direct experimental evidence was not reported for their existence in aqueous phase. The only exception is the work by Valdes-Aguilera and coworkers on the bromine−chlorine(III) reaction, in which spectral changes were assigned to the formation of $BrClO_2$.[8]

Recently, we developed a ten-step kinetic model for the oxidation of chlorine(III) by bromine in aqueous solution and concluded that the overall reaction proceeds via competing paths with Br_2, HOBr, Br_2^-, and Br as oxidants.[16] Hypobromous acid is in fast hydrolytic equilibrium with bromine, and the last two species are formed as intermediates in the reaction. The formation of $BrClO_2$ was also postulated in the model, but in disagreement with the results by Valdes-Aguilera et al., we could not find appropriate experimental conditions for detecting this intermediate.

In order to validate the kinetic model and to explore further details of the mechanism, a series of new experiments were designed to evaluate independently the rate law for some of

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the component reactions. The results of a recent laser flash photolytic study on the reverse step of the $Br_2 + ClO_2^- \rightleftharpoons Br_2^- + ClO_2$ reaction were fully consistent with our earlier conclusions and lent strong support to the model proposed.[21]

Hypobromous acid was shown to contribute to the initial part of the Br_2–Cl(III) reaction in the absence of added bromide ion.[16] The concentration of HOBr sharply decreased, and the corresponding reaction path vanished at longer reaction times when the hydrolysis of bromine was suppressed by Br^- formed in the reaction. In general, the contribution of the HOBr-path to the overall redox process was apparent but not large enough to establish the corresponding rate law, and certain approximations had to be introduced for the evaluation of the experimental data. Our early attempts to eliminate the uncertainties associated with the HOBr-path were unsuccessful because the kinetic traces obtained with different HOBr stock solutions were not reproducible. Apparently, literature procedures were not suitable to prepare HOBr stock solutions of appropriate quality. The solutions contained halogenide ions and in some cases presumably BrO_3^- as impurities, and these species had profound effects on the kinetics under acidic conditions. Eventually, this problem could be circumvented by using a somewhat modified procedure for the preparation of hypobomous acid stock solutions, as will be discussed in this paper.

Now we report a thorough kinetic study on the HOBr–Cl(III) reaction in the pH < 3.0 region. The results presented here complement a related study by Furman and Margerum on the HOBr–ClO_2^- system in the pH 5.0–9.0 range.[14] According to those authors, the oxidation of the base form of Cl(III) is general-acid-catalyzed and first-order in each reactant. However, they did not test the validity of the rate law under acidic conditions where the overall redox process becomes faster by orders of magnitude. Calculations on the basis of these literature data predicted reaction rates considerably slower than experimentally observed at low pH in preliminary studies. In this paper, we confirm that an alternative reaction path needs to be considered for proper interpretation of the experimental data in acidic solution. The combination of our results with those of Furman and Margerum provides a coherent description of the hypobromous acid–chlorine(III) reaction in the 1.0–9.0 pH range. A quantitative description of the redox properties of the $BrClO_2$ intermediate in aqueous solution is also given.

Experimental Section

Chemicals. Sodium chlorite (Fluka, 80% purity) and Br_2 (Ferak) were purified as described earlier.[22,23] All measurements were made at 25 ± 0.1 °C and 1.00 M ionic strength set by sodium perchlorate prepared from perchloric acid (Carlo Erba) and Na_2CO_3 (Reanal). Other reagents were of the highest available quality and were used without further purification. The preparation of halogenide-free acidic HOBr stock solution will be discussed in the next chapter. The HOBr solutions were always freshly prepared and used within a few hours. The pH was set by using acetic acid/acetate buffer ($pK_a = 4.61$) in the hydrolytic experiments. Reagent solutions were prepared with doubly deionized and ultrafiltered water obtained from a Milli-Q RG, Millipore system. The pH ($= -\log[H^+]$) was either measured with a Metrohm 6.0202.000 combined glass elctrode connected to a Radiometer PHM85 Precision pH-meter or calculated from the total concentrations of the reactants by using the appropriate equilibrium constants for the pH-dependent equilibrium steps. The electrode was calibrated for two buffers in accordance with IUPAC recommendations,[24] and the pH readings were converted to $-\log[H^+]$ using a correction coefficient determined by measuring the pH of standardized perchloric acid in 1.0 M $NaClO_4$.[25]

Methods. Hypobromous acid stock solutions were standardized by using two independent analytical methods. First, NaI was added to a portion of the stock solution under acidic conditions, and the product I_2 was titrated with standardized $Na_2S_2O_3$ solution using a Metrohm 721 NET Titrino potentiometric titrating system equipped with a Metrohm 6.0420.100 combined Pt wire electrode. This method overestimates the HOBr concentration when bromate ion is present as impurity. In another set of experiments, aliquots of the stock solution were made alkaline (pH > 10), and their spectra were recorded on a Unicam Helios Alpha spectrophotometer. The concentration was determined at the 332 nm absorbance maximum of OBr^- ($\epsilon = 316.7\ M^{-1}\ cm^{-1}$). The HOBr stock solutions were considered to be of acceptable quality when the two analytical results agreed within the experimental error. The free acid concentration of the stock solution was determined potentiometrically by acid–base titration.

Bromine hydrolysis was studied by spectrophotometry with an HP-8453 diode-array spectrophotometer. The sample is exposed to a high-intensity continuous light source in such an instrument, and photochemical decomposition of the reactant(s) should always be a major concern during the measurements.[26,27] Our test experiments confirmed that this photometer is unfit for kinetic studies on the HOBr–Cl(III) reaction because repeated irradiation of the same sample led to significant photodecay of hypobromous acid and chlorine dioxide during time-resolved spectral scans. Nevertheless, photochemical reactions did not interfere with our equilibrium studies because the exposure of each sample to the photometer light lasted only for the duration of one scan, 0.5 s.

Kinetic runs were made with an Applied Photophysics DX-17 MV sequential stopped flow instrument in the single wavelength detection mode at 370 nm. This wavelength was selected in order to use the same conditions as in our related study on the bromine–chlorine(III) reaction.[16] Each kinetic trace was obtained as an average of 5 replicate runs. The initial rates were obtained at $t = 0$ using the first derivative of an appropriate polynomial function fitted to the experimental traces with the program package SCIENTIST;[28] $v_0 = -d[HOBr]_0/dt = (dA_{370\ nm}/dt)/\epsilon_{ClO_2}/2$, $\epsilon_{ClO_2} = 962\ M^{-1}\ cm^{-1}$ (the molar absorbance of ClO_2 at 370 nm).[16] This expression implies that the contribution of the reactants and intermediate(s) to the measured absorbance change is negligible

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and the spectral effects are exclusively due to the formation of chlorine dioxide at this wavelength. These assumptions are corroborated by the results presented in this paper. Comprehensive evaluation of the data was made with the program package ZITA.[29]

Results and Discussions

Preparation of Halogenide-Free HOBr Solution. Several methods were reported for the preparation of hypobromous acid in the literature. The procedure described by Orlando and Burkholder is similar to the preparation of high purity HOCl.[30] In this case, bromine is oxidized with yellow HgO, and the product Br_2O is flushed into an alkaline solution with a steady stream of nitrogen gas. While Cl_2 can completely be eliminated from the HOCl solution, the final HOBr solution is always contaminated with relatively large quantities of unoxidized Br_2. This renders these stock solutions useless for kinetic studies under acidic conditions.

The oxidation of Br^- to bromate ion by ozone proceeds via HOBr.[31] This offers a possibility to prepare hypobromous acid in adequate quality provided that the oxidation is terminated at suitable conversion. A particular advantage of this procedure would be that the presence of the byproduct dioxygen does not affect the reactions of oxyhalogen species. Our attempts failed to control the ozonation process quantitatively, and the method was abandoned.

Gazda and Margerum oxidized bromide ion quantitatively to hypobromite ion with an equivalent amount of OCl^- at pH ∼ 9.0.[32] Apparently, the product Cl^- did not interfere with their studies in the slightly acidic−neutral pH range. However, the presence of chloride ion clearly affected the kinetic traces at lower pH in our experiments. This phenomenon is presumably the consequence of the formation of BrCl at low concentration levels which, in turn, can initiate alternative reaction paths for the oxidation of Cl(III) or some other unidentified side reactions. The problem was not studied in any further detail, but the method was considered to be inappropriate for our purposes.

In the most promising procedure, Br_2 is fully hydrolyzed into OBr^- and Br^- by dissolving liquid bromine in alkaline solution, and bromide ion is precipitated by adding freshly prepared Ag_2O to the solution in excess.[33] However, kinetic runs were highly irreproducible with samples prepared from different batches of HOBr stock solutions. This problem was attributed to Ag_2O-catalyzed disproportionation of hypobromite ion. Such a catalytic activity of various metal oxides and hydroxides in the disproportionation of hypohalites was reported in the earlier literature.[34,35] The analysis of the solutions prepared with Ag_2O was consistent with the presence of bromate ion in that iodometry always yielded considerably higher OBr^- concentration than spectrophotometry.

In order to prepare HOBr solution of acceptable quality, the previous procedure was modified by eliminating the use of Ag_2O. A known amount of Br_2 was dissolved in NaOH, and the pH was set between 7.5 and 7.8 by adding appropriate amounts of $HClO_4$. The Br^- content was removed with an equivalent amount of $AgClO_4$. Strict control of the pH of the solution is a crucial element of the procedure. The precipitation of the catalytically active Ag_2O is unavoidable at pH > 7.8, and experimental complications arise from the formation of colloidal AgBr at pH < 7.5. In the final step, AgBr was filtered off, and the stock solution was made slightly acidic by adding a known amount of $HClO_4$. The noted reproducibility problems were not observed with these solutions, and the analytical results obtained by iodometry and spectrophotometry agreed within 1%.

Equilibrium Constant for the Hydrolysis of Bromine. Literature values for the equilibrium constant of reaction 1 cover more than an order of magnitude range, $(0.6-11) \times 10^{-9}$ M^2.[36−45]

$$Br_2 + H_2O \rightleftharpoons HOBr + Br^- + H^+ \qquad (1)$$

$$K_1 = \frac{[HOBr][Br^-][H^+]}{[Br_2]}$$

The variation in the experimental conditions does not explain this discrepancy, and a thorough review of the relevant publications did not reveal the source of the unusually large differences. It should be added that the evaluation of the experimental data typically involved approximations which could lead to biased results. Thus, the hydrolysis constant of bromine was redetermined spectrophotometrically for the conditions applied here.

Individual samples were prepared by mixing solutions of HOBr and Br^- in a stoppered spectrophotometric cell such that the headspace was minimized. The hydrolytic equilibrium was shifted between 0 and 100% completion by varying the pH and the concentrations of the reactants systematically. The hydrolysis constant and the molar absorbtivities of Br_2, Br_3^-, and HOBr were calculated by fitting the experimental data at 80 wavelengths in the 255−450 nm wavelength range with the program package PSEQUAD.[46] The molar absorptivities of OBr^- were determined in separate experiments

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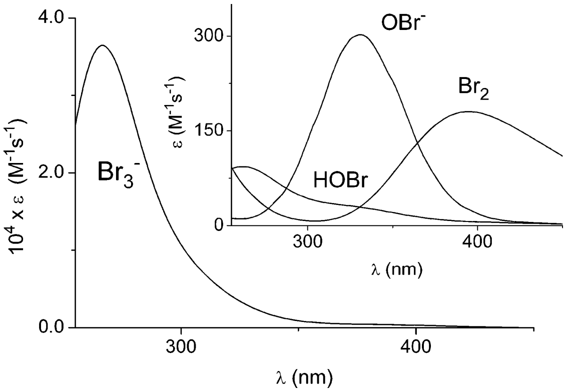

Figure 1. Spectra of absorbing bromine species.

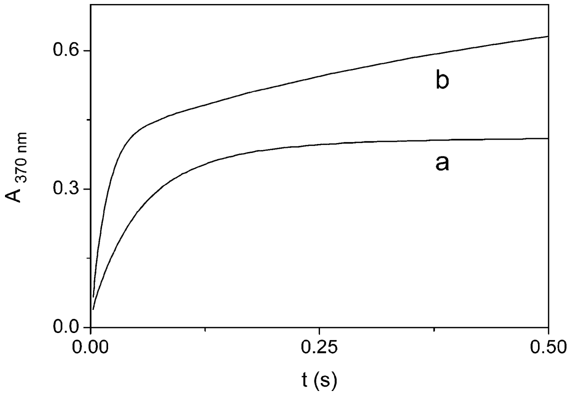

Figure 2. Typical kinetic traces at HOBr excess: $[HOBr]_0 = 1.0 \times 10^{-3}$ M, $[Cl(III)]_0 = 4.0 \times 10^{-4}$ M, pH = 1.50 (a). At Cl(III) excess: $[HOBr]_0 = 4.0 \times 10^{-4}$ M, $[Cl(III)]_0 = 2.0 \times 10^{-3}$ M, pH = 1.50 (b). $T = 25$ °C, $I = 1.0$ M.

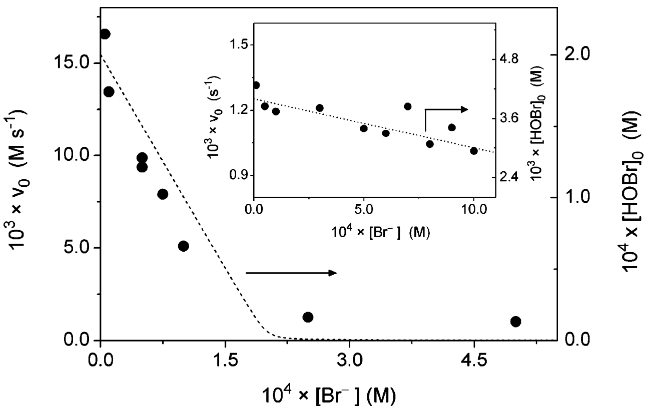

Figure 3. The initial rate (●) and the initial hypobromous acid concentration (- - -) as a function of added bromide ion concentration at Cl(III) excess: $[HOBr]_0 = 2.0 \times 10^{-4}$ M, $[Cl(III)]_0 = 4.0 \times 10^{-3}$ M, pH = 1.50. At HOBr excess (inset): $[HOBr]_0 = 4.0 \times 10^{-3}$ M, $[Cl(III)]_0 = 3.0 \times 10^{-4}$ M, pH = 1.50. $T = 25$ °C, $I = 1.0$ M.

and used as fixed parameters in the calculations. The equilibrium model also included the formation of tribromide ion and the protonation of hypobromite ion using literature values for the corresponding equilibrium constants: $K_{Br_3^-} = 19.3$ M^{-1},[16] and log $K_{OBr^-} = 8.59$,[47] respectively. This data treatment is expected to provide the most accurate estimate for the equilibrium constant of bromine hydrolysis because it does not involve any simplifying assumption. The calculations yielded $K_1 = (7.17 \pm 0.04) \times 10^{-9}$ M^2 in reasonable agreement with some of the literature data. The spectra of the absorbing species are shown in Figure 1.

Kinetic Observations. The kinetic traces exhibited distinct features depending on the concentration ratios of the reactants (Figure 2). In large excess of HOBr, the formation of ClO_2 could be approximated by single exponential traces up to 70−80% conversion in most cases. The final amount of ClO_2 formed was consistent with the following overall stoichiometry:

$$HOBr + 2ClO_2^- + H^+ = Br^- + 2ClO_2 + H_2O \qquad (2)$$

When the concentration ratio of the reactants was reversed, the formation of chlorine dioxide occurred for an extended period of time, and composite kinetic profiles were observed. These observations are qualitatively consistent with the assumption that the oxidation of Cl(III) by HOBr is relatively fast. When chlorine(III) is the limiting reagent, it is predominantly oxidized by HOBr. This reaction swiftly removes Cl(III), and other reactions have a marginal role in the overall process. In excess chlorine(III), the reaction between HOBr and the product Br^- leads to the fast formation of Br_2 which reacts with Cl(III) relatively slowly. Acid-catalyzed decomposition of unoxidized chlorine(III) also generates chlorine dioxide in a side reaction on the same time scale.

Reaction Orders, pH-Dependence. According to the initial rate method, the order of the reaction is one with respect to HOBr and varies between 1 and 2 in chlorine(III). In contrast, first-order kinetics was reported with respect to both reactants in the 5.0−9.0 pH range.[14] These results confirm that the kinetic behavior of the reaction is strongly dependent on the conditions applied and different reaction paths may become operative by varying the pH.

Figure 3 demonstrates the retarding effect of bromide ion on the initial rate. Bromide ion shifts equlibrium 1 to the left even at low concentration levels and efficiently converts HOBr into the less reactive Br_2. Hypobromous acid is fully removed when its concentration is low, while the rate decreases proportionally to the added amount of Br^- at large [HOBr] (cf. inset, Figure 3). There is an excellent correlation between the concentration of HOBr and the initial rate in both cases. This indicates again that the reaction is first-order in HOBr.

Earlier, we proposed the following reaction sequence for the oxidation of chlorine(III) by HOBr:[16]

$$HClO_2 + HOBr \rightleftharpoons BrClO_2 + H_2O \quad k_3, k_{-3} \qquad (3)$$

$$BrClO_2 + ClO_2^- \rightleftharpoons 2ClO_2 + Br^- \quad k_4, k_{-4} \qquad (4)$$

Provided that $BrClO_2$ is in steady state and the reverse step of eq 4 is negligible (or the reaction is irreversible), the following equation can be derived for the initial rate of the reaction:

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$$-\frac{\mathrm{d[HOBr]}}{\mathrm{d}t} = v_0 = \frac{k_3k_4[\mathrm{HOBr}][\mathrm{HClO_2}][\mathrm{ClO_2}^-]}{k_{-3} + k_4[\mathrm{ClO_2}^-]} \quad (5)$$

Equation 5 predicts either a first-order ($k_{-3} \ll k_4[\mathrm{ClO_2}^-]$) or a second-order ($k_{-3} \gg k_4[\mathrm{ClO_2}^-]$) rate law with respect to chlorine(III) in the two limiting cases. The fractional reaction order ($1 < n < 2$) found for Cl(III) clearly indicates that such approximations cannot be applied for the whole concentration range; i.e., the conversion of $BrClO_2$ back into its precursors and its reaction with chlorite ion proceed at comparable rates at low chlorine(III) concentrations. The reaction becomes first-order in chlorine(III) only at relatively high concentrations (Figure 4).

The oxidation rate shows a very characteristic acid concentration dependence (Figure 5). The dissociation of HOBr is negligible under acidic conditions, and the observations need to be interpreted in terms of the protolytic reaction of chlorine(III):

$$\mathrm{ClO_2}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{HClO_2} \quad K_\mathrm{p} \quad (6)$$

According to earlier results, $\log K_\mathrm{p} = 1.72$, and the conjugate acid and base forms of chlorine(III) are always present at comparable concentration levels in the 1.0−2.5 pH range.[22] Thus, the pH dependence of the reaction rate is expected to reflect the variation of the concentration ratio of these two species as a function of pH. Equation 5 can be converted into the following form by including reaction 6 as a diffusion controlled equilibrium step:

$$v_0 = \frac{k_3k_4[\mathrm{C1(III)}]_0^2K_\mathrm{p}[\mathrm{H}^+]}{(k_{-3}(1 + K_\mathrm{p}[\mathrm{H}^+]) + k_4[\mathrm{C1(III)}]_0)(1 + K_\mathrm{p}[\mathrm{H}^+])}[\mathrm{HOBr}] \quad (7)$$

At constant pH, the [Cl(III)] dependence of the initial rate can be expressed as follows:

$$v_0 = \frac{a[\mathrm{HOBr}][\mathrm{C1(III)}]_0^2}{1 + b[\mathrm{C1(III)}]_0} \quad (8)$$

where

$$a = \frac{k_3k_4K_\mathrm{p}[\mathrm{H}^+]}{k_{-3}(1 + K_\mathrm{p}[\mathrm{H}^+])^2} \quad b = \frac{k_4}{k_{-3}(1 + K_\mathrm{p}[\mathrm{H}^+])}$$

Fitting of the initial rates to eq 8 with a nonlinear least squares routine yielded $a = (4.5 \pm 0.4) \times 10^7$ M^{-2} s^{-1} and $b = (1.3 \pm 0.2) \times 10^3$ M^{-1} at pH = 1.50 (Figure 4).

The effect of acid concentration on the reaction rate was studied at constant reactant concentrations by using the following form of eq 7:

$$v_0 = \frac{d[\mathrm{HOBr}][\mathrm{C1(III)}]_0^2K_\mathrm{p}[\mathrm{H}^+]}{(1 + K_\mathrm{p}[\mathrm{H}^+] + e[\mathrm{C1(III)}]_0)(1 + \mathrm{Kp}[\mathrm{H}^+])} \quad (9)$$

where

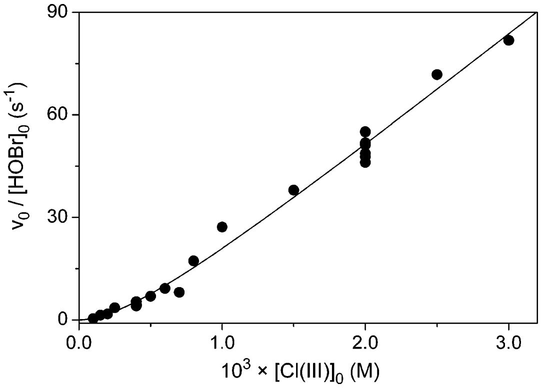

Figure 4. The normalized initial rate as a function of [Cl(III)] at constant pH. Solid line (—): fitted curve on the basis of eq 8. $[\mathrm{HOBr}]_0 = (0.1-2.0) \times 10^{-3}$ M, pH = 1.50. $T = 25$ °C, $I = 1.0$ M.

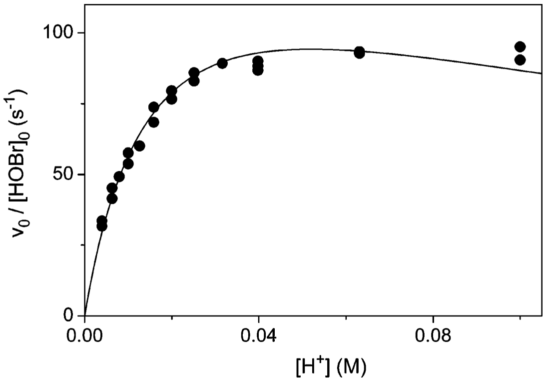

Figure 5. The normalized initial rate as a function of [H$^+$] at constant reactant concentrations. Solid line: fitted curve on the basis of eq 9. $[\mathrm{HOBr}]_0 = 2.0 \times 10^{-4}$ M, $[\mathrm{Cl(III)}]_0 = 4.0 \times 10^{-3}$ M. $T = 25$ °C, $I = 1.0$ M.

$$d = -\frac{k_3k_4}{k_{-3}} \quad e = \frac{k_4}{k_{-3}}$$

The equation predicts that the reaction rate should eventually decrease by increasing [H$^+$], but experimental limitations did not make it possible to work at sufficiently high acid concentrations to demonstrate this effect (Figure 5). By fixing $\log K_\mathrm{p}$ at 1.72,[22] the estimated values for c and d are $(8.2 \pm 0.7) \times 10^7$ M^{-2} s^{-1} and $(1.6 \pm 0.2) \times 10^3$ M^{-1}, respectively. The combination of parameters a, b, and K_p as well as d and e predicts that the value of k_3 is somewhere around $(3.5-5.0) \times 10^4$ M^{-1} s^{-1}.

Comprehensive Data Treatment. In order to overcome the constraints of the initial rate method and to explore further details of the reaction, the kinetic model was validated by using a comprehensive data fitting method. This procedure comprises numerical integration of a differential equation system representing the kinetic model and fitting the calculated kinetic traces to the experimental data by a nonlinear least squares algorithm. The advantages of this approach over classical data treatment in complex reactive systems were demonstrated in some of our earlier studies.[16,48−53] In the present study, 19 kinetic traces (ca. 5000

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Table 1. Kinetic Model for the Oxidation of Chlorine(III) by HOBr ($I = 1.0$ M $NaClO_4$, $T = 25.0$ °C)

reaction	log K	ref	rate constant[a]	ref
$HOBr + HClO_2 \rightleftharpoons BrClO_2 + H_2O$			k_3 $(3.34 \pm 0.02) \times 10^4$	*b*
			k_{-3} $(3.5 \pm 1.3) \times 10^3$	*b*
$BrClO_2 + ClO_2^- \rightleftharpoons 2ClO_2 + Br^-$			k_4 $(2.9 \pm 1.0) \times 10^7$	*b*
			k_{-4} n.a.	*c*
$Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^-$	−8.14	*b*	k_5 110	39, *f*
			k_{-5} 1.5×10^{10}	*d*
$Br_2 + Br^- \rightleftharpoons Br_3^-$	1.28	16	k_6 1.5×10^9	54
			k_{-6} 7.8×10^7	*d*
$ClO_2^- + H^+ \rightleftharpoons HClO_2$	1.72	22	k_7 1.0×10^{10}	*e*
			k_{-7} 1.9×10^8	*d*

[a] The units for the first-, second-, and third-order rate rate constants are s^{-1}, M^{-1} s^{-1}, and $M^{-2}s^{-1}$, respectively. [b] This work. [c] Too small to be determined. [d] $k_- = k_+/K$. [e] Estimated value assuming diffusion control. [f] $I = 0.1$ M, $T = 20.0$ °C.

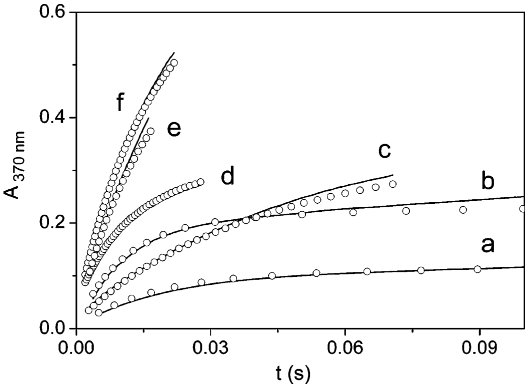

Figure 6. Experimental (○) and fitted (—) kinetic traces at pH = 1.50: $[HOBr]_0 = 1.0 \times 10^{-4}$ M, $[Cl(III)]_0 = 2.0 \times 10^{-3}$ M (a); $[HOBr]_0 = 2.0 \times 10^{-4}$ M, $[Cl(III)]_0 = 3.0 \times 10^{-3}$ M (b); $[HOBr]_0 = 1.0 \times 10^{-3}$ M, $[Cl(III)]_0 = 4.0 \times 10^{-4}$ M (c); $[HOBr]_0 = 4.0 \times 10^{-4}$ M, $[Cl(III)]_0 = 2.0 \times 10^{-4}$ M (d); $[HOBr]_0 = 6.0 \times 10^{-4}$ M, $[Cl(III)]_0 = 2.0 \times 10^{-3}$ M (e); $[HOBr]_0 = 2.0 \times 10^{-3}$ M, $[Cl(III)]_0 = 8.0 \times 10^{-4}$ M (f); $T = 25$ °C, $I = 1.0$ M. For sake of simplicity, only a portion of the experimental data points is shown in each experimental trace.

data points) obtained at various reactant concentrations and recorded at 370 nm were evaluated simultaneously. Some of the traces were truncated in order to avoid the interference by the slow acid-catalyzed decomposition of Cl(III) at longer reaction times. While only about the first half of the kinetic curves were useful when the chlorine(III) concentration was relatively high, considerably larger sections of the traces could be used at HOBr excess.

The kinetic model includes the actual redox steps, the acid−base equilibrium of chlorine(III), as well as the hydrolysis of Br_2 and the formation of the tribromide ion (Table 1). These latter reactions have minor but increasing role as the oxidation proceeds due to the formation of Br^- in increasing amounts. The forward rate constants for these steps are available from the literature, and the reverse rate constants were calculated on the basis of $k_- = k_+/K$ using the appropriate equilibrium constants. Rate constants k_3, k_{-3}, and k_4 were fitted, and all other kinetic parameters were included with fixed values in the calculations. We also made several attempts to fit k_{-4} by assuming that reaction 4 is an equilibrium step. However, these trials failed, indicating that the oxidation of chlorite ion by $BrClO_2$ is completely shifted to the right.

The fitted value for k_3 is in excellent agreement with those obtained from the initial rate method. In addition, estimates for the other two fitted parameters were also calculated. A comparison of experimental and fitted kinetic traces (Figure 6) confirms that the model provides excellent interpretation of the experimental observations. Nevertheless, there is an about 30% error in k_{-3} and k_4 due to the fact that the contributions of the corresponding competing steps are very similar and always comparable. Experimental conditions could not be found to resolve better the strong cross-correlation between these parameters.

The Kinetic Role of the $BrClO_2$ Intermediate. There are some similarities between the kinetic models postulated here and proposed by Furman and Margerum at higher pH.[14] In both cases, the reaction is assumed to proceed via the formation of the $BrClO_2$ intermediate, but the reaction sequences leading to this species are different. In the HOBr−ClO_2^- reaction, the formation of $HOBrOClO^-$ was considered to be the first step which is transformed into $BrClO_2$ in general acid-catalyzed subsequent reactions:[14]

$$HOBr + ClO_2^- \rightleftharpoons HOBrOClO^- \tag{10}$$

$$HOBrOClO^- + HA = BrClO_2 + H_2O + A^- \tag{11}$$

$$BrClO_2 + ClO_2^- = 2ClO_2 + Br^- \tag{12}$$

$$BrClO_2 + H_2O = ClO_3^- + Br^- + 2H^+ \tag{13}$$

Assuming that $HOBrOClO^-$ and $BrClO_2$ are in steady state, $HClO_2$ acts as a general acid, and the reaction with H^+ is negligible in eq 11, the model predicts the same concentration dependencies of the overall rate as shown in eq 7. However, this is only a formal analogy because on the basis of our data the forward rate constant for reaction 10 would be about 2 orders of magnitude larger than reported earlier. It follows that an alternative path, i.e., reactions 3 and 4, needs to be operative in the formation of $BrClO_2$ under acidic conditions.

Despite great many efforts to explore the intimate nature of the X_2O_2 intermediates in solution phase, very limited quantitative information is available for these species in the literature. To our knowledge, this is the first time that thermodynamic and redox properties of a member of the X_2O_2 family are quantified in aqueous solution. The k_3/k_{-3} ratio yields $K_3 = 9.5$ M^{-1} for the equilibrium constant of reaction 3 indicating that the formation of $BrClO_2$ is slightly favored from HOBr and $HClO_2$.

The relatively small equilibrium constant clearly explains why direct detection of $BrClO_2$ failed in previous studies. Under typical experimental conditions, the reactants are used at concentration levels on the order of 10^{-3} M or less. It follows that the conversion of the reactants into $BrClO_2$ would be marginal, i.e., less than 10%, even if other reactions did not occur. Due to subsequent fast reactions, the steady

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state concentration of this species is probably orders of magnitude smaller than calculated on the basis of reaction 3. For example, the concentration of this species is estimated to be less than 10^{-5} M even at the largest reactant concentrations applied in our experiments. Consequently, the spectral change associated with the formation of $BrClO_2$ is expected to be negligible.

The oxidation power of the kinetically significant intermediates is an intriguing question of oxyhalogen chemistry. The $BrClO_2$ intermediate is assumed to be a relatively strong oxidant which is capable of oxidizing chlorine(III) to chlorine dioxide (eq 4). Now that the equilibrium constant is available for reaction 3, the relevant redox potential can be estimated by using log $K_p = 1.72$ for the protonation constant of chlorite ion,[22] and $\epsilon_0 = 1.341$ V[55] and 0.934 V[56] for the HOBr/Br^- and ClO_2/ClO_2^- redox couples, respectively:

$$BrClO_2 + e^- = Br^- + ClO_2 \quad \epsilon_0 \sim 1.70 \text{ V} \qquad (14)$$

The calculations confirm that the redox potential of $BrClO_2$ is comparable to or even higher than that of the strongest inorganic oxidants such as permanganate ion, dichromate ion, bromate ion, chlorine, etc. Consequently, reaction 4 is very favorable and should be regarded as an irreversible step for all practical purposes.

The connectivity of the X_2O_2 intermediates has been discussed extensively in recent years. In their pioneering work, Taube and Dodgen concluded that the two halogen atoms are not equivalent in Cl_2O_2.[1] These results were widely adopted in subsequent studies and also extended to other members of the X_2O_2 family by assuming a Y-shape geometry for these intermediates. However, recently Furman and Margerum have presented arguments that, after all, the X−O−X−O type structure cannot be ruled out,[14] and later studies from that group postulated a series of chainlike intermediates in the reactions between various oxychlorine and oxybromine species.[18,19] Gas phase studies confirmed the existence of both isomers,[57−59] but according to a functional density study, the Y-shaped geometry of $BrClO_2$ is somewhat more stable than the other form.[60] However, the relevance of these results in aqueous solution is dubious because solvation effects can significantly alter the stability order of these species.

In the HOBr−ClO_2^- reaction, the formation of the precursor $HOBrOClO^-$ intermediate (eq 10) implies direct interaction between bromine and one of the oxygen atoms of chlorite ion.[14] In the subsequent general-acid-catalyzed step, the $BrClO_2$ species is formed by retaining the chainlike connectivity. This reaction was explained in terms of a H-bond formed between the proton of the acid and the OH group of the precursor complex. However, it should be noted that an alternative path leading to the formation of the Y-shaped isomer cannot be excluded. In this case, the precursor complex would involve direct halogen−halogen interaction and be stabilized by a H-bond between the OH group of hypobromous acid and a chlorite oxygen. Our pressure dependent kinetic studies were consistent with the formation of such an intermediate in the BrO_3^-−I^- system.[61]

The formation of a chainlike species does not seem to be appropriate in the HOBr−$HClO_2$ reaction for the following reasons. Protonation would clearly weaken the interaction between HOBr and the chlorite oxygen and reduce the stability of the corresponding precursor complex. In addition, the partial negative charge of the OH oxygen would also be smaller making the acid catalyzed step less favorable. As a consequence, chlorous acid should react considerably slower with HOBr than chlorite ion. The experimental results do not support these expectations, and in fact, we observe the opposite trend.

The formation of a halogen−halogen bonded adduct may account for the kinetic effects of protonation better. The higher electron deficiency of chlorine in $HClO_2$ compared to ClO_2^- may strengthen the X−X bond and stabilize the precursor complex. Furthermore, there are two possibilities for the formation of the H-bond via the OH group of either HOBr or $HClO_2$. This makes the formation of the adduct statistically more favorable. These considerations lend support to our earlier assumption that the $BrClO_2$ intermediate is formed via a cyclic hydrogen bonded precursor complex and has a Y geometry.[16] Having said that, we also have to emphasize that direct experimental evidence is not available to distinguish between the alternative isomers of $BrClO_2$ in solution phase. Thus, any conclusion regarding the geometries of this and related intermediates is vague and should be the subject of scrutiny.

In conclusion, the results presented here clarify mechanistic aspects of the HOBr−$HClO_2$ reaction under acidic conditions and provide coherent interpretation of the kinetic data obtained at different reactant concentrations and concentration ratios. Despite the noted ambiguity in its geometry, the importance of the $BrClO_2$ intermediate is well established, and for the first time, its redox properties are quantified.

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