the hydrolysis equilibrium toward the products, whereas addition of chloride ion minimizes hydrolysis. (2) Using stoichiometric amounts of sodium chlorite and chlorine, Emmenegger and Gordon observed that the yield of chlorate ion increases with decreasing concentration of the reactants.[5] Decreasing the initial chlorine concentration increases the ratio $[HOCl]/[Cl_2]$ at equilibrium. (3) In their study of the reaction between chlorine(III) and hypochlorous acid, Emmenegger and Gordon showed that the chlorate ion yield is larger when hypochlorous acid is in excess. When chlorine(III) is the reactant in excess, chlorine dioxide is formed preferentially.

Formation of the $XClO_2$-type intermediate, reaction VI, is a process common to the three halogens. The influence of the halogen on the value of the rate constant cannot be fully ascertained because of the qualitative nature of the data available for the chlorine(III)–Cl_2 reaction, where the rate-determining step has not been identified.[5,9]

In the oxidation of iodine by chlorine(III) the reaction $ClO_2^- + I_2 \rightarrow IClO_2 + I^-$ is one of the rate-determining processes, with a rate constant of 11 $M^{-1}\ s^{-1}$.[6] Our results for the chlorine(III)–bromine reaction imply that the step forming $BrClO_2$, reaction 2 in Table I, is not rate-determining, and we derive a minimum value for its rate constant, $k_3 > 1.7 \times 10^5\ M^{-1}\ s^{-1}$.

Since iodide ion is a better leaving group than bromide ion, we interpret the values of the rate constants for the formation of $BrClO_2$ and $IClO_2$ as evidence that the process determining the rate of formation of the intermediates is attack on the halogen followed by electron transfer, and not the leaving of the halide. Reasoning along this line we would predict that the formation of Cl_2O_2 in the chlorine(III)–chlorine reaction is faster than the formation of $BrClO_2$ and $IClO_2$. However, we must bear in mind that chlorine is a better electron acceptor than bromine and iodine[25] and that chloride ion is a poorer leaving group than bromide and iodide ions. Thus, in this case the exiting of the chloride ion may become the rate-determining process. A definitive answer cannot be advanced until more quantitative rate data for the chlorine(III)–chlorine reaction are available.

We have proposed a mechanism for the chlorine(III)–bromine reaction involving the participation of the intermediate $BrClO_2$ in the rate-determining step. Hydrogen ion decreases the rate of the reaction due to the formation of the less reactive species $BrClO_2H^+$. From the analysis of the effect of $[H^+]$ on the reaction rate we have determined a value for the acidity constant of $BrClO_2H^+$ and for the rate constant of the rate-determining step. This work, together with our study of the chlorine(III)–bromide reaction should make it possible to develop a molecular mechanism for the oscillations observed when the chlorine(III)–bromide reaction is carried out in a flow reactor.

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Kinetics and Mechanism of the Reaction between Chlorine(III) and Bromide Ion[1]

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The stoichiometry and kinetics of the reaction between chlorine(III) and bromide ion were studied spectrophotometrically at 25.0 ± 0.5 °C and ionic strength 1.2 M ($NaClO_4$). The main products are Br_3^- and Cl^- when bromide ion is in excess, ClO_2 and Br_2 when chlorine(III) is in excess. With sufficient acid and excess bromide ion, the stoichiometry of the reaction is $HClO_2 + 6Br^- + 3H^+ \rightarrow 2Br_3^- + Cl^- + 2H_2O$. The rate law for this reaction is $(1/2)d[Br_3^-]/dt = k[H^+][Br^-][Cl(III)]$ where $k = (9.51 \pm 0.14) \times 10^{-2}\ M^{-2}\ s^{-1}$. When the reaction is carried out with $[Cl(III)] > [Br^-]$, the stoichiometry is difficult to define. In the range $[Cl(III)] \approx (1.50\text{–}2.00) \times 10^{-3}$ M, $[Br^-] \approx 5.00 \times 10^{-4}$ M, and [perchloric acid] ≈ 0.20 M, a "clock" reaction occurs, the lag time of which decreases with addition of small amounts ($<10^{-4}$ M) of molecular bromine. The complex rate law for the chlorine(III)–bromide ion reaction with excess Cl(III) can be explained by a 16-step mechanism including oxidation of bromide ion to bromine by chlorine(III), reduction of bromine to bromide ion, and decomposition of chlorous acid. A reduced set of 10 reactions and associated rate and equilibrium constants successfully modeled the clock reaction by computer simulation.

Introduction

Chlorine(III)-based reaction systems form a large class of oscillators,[3] and exhibit a wide range of complex dynamical behavior in closed (batch) and open (flow) reactors.[4-6] Especially interesting because they are amenable to full kinetics analysis and computer simulation are reactions between chlorine(III) and molecular halogen/halide systems.[7]

In the preceding article,[8] we describe the interaction between molecular bromine and chlorine(III). In this article we report our results on the complex stoichiometry and kinetics of the chlorine(III)–bromide ion interaction.[9] First, we review the kinetics of chlorine(III) with chloride and iodide ions.

Chlorine(III) does not oxidize chloride ion; instead, chloride ion catalyzes the decomposition of chlorous acid, yielding chlorine

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dioxide, chlorate, and chloride ion. The reaction is complex; the stoichiometry depends on the initial chloride ion concentration,[10-14] and the reaction is catalyzed by traces of ferric ion.[10,11] Proposed mechanisms involve competing reactions of chlorine(III) with Cl_2O_2, Cl_2, and HOCl.

Chlorine(III) oxidizes iodide ion to iodate ion.[15,16] The reaction shows clock behavior in batch, and bistability and oscillations in a flow reactor.[17] Recently Epstein and Kustin have proposed a mechanism consisting of 15 elementary steps to explain the oscillatory behavior.[7] Formation of the mixed halogen species $IClO_2$ plays a key role in the mechanism of this oscillator.

Experimental Section

Most of the chemicals employed were of the highest grade commercially available and were used as received. The exception was sodium perchlorate; it was dried overnight in a vacuum oven at 50 °C and stored in a desiccator over silica gel.

The purity of the sodium chloride (Kodak) was determined by adding an excess of potassium iodide and titrating the liberated iodine with standardized sodium thiosulfate solution. The chlorite content obtained was 82.3% and the main impurity is chloride ion.[6] At the sodium chlorite concentrations employed, the chloride ion present in the reactant does not affect the stability of chlorine(III) in solution.[10-14] Perchloric acid solutions of known concentrations were prepared by dilution of a stock solution previously titrated with sodium hydroxide solution (Fisher).

Stock solutions of sodium chlorite were prepared in 1.0×10^{-3} M sodium hydroxide to retard decomposition. Solutions prepared this way are stable for about a week;[18] they were used or discarded within 4 days of their preparation.

Chloroacetic acid, sodium sulfate, and sodium bisulfate were used to prepare buffers with pHs in the range 1.00–3.00. For pHs lower than 1.00 perchloric acid solutions were used as the reaction medium. Hydrogen ion concentrations of the buffer solutions were measured potentiometrically with a calibrated Orion 91-04 combination-glass electrode, the voltage being displayed on an Orion Research Digital Ionalyzer Model 801 A.

The reaction was studied spectrophotometrically in a Beckman 25 spectrophotometer. Reaction was initiated by mixing equal volumes of sodium chlorite and sodium bromide solutions in the spectrophotometric cuvette. The reaction mixture was shaken several times, placed in the cell compartment, and the absorbance at 360 or 390 nm monitored as a function of time. The spectrophotometer's digital output was transmitted to a PDP-11 computer for analysis and storage. Temperature was maintained at 25.0 ± 0.5 °C and ionic strength was adjusted to 1.2 M with sodium perchlorate.

Results

Experiments were carried out in the presence of either excess bromide ion or excess chlorine(III). We found that the products of the reaction depended on the experimental conditions: Br_3^- was the product detected when bromide ion was in excess, whereas at low bromide ion concentrations chlorine dioxide was the final product detected spectrophotometrically. Therefore, we present our results in two separate sections.

High Bromide Ion Concentration. Under these conditions tribromide ion is one of the products of the reaction. As an example, Figure 1 shows the spectrum obtained when 7.94×10^{-4} M sodium chlorite was reacted with 0.80 M sodium bromide in 0.583 M perchloric acid. For comparison, the figure also includes the spectrum of 1.26×10^{-3} M bromine in the same bromide ion and acid concentrations.

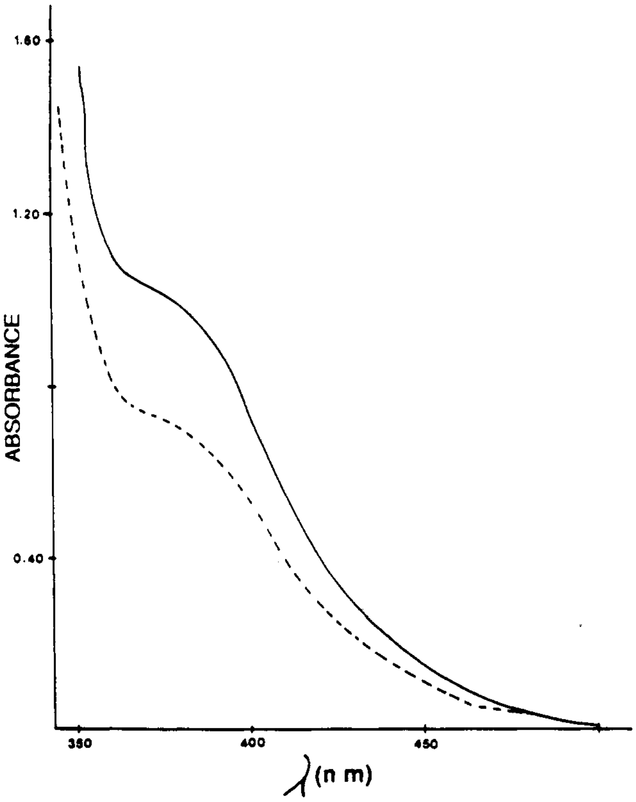

Figure 1. UV–visible spectrum in the chlorine(III)–bromide ion reaction, excess bromide ion. Conditions: solid line, UV–vis spectrum obtained when 7.94×10^{-4} M sodium chloride reacted with 0.813 M sodium bromide, $[HClO_4]$ = 0.583 M; broken line: comparison UV–visible spectrum of 1.26×10^{-3} M bromine in 0.813 M sodium bromide, $[HClO_4]$ = 0.583 M.

Strictly speaking, the spectra shown in Figure 1 correspond to the mixture ($Br_2 + Br_3^-$). At the bromide ion concentrations considered in this section Br_3^- is the dominant species ($K_{Br_3^-} = 17\ M^{-1}$) and we will refer to tribromide ion as the product of the reaction.

The stoichiometry of the reaction was determined in 1.0 M sodium bromide. To determine the amount of product obtained, we measured the "apparent molar absorptivity" of bromine in 1.0 M sodium bromide. A plot of absorbance at 390 nm against bromine concentration under these conditions yields a value for the apparent molar absorptivity equal to 618 ± 28 $M^{-1}\ cm^{-1}$.

In one experiment 3.47×10^{-3} M sodium chlorite was reacted with 1.0 M sodium bromide in 0.117 M perchloric acid and the absorbance at 390 nm was measured. The ratio [product]/$[NaClO_2]$ was 2.1. Eight replicate measurements yield a value of 2.0 ± 0.2. These results, together with that shown in Figure 1, suggest that the stoichiometry of the reaction in excess bromide ion is

$$HClO_2 + 6Br^- + 3H^+ \rightarrow 2Br_3^- + Cl^- + 2H_2O \qquad (I)$$

The kinetics of the reaction in excess bromide ion were studied spectrophotometrically at 390 nm. The kinetics curve can be described by an exponential function, implying that the reaction is first order with respect to chlorine(III). A value of the pseudo-first-order rate constant was obtained by using a least-squares fit to the function $A = B_1 + B_2 \exp(-B_3 t)$, where A is the absorbance at time t, B_1 is the absorbance after no further reaction is observed, and B_3 is the rate constant. The value of the pseudo-first-order rate constant was independent of the initial chlorine(III) concentration in the range 5.54×10^{-5} to 1.09×10^{-3} M, which is further evidence that the reaction is first order with respect to chlorine(III).

For the determination of the order with respect to bromide ion, the pseudo-first-order rate constant was determined at five con-

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TABLE I: Variation of Pseudo-Second-Order Rate Constant with Hydrogen Ion Concentration[a]

$[H^+]$, M	k_{app}, M^{-1} s^{-1}
9.12×10^{-3c}	$(5.61 \pm 0.06) \times 10^{-4}$
2.04×10^{-2b}	$(5.87 \pm 0.12) \times 10^{-3}$
6.45×10^{-2}	$(4.12 \pm 0.12) \times 10^{-3}$
6.46×10^{-2b}	$(6.76 \pm 0.05) \times 10^{-3}$
0.117	$(8.70 \pm 0.26) \times 10^{-3}$
0.233	$(1.92 \pm 0.04) \times 10^{-2}$
0.583	$(5.10 \pm 0.26) \times 10^{-2}$
1.17	0.110 ± 0.003

[a] Reaction carried out in the presence of excess bromide ion. Unless specified otherwise, the rate constants were measured in perchloric acid. [b] In sulfate/bisulfate buffer (buffer concentration = 0.2 M). [c] In chloroacetic acid buffer (buffer concentration = 0.2 M).

centrations of sodium bromide in the range 0.06–1.00 M. A linear plot was obtained, indicating that the reaction is first-order with repect to bromide ion. The slope of the line gives a value for the pseudo-second-order rate constant.

The variation of the pseudo-second-order rate constant with hydrogen ion concentration is shown in Table I. Rate constants measured in sulfate/bisulfate buffer are higher than predicted from those obtained in chloroacetic acid buffer or in perchloric acid. Thus, sulfate/bisulfate buffer seems to catalyze the reaction, and we discontinued its use. The slope of a line generated by the data obtained in chloroacetic acid buffer and in perchloric acid is 1.09 ± 0.01, indicating that the reaction is approximately first order with respect to $[H^+]$.

Combining the results presented in this section we obtain a rate law for reaction I of the form

$$\frac{1}{2}\frac{d[Br_3^-]}{dt} = k[H^+][Br^-][Cl(III)] \qquad \text{(RI)}$$

with $k = (9.51 \pm 0.14) \times 10^{-2}\ M^{-2}\ s^{-1}$ at 25 °C and ionic strength 1.2 M.

Low Bromide Ion Concentration. When the reaction is carried out with $[Cl(III)] > [Br^-]$, chlorine dioxide is obtained. Using a value of 1260 M^{-1} cm^{-1} for the molar absorptivity of chlorine dioxide at 360 nm,[19] we find that the ratio $[ClO_2]/[Cl(III)]$ is 0.64 ± 0.01 (average of four determinations). We interpret these results as evidence that, under these conditions, bromide ions induce the decomposition of chlorine(III).

The ratio $[ClO_2]/[Cl(III)]$ obtained above is intermediate between that observed for the decomposition of chlorous acid[9-14]

$$4HClO_2 \rightarrow 2H^+ + ClO_3^- + Cl^- + 2ClO_2 + H_2O \qquad \text{(II)}$$

and that expected from the combination of the oxidation of bromide ion according to $HClO_2 + 4Br^- + 3H^+ \rightarrow 2Br_2 + Cl^- + 2H_2O$ with the reduction of bromine by chlorine(III), $Br_2 + 2HClO_2 \rightarrow 2ClO_2 + 2Br^- + 2H^+$,[8] which gives

$$5HClO_2 \rightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O \qquad \text{(III)}$$

A plausible explanation of our results is that reactions II and III occur simultaneously. The relative importance of these two reactions may depend on the bromide ion concentration. In addition, it is possible that not all the bromine produced by oxidation of bromide ion reacts with chlorine(III), leading to a reduced $[ClO_2]/[Cl(III)]$ ratio. These complications make it difficult to define the stoichiometry of the reaction and introduce some uncertainty in our kinetics analysis.

Under the experimental conditions indicated above, a clock reaction occurs, the lag time of which decreases upon addition of small amounts of bromine. An example of these results is shown in Figure 2.

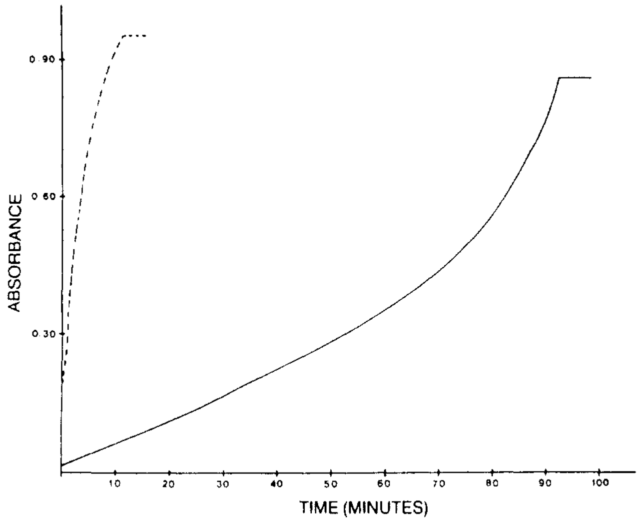

Figure 2. Effect of added bromine on the rate of the Cl(III)–Br^- reaction with $[Cl(III)] > [Br^-]$. Conditions: 5.0×10^{-4} M sodium bromide reacted with 1.65×10^{-3} M sodium chlorite; $[HClO_4] = 0.20$ M; absorbance monitored at 390 nm; solid line = no bromine initially added, broken line = initial $[Br_2]$ $(2.26 \times 10^{-4}$ M).

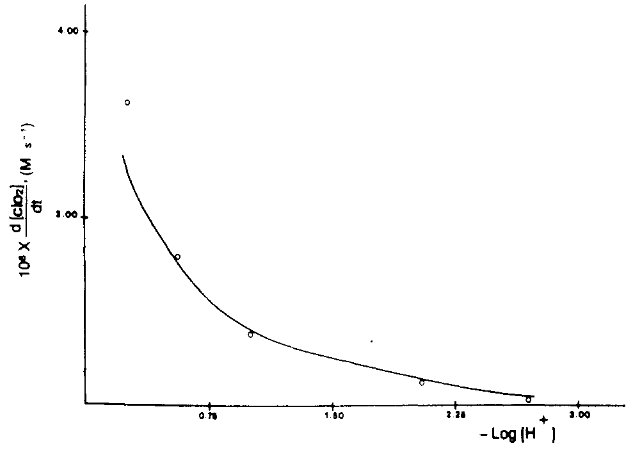

Figure 3. Effect of hydrogen ion concentration on the rate of chlorine dioxide production: $[NaClO_2] = 1.00 \times 10^{-2}$ M; $[NaBr] = 7.00 \times 10^{-4}$ M; circles = experimental points, solid line = calculated from the equation $Y = \{(A[H^+] + B)[H^+]\}/\{C + [H^+]\} + D[H^+]^2/\{(C + [H^+])^2\}$, with $A = 3.64 \times 10^{-6}\ s^{-1}$, $B = 1.40 \times 10^{-7}\ M\ s^{-1}$, $C = 3.5 \times 10^{-3}$ M, $D = 3.40 \times 10^{-7}\ M\ s^{-1}$.

The kinetics of the reaction in the absence of added bromine were studied spectrophotometrically at 360 nm. The ratio $[Cl(III)]/[Br^-]$ was between 4 and 70, and the ratio $[ClO_2]/[Cl(III)]$ was kept below 0.07. Under these conditions the absorbance increases linearly with time, and the slope of the line yields a value for the initial rate of chlorine dioxide production.

For the determination of the order with respect to bromide ion, the rate of ClO_2 production at constant $[Cl(III)]$ and $[H^+]$ was plotted against the initial concentration of sodium bromide. A linear plot with a nonzero intercept was obtained, indicating that two processes are present: one first order in $[Br^-]$, the other zeroth order in $[Br^-]$. The value of the bromide-independent term compares well with the rate of decomposition of chlorous acid reported in the literature.[9,12]

The variation of the rate of chlorine dioxide production with hydrogen ion concentration is presented in Figure 3. The points were fitted to the equation

$$Y = \frac{(A[H^+] + B)[H^+]}{C + [H^+]} + \frac{D[H^+]^2}{(C + [H^+])^2}$$

which is derived from the mechanism given in Table II. The value of C was fixed at the literature value[19] of K_a for $HClO_2$.

Figure 4 shows a plot of the rate of chlorine dioxide production against the initial concentration of chlorine(III). The data can be described by an equation of the form $c[Cl(III)] + d[Cl(III)]^2$, indicating that two processes are present: one first order in $[Cl(III)]$, the other second order in $[Cl(III)]$.

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TABLE II: Mechanism for the Chlorine(III)-Bromide Ion Reaction[a]

1.	$HClO_2 \rightleftarrows ClO_2^- + H^+$	K_a
2.	$Br^- + HClO_2 + H^+ \rightarrow BrClO + H_2O$	k_2, slow
3.	$BrClO + Br^- + H^+ \rightarrow Br_2 + HOCl$	k_3
4.	$Br^- + HOCl \rightarrow HOBr + Cl^-$	k_4
5.	$Br^- + HOBr + H^+ \rightleftarrows Br_2 + H_2O$	K_5
5′.	$2Br_2 + 2Br^- \rightleftarrows 2Br_3^-$	$K_{Br_3^-}$
6.	$HClO_2 + BrClO \rightarrow BrClO_2 + HOCl$	k_6
7.	$Br_2 + HClO_2 \rightleftarrows BrClO_2H^+ + Br^-$	K_7
8.	$BrClO_2H^+ \rightleftarrows BrClO_2 + H^+$	K_8
9.	$BrClO_2 + HClO_2 \rightarrow 2ClO_2 + Br^- + H^+$	k_9
10.	$BrClO_2 + Br^- + H_2O \rightarrow HBrO_2 + HOBr + Cl^-$	k_{10}
11.	$HBrO_2 + Br^- + H^+ \rightleftarrows 2HOBr$	K_{11}
12.	$Br^- + HClO_2 \rightleftarrows BrClO_2H^-$	k_{12}; k_{-12}, slow
13.	$BrClO_2H^- + HClO_2 \rightarrow ClO_3^- + HOCl + H^+ + Br^-$	k_{13}
14.	$2HClO_2 \rightarrow H^+ + ClO_3^- + HOCl$	k_{14} slow
15.	$HClO_2 + HOCl \rightarrow Cl_2O_2 + H_2O$	k_{15}
16.	$Cl_2O_2 + HClO_2 \rightarrow H^+ + Cl^- + 2ClO_2$	k_{16}

[a] Rate law:

$$\frac{d[ClO_2]}{dt} = \frac{(4k_2[H^+] + 2k_{12})[Br^-][Cl(III)]}{K_a + [H^+]} + \frac{2k_{14}[H^+]^2[Cl(III)]^2}{(K_a + [H^+])^2}$$

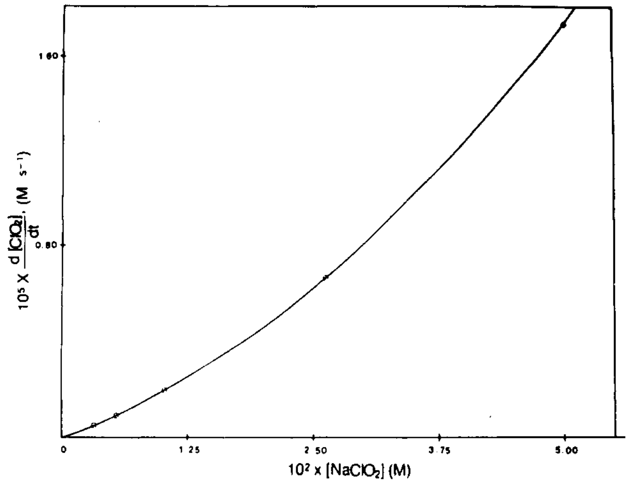

Figure 4. Effect of initial concentration of sodium chlorite on rate of ClO_2 production. [NaBr] = 7.00×10^{-4} M; [$HClO_4$] = 0.350 M. The points can be fitted by the equation Y = c[Cl(III)] + d[Cl(III)]^2, with $c = (1.47 \pm 0.04) \times 10^{-4}$ s^{-1} and $d = (3.95 \pm 0.08) \times 10^{-3}$ M^{-1} s^{-1}; circles = experimental points, solid line = calculated.

Mechanism

When the reaction is carried out in the presence of excess bromide ion, the stoichiometry is well-defined and the rate law is simple. Therefore, we analyze this regime first.

In the range of [H$^+$] considered, most of the Cl(III) is present as $HClO_2$. To explain the observed rate law, eq 1, we propose that the rate-determining step is

$$Br^- + HClO_2 + H^+ \rightarrow BrClO + H_2O \qquad (IV)$$

Formation of the products requires additional reactions, for example:

$$BrClO + Br^- + H^+ \rightarrow Br_2 + HOCl \qquad (V)$$

A complete mechanism for the reaction in the presence of excess bromide ion is given by eq 1–5′ of Table II. Adding reactions 2 through 5′ yields the stoichiometry represented by reaction I and a rate law

$$\frac{1}{2}\frac{d[Br_3^-]}{dt} = \frac{k_2[Br^-][Cl(III)][H^+]^2}{K_a + [H^+]} \qquad (RII)$$

In agreement with our expermental results, the rate law predicts that the reaction is first order with respect to bromide ion and chlorine(III). However, the predicted dependence on [H$^+$] is more complex than observed experimentally. Specifically, rate law (RII) predicts that the order with respect to [H$^+$] changes from second ([H$^+$] $\ll K_a$) to first ([H$^+$] $\gg K_a$), whereas our data can be fitted with a constant order of 1.09. The reason for this discrepancy is that, in the range of [H$^+$] considered (see Table I), more than 77% of chlorine(III) is present as $HClO_2$. The hydrogen ion concentrations employed are too large for the complex dependence to be observed. For five of the six hydrogen ion concentrations considered, [H$^+$] $\gg K_a$ and the rate law simplifies to that given in eq 1 with $k = k_2$. Therefore, $k_2 = k = (9.51 \pm 0.14) \times 10^{-2}$ M^{-2} s^{-1} at 25 °C and ionic strength 1.2 M.

TABLE III: Rate Parameters in the Chlorine(III)-Bromide Ion Reaction

1. with [Cl(III)] and [H$^+$] constant,

$$\frac{d[ClO_2]}{dt} = a + b[Br^-],$$

where

$$a = \frac{2k_{14}[Cl(III)][H^+]^2}{(K_a + [H^+])^2}$$

$$b = \frac{(4k_2[H^+] + 2k_{12})[H^+][Cl(III)]}{K_a + [H^+]}$$

2. with [Br$^-$] and [H$^+$] constant,

$$\frac{d[ClO_2]}{dt} = c[Cl(III)] + d[Cl(III)]^2,$$

where

$$c = \frac{(4k_2[H^+] + 2k_{12})[H^+][Br^-]}{K_a + [H^+]}$$

$$d = \frac{2k_{14}[H^+]^2}{(K_a + [H^+])^2}$$

3. with [Cl(III)] and [Br$^-$] constant,

$$\frac{d[ClO_2]}{dt} = \frac{(A[H^+] + B)[H^+]}{C + [H^+]} + \frac{D[H^+]^2}{(C + [H^+])^2},$$

where

$$A = 4k_2[Br^-][Cl(III)]$$

$$B = 2k_{12}[Br^-][Cl(III)]$$

$$C = K_a$$

$$D = 2k_{14}[Cl(III)]^2$$

Simoyi[5] studied the chlorine(III)–Br$^-$ reaction with bromide ion in excess and obtained the rate law

$$\frac{1}{2}\frac{d[Br_3^-]}{dt} = k[Br^-][H^+][ClO_2^-]$$

with $k = 0.13$ M^{-2} s^{-1} at an ionic strength of 0.5 M. The difference in rate constants can be attributed to the different ionic strengths employed. However, we are at a loss to explain a major discrepancy between Simoyi's and our rate law. Namely, we find that the reaction is first order with respect to chlorine(III) ([$HClO_2$] + [ClO_2^-]), eq RI, whereas Simoyi finds the reaction to be first order with respect to the equilibrium concentration of chlorite ion.

When the reaction is carried out with [Cl(III)] > [Br$^-$], a clock reaction occurs and the final product is chlorine dioxide. The stoichiometry is difficult to define and the rate law is complex (Tables II and III).

The full set of reactions in Table II constitutes a mechanism consistent with our kinetics results and with those of previous studies. Reactions 1–5′ account for the results obtained with excess bromide ion. Reactions 7–9 were introduced in the preceding article[8] to account for the kinetics of the reaction between chlo-

TABLE IV: Rate and Equilibrium Constants Derived from the Mechanism Shown in Table II and Results Obtained with [Cl(III)] > [Br⁻]

parameter	value	lit. value
k_2	0.13 ± 0.01 M^{-2} s^{-1}	
k_{12}	$(1.3 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1}	
K_a	$(3.5 \pm 0.7) \times 10^{-3}$ M	2.70×10^{-3} M[a]
k_{14}	$(2.0 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1}	2.75×10^{-3} M^{-1} s^{-1}[b]

[a] Reference 19. [b] Reference 12.

TABLE V: Reactions Used in the Computer Simulation of the Clock Reaction[a]

2.	$HClO_2 + Br^- + H^+ \rightarrow BrClO + H_2O$
3.	$Br^- + BrClO + H^+ \rightarrow Br_2 + HOCl$
5.	$HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O$
6.	$HClO_2 + BrClO \rightarrow BrClO_2 + HOCl$
a.	$Br_2 + HClO_2 \rightleftarrows BrClO_2 + Br^- + H^+$
9.	$HClO_2 + BrClO_2 \rightarrow 2ClO_2 + Br^- + H^+$
10.	$BrClO_2 + Br^- + H_2O \rightarrow HBrO_2 + HOBr + Cl^-$
11.	$HBrO_2 + Br^- + H^+ \rightleftarrows 2HOBr$
14.	$2HClO_2 \rightarrow H^+ + ClO_3^- + HOCl$
b.	$2HClO_2 + HOCl \rightarrow 2ClO_2 + H^+ + Cl^- + H_2O$

[a] Reaction numbers as in Table II. For reactions a and b, in terms of reaction numbers shown in Table II: (a) = (7) + (8); (b) = (15) + (16).

rine(III) and bromine. Participation of reactions 12 and 13 is inferred from the hydrogen ion dependence. Reactions 14–16 have been proposed to explain the decomposition of chlorous acid.[9–14] The clock reaction observed under the conditions of Figure 2 is accounted for by the sequence (7) + (8) + (10) + (11) + 3 × (5), having the stoichiometry

$$Br_2 + HClO_2 + 4Br^- + 3H^+ \rightarrow 3Br_2 + Cl^- + 2H_2O \qquad (VI)$$

The rate law shown in Table II can be used to identify the parameters with rate and equilibrium constants for different steps in the mechanism (Table III). We thus obtain the parameters collected in Table IV. Agreement with previously determined values is not perfect. We obtain values for k_{14} and K_a 27% lower and approximately 30% higher, respectively, than the literature values.[12,19] Similarly, the value of k_2 we derive from the analysis of our results obtained with [Cl(III)] > [Br⁻] is 37% higher than that measured in the presence of excess bromide, $(9.51 \pm 0.14) \times 10^{-2}$ M^{-2} s^{-1}. However, taking into account the complexity of the system and the fact that, as mentioned earlier, the stoichiometry of the reaction carried out with [Cl(III)] > [Br⁻] is ambiguous, we consider the agreement to be satisfactory.

Computer Simulations

The clock reaction observed in batch (Figure 2) can be simulated by the mechanism shown in Table II. To make the problem tractable, we have used a simplified version of the mechanism. At $[H^+] = 0.2$ M essentially all the chlorine(III) is present as $HClO_2$; therefore, reaction 1 has not been included in the calculations. For simplicity, we have neglected reactions 4, 5′, 12, and 13. We have combined reactions 7 and 8, thus eliminating the intermediate $BrClO_2H^+$. To eliminate the species Cl_2O_2, we have combined reactions 15 and 16. The resulting set of reactions is shown in Table V.

The model used in the calculations consisted of the rate equations derived from the reactions of Table V and the rate constants shown in Table VI. Initial concentrations of $HClO_2$, Br^-, and Br_2 were determined by our experimental conditions. Since $[H^+]$ is large compared with $[HClO_2]$ and $[Br^-]$, it was maintained constant during the calculations. Water is the solvent and, therefore, its activity is set to unity in the computation. The concentrations of all other species were set initially to zero. The resulting set of differential equations was integrated numerically by using Hindmarsh's version[20] of the Gear method.[21]

TABLE VI: Rate Constants for Reactions Shown in Table V

rate const	value
k_2	9.5×10^{-2} M^{-2} s^{-1}
k_3	8×10^{9} M^{-2} s^{-1}
k_5	8×10^{9} M^{-2} s^{-1}
k_{-5}	110 s^{-1}
k_6	5×10^{9} M^{-1} s^{-1}
k_a	1×10^{6} M^{-1} s^{-1}
k_{-a}	1×10^{8} M^{-2} s^{-1}
k_9	1.81×10^{2} M^{-1} s^{-1}
k_{10}	1.77×10^{2} M^{-1} s^{-1}
k_{11}	2×10^{9} M^{-2} s^{-1}
k_{-11}	5×10^{-5} M^{-1} s^{-1}
k_{14}	2.8×10^{-3} M^{-1} s^{-1}
k_b	1×10^{9} M^{-2} s^{-1}

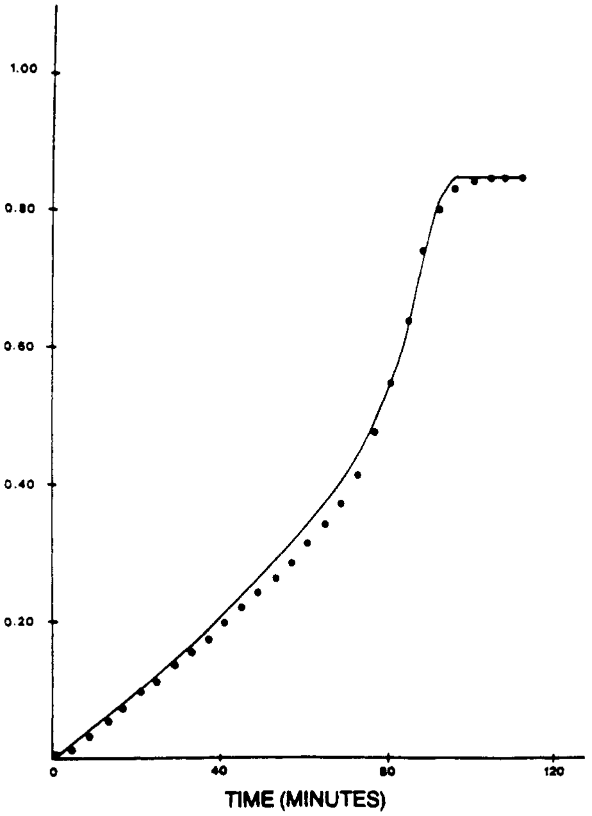

Figure 5. Comparison between experimental results and computer simulation of chlorine(III)–bromide ion reaction with [Cl(III)] > [Br⁻]. Mechanism is shown in Table I. (A) Initial concentrations: $[NaBr] = 5.00 \times 10^{-4}$ M, $[NaClO_2] = 1.65 \times 10^{-3}$ M, $[Br_2] = 0.0$ M, and $[HClO_4] = 0.200$ M. (B) Solid line = experimental, circles = calculated by using rate constants in Table VI.

Reactions 3, 6, and b of Table V are expected to be fast, and the rate constants we have used correspond to those for diffusion-controlled reactions. Decreasing the values of the rate constants for these reactions by a factor of 10 has no effect on the calculated results. The value of k_2 is that determined experimentally in our study of the chlorine(III)–Br⁻ reaction, carried out in the presence of excess bromide ion. The rate constants for the hydrolysis of bromine, k_5 and k_{-5}, have been determined experimentally by temperature-jump.[22] Rate constant k_9 has been obtained from our results for the chlorine(III)–Br_2 reaction.[8] The values of k_{11} and k_{-11} are those deduced by Field, Körös, and Noyes in their study of the Belousov–Zhabotinskii reaction,[23] and k_{14} was taken from ref 12.

The values of k_a, k_{-a}, and k_{10} were adjusted so as to give a good fit to the experimental curves obtained in the absence of added

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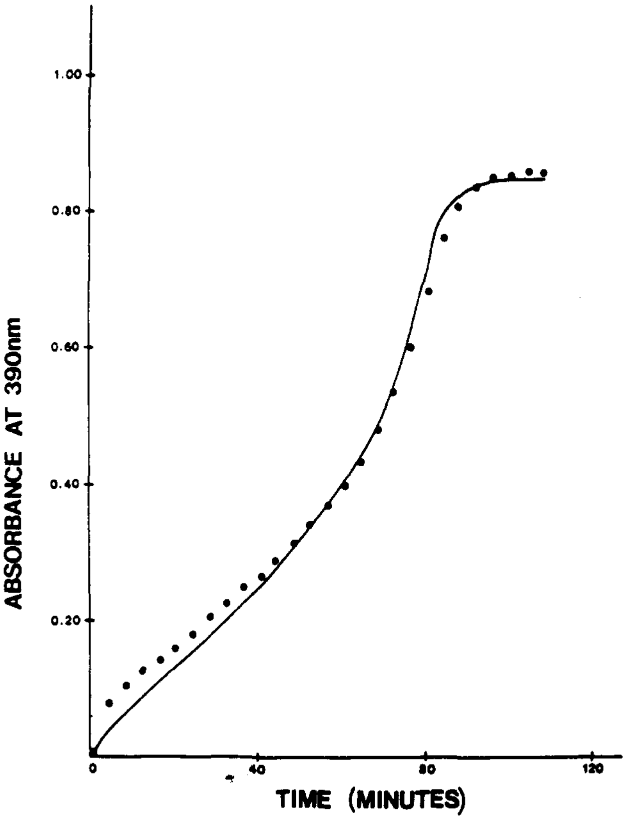

Figure 6. As in Figure 5, initial concentrations: [NaBr] = 5.00×10^{-4} M, [$NaClO_2$] = 1.65×10^{-3} M, [Br_2] = 2.26×10^{-5} M, [$HClO_4$] = 0.200 M; solid line = experimental, circles = calculated with $k_{10} = 1.54 \times 10^2$ M^{-2} s^{-1}; other rate constants as in Table VI.

bromine. An example of these results is shown in Figure 5. Changing the values of k_a and k_{-a} by an order of magnitude did not affect the results so long as the ratio k_a/k_{-a} was unchanged. Lowering the ratio k_a/k_{-a} decreases the calculated absorbances; to obtain better agreement with the experimental curve, k_{10} must then be increased. Conversely, if we increase k_a/k_{-a}, k_{10} must then be decreased. However, our freedom to change k_a/k_{-a} is somewhat restricted in view of our study of the oxidation of chlorine(III) by bromine.[8] Those results require that $k_a/k_{-a} > 4 \times 10^{-3}$ M.

Figure 6 shows the results obtained with an initial bromine concentration of 2.26×10^{-5} M. Good agreement with experiment is found with $k_{10} = 1.54 \times 10^{-2}$ M^{-2} s^{-1}, a value 13% lower than that shown in Table VI.

Less satisfactory agreement is obtained when the initial concentration of bromine is 2.26×10^{-4} M, Figure 7. Two problems can be seen: first, the experimental absorbance at time zero is 3.5 times the calculated value; second, most of the calculated absorbances are larger than the experimental values. Decreasing k_{10} even more improves the fit in the central portion of the figure, but underestimates the final absorbance by a larger amount than that shown in Figure 7.

A possible explanation of this discrepancy is that, because reactions a, 9, 10, and 11 are fast, when we start monitoring the reaction in the Beckman spectrophotometer, $t = 0$ in Figure 7, the concentrations of bromine, bromide, and chlorine(III) are different from those shown in the figure. In particular, we have shown that the chlorine(III)–Br_2 reaction is finished in 1 s or less. The occurrence of this process, reactions a and 10 in Table V, will significantly increase the bromide concentration and decrease that of chlorine(III). Similarly, we have set the initial concentrations of all the other species equal to zero. Because of the fast reactions, this is clearly not true at $t = 0$ in Figure 7.

Discussion

It is interesting to compare reactions 2 and 12 since both involve attack by bromide ion on chlorine(III), but the products are different and a proton is required in reaction 2. To make the comparison, we consider reaction 2 as the combination of processes VII and VIII.

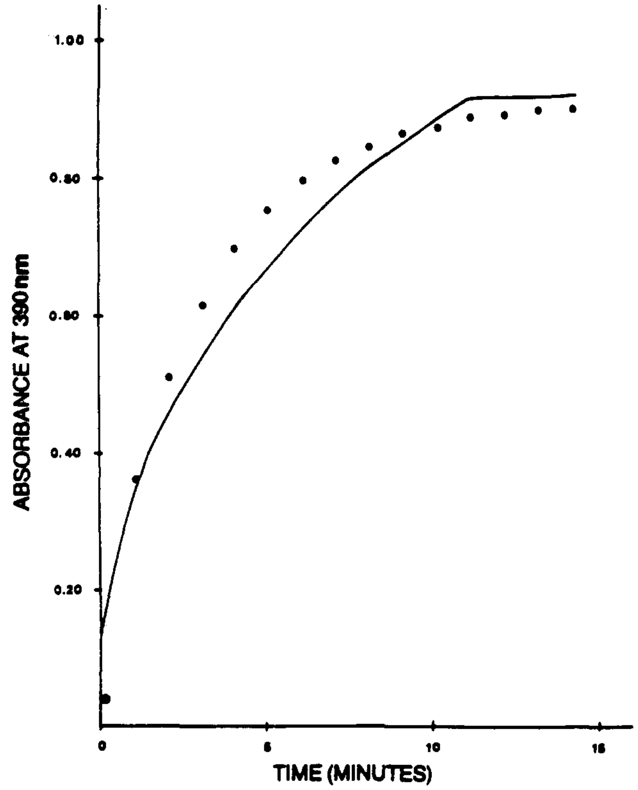

Figure 7. As in Figure 5, initial concentrations: [NaBr] = 5.00×10^{-4} M, [$NaClO_2$] = 1.65×10^{-3} M, [Br_2] = 2.26×10^{-4} M, [$HClO_4$] = 0.200 M; solid line = experimental, circles = calculated with $k_{10} = 1.43 \times 10^2$ M^{-2} s^{-1}; other rate constants as in Table VI.

$$HClO_2 + H^+ \rightleftarrows H_2ClO_2^+ \qquad K, \text{ fast} \qquad \text{(VII)}$$

$$Br^- + H_2ClO_2^+ \rightarrow BrClO + H_2O \qquad k, \text{ slow} \qquad \text{(VIII)}$$

From the hydrogen ion dependence of the rate constant for the chlorine(III)–Br^- reaction carried out with excess bromide ion, we deduce that $K < 1$ since no curvature is observed up to [H^+] = 1.17 M; thus, we obtain $k/k_{12} > 7$. This result is expected, since the increased positive charge on the chlorine in $H_2ClO_2^+$ facilitates attack by bromide ion. We should point out that our experimental results do not provide evidence for the existence of $H_2ClO_2^+$ and, therefore, reactions VII and VIII should be considered primarily as a convenience useful in the visualization of reaction 2.

Comparisons among the reactions of chlorine(III) with chlorine ion,[9-14] bromide ion (this work), and iodide ion[15,16] reveal similarities and differences. Chloride ion induces decomposition of chlorine(III) to bromine; when [Cl(III)] > [Br^-], bromide ion induces decomposition of chlorine(III). Iodide ion is oxidized to iodate ion in the presence of excess chlorine(III). No study has been reported for the Cl(III)–I^- reaction with iodide ion in excess; however, the available evidence[15,16] suggests that iodine would be the final product under these conditions.

The initial interaction of chlorine(III) with the halides results in the oxidation of the halides to the halogens. The reactivity increases in the order $Cl^- < Br^- < I^-$, a pattern that can be explained in terms of the redox properties of the halides.[24] The different net effects of the halides are due to the differences in the reactions between chlorine(III) and the halogens.[8]

Significant differences exist between the mechanism proposed here for the oxidation of bromide ion by chlorine(III) (Table II) and those reported in the literature for reaction between Cl(III)

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and chloride ion,[9-14] or iodide ion.[15,16] We analyze these differences in the following paragraphs.

The chlorine(III)–I^- reaction has been studied in the pH range between 4 and 8,[15,16] where the rate-determining step is (IX). By

$$ClO_2^- + H^+ + I^- \rightarrow HOCl + OI^- \qquad (IX)$$

$$k_{IX} = 4.6 \times 10^2\ M^{-2}\ s^{-1}$$

contrast, the Cl(III)–Cl^- and Cl(III)–Br^- reactions are too slow to be detected at pH 4–8, and they have been studied at acidities where $HClO_2$ is the predominant species. In the case of the chlorine(III)–Cl^- reaction,[9-14] the rate-determining step, reaction X, is similar to reaction IX.

$$HClO_2 + H^+ + Cl^- \rightarrow 2HOCl \qquad (X)$$

$$k_X = 4.83 \times 10^{-3}\ M^{-2}\ s^{-1}$$

For the oxidation of bromide ion by chlorine(III) we have proposed formation of the intermediate BrClO, reaction IV, in the rate-determining step (Table II).

$$HClO_2 + H^+ + Br^- \rightarrow BrClO + H_2O \qquad (IV)$$

$$k_{IV} = 9.51 \times 10^{-2}\ M^{-2}\ s^{-1}$$

Reactions IX and X involve oxygen transfer from Cl(III) to the halide. Since the oxygen in chlorine(III) has a partial negative charge, this process is difficult to visualize as an elementary step. We feel that reaction IV is conceptually simpler since it involves nucleophilic attack by the halide on a chlorine atom having a partial positive charge.[14] Thus, if we consider that the initial interaction between chlorine(III) and the halides is attack on the chlorine atom, we can interpret the reactivity pattern $I^- > Br^- > Cl^-$ in terms of the nucleophilicities of the halides in aqueous solution.

Autocatalysis is a common feature of all known chemical oscillators. The chlorine(III)–Br^- reaction is no exception; oscillations have been observed when the reaction is carried out in a flow reactor,[6] and our study of the system in batch has shown that autocatalysis is present and can be accounted for by our mechanism. A more stringent test of the mechanism we have developed will be possible when more detailed studies of the oscillatory behavior become available.

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Registry No. $HClO_2$, 13898-47-0; Br^-, 24959-67-9.

NaCl Effect on the Excited-State Proton Dissociation Reaction of Naphthols: Water Structure in the Presence of NaCl

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The NaCl effect on the proton dissociation reaction in water at 300 K has been studied by means of nanosecond and picosecond spectroscopy with fluorimetry. The proton dissociation rate constant k_1 decreased with an increase of NaCl according to the equation $k_1 = k_0[(H_2O)_4](1 - \alpha[NaCl])$, where k_0 denotes the second-order rate constant for the proton transfer from excited naphthols to water clusters $(H_2O)_4$ and α is a constant value. This means that the decrease in the k_1 value is caused by NaCl-induced destruction of water clusters resulting in production of the hydrated ions $(Na^+)_{hyd}$ and $(Cl^-)_{hyd}$. The average hydration number of Na^+ or Cl^- in water is obtained to be 4.4 or 6.6, respectively. The kinetic H–D isotope effect for k_1 in the presence of NaCl was also examined.

Proton-transfer reactions in the excited state of aromatic compounds are elementary processes in both chemistry and biochemistry.[1-10] There has been considerable interest in the photochemical and photophysical properties of aromatic compounds involving proton-transfer reactions:[11] proton-transfer reactions in the excited state and proton-induced quenching,[12,13] a one-way proton-transfer reaction of aromatic ammonium ion–18-crown-6 complexes,[14-16] examples for non-excited-state prototropic equilibrium,[17,18] hydrogen atom transfer reaction from triplet aromatic

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