Analogous correction for enthalpies of solution give $\Delta H_c^{\circ}_{298}$ = -40.1 kcal for $\text{Re}_2(\text{CO})_{10}(c)$ reacting with $I_2(c)$ to give Re(C)O)₅I (c) and $\Delta H_c^{\circ}_{298} = -56.8$ kcal for the analogous reaction of MnRe(CO)₁₀(c). In this last case, we take the heat of solution of $MnRe(CO)_{10}(c)$ to be the average of the values for Mn_2 - $(CO)_{10}(c)$ and $Re_2(CO)_{10}(c)$.

Gas-Phase Bond Energies. Gas-phase bond energy quantities are "simpler" than D_s ones in that solvation effects are eliminated and are thus of interest theoretically. Our data may be referred to the gas phase through the Hess' law tableau of Scheme I. Thus

$$\Delta H_1 + \Delta H_2^{\circ} + D_{Mn-Mn} + \Delta H_4 + \Delta H_5^{\circ} + \Delta H_6^{\circ} - 2D_{Mn-I} = \Delta H_5 + \Delta H_7 + \Delta H_8^{\circ} (18)$$

Superscript degrees are omitted if the enthalpy quantity involves species in solution since our values are not corrected to the solution standard state; the correction should be quite small, however. On substitution of the various numerical values, we have

$$D_{\rm Mn-Mn} - 2D_{\rm Mn-I} = \Delta H_{\rm s} - 35.4 = -80.3 \text{ kcal}$$
 (19)

Equation 19 differs little from the analogous equation containing $D_{\rm s}$, eq 11, due to the fortuitous manner in which the numbers combine. Thus, as noted above, the numerical distinction between D and D_s bond energies is not important in the present case. The difference of 9.6 kcal between our ΔH_c° value and that of Connor et al³ carries through the cycle, of course. If, for example, we take D_{Mn-Mn} to be 22.4 kcal, then our inferred value of D_{Mn-I} is 9.6/2 or 4.8 kcal more negative than their value, that is 51.4 vs. 46.6 kcal.

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Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Re_2(CO)_{10}$, 14285-68-8; $MnRe(CO)_{10}$, 14693-30-2; I_2 , 7553-56-2; Mn, 7439-96-5; Re, 7440-15-5; cyclohexane, 110-82-7.

Kinetics and Mechanism of the Reaction between Chlorine(III) and Molecular Bromine¹

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Reaction between chlorine(III) and bromine results in the oxidation of chlorine(III) to chlorine dioxide according to $2ClO_2^{-1}$ (or $2HClO_2$) + $Br_2 \rightarrow 2ClO_2 + 2Br^-$ (+ $2H^+$) (reaction A). The kinetics of reaction A were studied by stopped-flow spectrophotometry in the pH range 0.58-4.23, leading to a proposed mechanism in which the rate-determining step is BrClO₂ + ClO_2^- (or $HClO_2$) $\rightarrow 2ClO_2 + Br^-$ (+ H⁺) (reaction B). The rate data obtained at 25 °C and ionic strength 0.66 M yield the rate constant of reaction B, $k_{\rm B} = (2.94 \pm 0.25) \times 10^3 \,{\rm M}^{-1} \,{\rm s}^{-1}$, and the acidity constant of the intermediate BrClO₂H⁺, $K_{\rm a} = (1.23 \pm 0.02) \times 10^{-2} \,{\rm M}$. At pH 7.41 bromine is present as BrOH and Cl(III) as ClO₂⁻. Consequently the rate constant for the reaction between BrOH and ClO_2^- , 20.6 M⁻¹ s⁻¹, indicates that BrOH is less reactive than Br₂ toward Cl(III). Formation of the intermediate is a complex process involving attack by chlorine(III) on molecular bromine followed by electron transfer and leaving of bromide ion.

Introduction

Chlorite-based oscillators are important and numerous,³ but information concerning the kinetics of the elementary steps is scarce. To describe the oscillators, multistep mechanisms are constructed and tested by modeling the system's observed behavior with them. However, the validity of a mechanism may not be ascertained properly if insufficient rate data exist for the elementary steps in the mechanism.

Considerable information on the reactions of chlorine and iodine species with chlorine(III) is available, but very little is known about the dynamics of reactions between bromine species and chlorine(III). These reactions are important in describing the oscillations observed when sodium chlorite and bromide ion are mixed in a flow reactor.⁴ Therefore, we have undertaken a study of the stoichiometry and kinetics of the reaction between chlorine(III) and bromine.

A common feature in the reactions of molecular chlorine⁵ or iodine⁶ is participation of $XClO_2$ (X = Cl or I) species as transient intermediates. For example, chlorine oxidizes chlorite to chlorine dioxide and chlorate ion, the stoichiometry of the reaction depending on the conditions.⁵ This fact prevented Emmenegger and Gordon from undertaking a quantitative study of the reaction. Based on their qualitative observations they suggested a mechanism, similar to that proposed by Taube and Dodgen,⁹ in which the intermediate Cl_2O_2 is formed by reaction of chlorine(III) and Cl₂ or HOCl.

Grant and co-workers studied the reaction between chlorite ion and molecular iodine.⁶ Chlorite ion oxidizes iodine in a reaction having a well-defined stoichiometry to yield iodate and chloride ions as the exclusive products. The kinetics results were interpreted in terms of a mechanism in which $IClO_2$ is formed by reactions of chlorite ion with $I_2,\ I_2OH^{\text{-}},\ \text{and}\ IO{H_2}^{\text{+}},\ \text{reaction}$ between chlorite ion and HOI being unimportant.

⁽¹²⁾ In this paper the periodic group notation (in parentheses) is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

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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 $^{\circ}$ C and stored in a desiccator over silica gel.

The purity of the sodium chlorite (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%. The major impurity is chloride ion; the most significant metal ion contaminants, present at parts per million levels, are Fe(II), Ag(I), Cu(II), and Hg(II).

Studies by Simoyi⁷ on the chlorite-bromide reaction and by Nagypal et al.⁸ on the chlorite-thiosulfate reaction in which the chlorite was recrystallized from water suggest that under the conditions employed here, the presence of chloride ion should have no effect on the reaction studied nor on the stability of Cl(III) in solution.

A stock solution of bromine in 1.0×10^{-3} M perchloric acid was prepared and kept in the dark. Its concentration was determined at least once a day either by measuring the absorbance at 390 nm in a Beckman 25 spectrophotometer, or by adding an excess of potassium iodide and titrating the liberated iodine with standardized sodium thiosulfate solution. The molar absorptivity of bromine at 390 nm was obtained from a plot of absorbance against bromine concentration in the concentration range from 6.0×10^{-4} to 7.0×10^{-3} M. The slope yields a molar absorptivity of (168 ± 6) M⁻¹ cm⁻¹ in good agreement with the value reported in the literature.⁹

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;¹⁰ they were used or discarded within 4 days of their preparation.

Acetic acid, chloroacetic acid, sodium sulfate, and sodium bisulfate were used to prepare buffers with pH in the range 1.00-5.00. For pH's lower than 1.00, perchloric acid solutions were used as the reaction medium. A buffer solution of pH 7.41 was prepared by dissolving Fisher certified buffer salt in water. Hydrogen ion concentrations were measured potentiometrically (except at pH 7.41) with a calibrated Orion 91-04 combination-glass electrode, the voltage being displayed on an Orion Research Digital Ionalyzer Model 801 A.

Bromide ion was monitored with an Orion Research bromide-sensitive electrode using a mercurous sulfate reference electrode (Radiometer A/S K601). The bromide-sensitive electrode was calibrated with sodium bromide for concentrations between 2×10^{-5} and 1.1×10^{-2} M. The concentration of chlorine dioxide was determined spectrophotometrically at 360 nm by using a value of 1260 M⁻¹ cm⁻¹ for the molar absorptivity at this wavelength.¹¹

The kinetics of the reaction between chlorine(III) and bromine were studied by using stopped-flow spectrophotometry¹² with a path length of 0.91 cm and a dead time of 3 ms.¹³ The photomultiplier output was digitized (Biomation 610B) and transmitted to a PDP-11 computer for analysis and storage.

Results

Stoichiometry. As a first step in the determination of the stoichiometry, the bromide ion concentration was measured with the bromide-sensitive electrode. Figure 1 shows the response of the electrode as a function of time when 0.052 mmol of bromine were reacted with 1.46 mmol of sodium chlorite. In this experiment, the ratio (moles of bromide ion produced)/(moles of bromine reacted) equals 1.97. Three determinations of this ratio yielded the value 1.96 ± 0.08 . The temperature in these experiments was between 24 and 26 °C and [H⁺] was 1.58×10^{-3} M. From these results we conclude that at this [H⁺], bromine is

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Figure 1. Response of bromide electrode when 5.2×10^{-2} mmol of bromine was reacted with 1.46 mmol of sodium chlorite at $[H^+] = 1.58 \times 10^{-3}$ M. The final volume was 110 mL and the temperature 24 °C. The voltage reading when no further reaction is observed corresponds to $[Br^-] = 1.03 \times 10^{-3}$ M.



Figure 2. Response of bromide electrode when 9.23×10^{-2} mmol of bromine was reacted with 2.0 mmol of sodium chlorite in 1 M sulfuric acid. The final volume was between 100 and 110 mL and the temperature 24 °C. The voltage reading at the maximum of the trace corresponds to [Br⁻] < 6.4×10^{-4} M.

reduced to bromide ion by chlorine(III).

When bromine was reacted with an excess of sodium chlorite, the UV-vis spectrum of chlorine dioxide was obtained. The ratio (moles of chlorine dioxide produced)/(moles of bromine reacted) was determined by measuring the absorbance at 360 nm. In one experiment, 4.1×10^{-4} mmol of bromine was reacted with 2.03 $\times 10^{-2}$ mmol of sodium chlorite and the absorbance at 360 nm was measured. In this experiment the ratio (moles of chlorine dioxide produced)/(moles of bromine reacted) was 2.03; six determinations of this ratio yielded a value of 1.95 \pm 0.10.

Experiments were carried out with excess bromine; for example, 0.141 mmol of bromine was reacted with 7.87×10^{-3} mmol of sodium chlorite. The solution was boiled (to eliminate ClO₂) until it became colorless, allowed to cool to room temperature, and the unreacted bromine was extracted with carbon tetrachloride. The aqueous phase was diluted to 100 mL with buffer ([H⁺] = 1.58 \times 10⁻³ M) and the response of the bromide-sensitive electrode determined. In three replicate experiments, the ratio (moles of bromide ion)/(moles of chlorite ion reacted) was found to be 1.00 \pm 0.09. The results presented imply that the reduction of bromine by chlorine(III) proceeds according to

$$2\mathrm{ClO}_2^- + \mathrm{Br}_2 \to 2\mathrm{ClO}_2 + 2\mathrm{Br}^- \tag{I}$$

Experiments performed with excess sodium chlorite at hydrogen ion concentrations higher than 1.58×10^{-3} M showed that the amount of bromide ion produced depends on the acidity, less bromide ion being detected the higher the acid concentration. At $[H^+] < 0.1$ M the curves obtained resemble that shown in Figure

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1. At $[H^+] \ge 0.1$ M there is a significant difference: bromide ion is produced initially and disappears after a period of time. The length of this period decreases as [H⁺] is increased.

Figure 2 shows the result obtained in 1 M sulfuric acid. In this experiment, the amount of bromide ion produced corresponds to a yield of less than 39%. At this acid concentration, determination of chlorine dioxide is hampered by the decomposition of chlorous acid, even when the reaction is monitored for only 13 s. In 0.3 M perchloric acid the decomposition of chlorous acid is slow enough not to be detected in 13 s. When sodium chlorite and bromine were reacted under these conditions we found that the amount of chlorine dioxide produced corresponded to the stoichiometry of reaction I. Observation of the reaction for longer than 30 s shows that chlorine dioxide does not disappear, but its concentration increases owing, presumably, to the decomposition of chlorous acid.

On the basis of the results presented we conclude that, at all acidities employed, the result of the interaction between bromine and chlorine(III) is the oxidation of the latter to chlorine dioxide according to reaction I. Bromide ion disappears via reaction with excess chlorine(III). The reaction between bromide ion and chlorine(III) is the subject of the following article.

Kinetics

Control Experiments. Chlorous acid is unstable, decomposing by a complex process to give chlorine dioxide at a rate that increases with decreasing pH.^{15,16} In addition, the photochemical decomposition of sodium chlorite produces chlorine dioxide with a quantum yield approaching unity at pH 6 or below.¹⁷ Therefore, in order to ascertain the influence of these processes on our kinetics results, control experiments were carried out.

When sodium chlorite was mixed with buffer in the stopped-flow apparatus to give a chlorite ion concentration of 2.0×10^{-2} M and $[H^+] = 1.58 \times 10^{-3}$ M, an increase in the absorbance at 360 nm was observed, indicating that chlorine dioxide is formed under these conditions. The following results convinced us that the observed production of chlorine dioxide is the result of the photochemical decomposition of sodium chlorite induced by the monitoring 150-W tungsten filament lamp. (a) The rate of chlorine dioxide production depends on the band-pass employed. When the monochromator was set at 360 nm, we obtained rates, in absorbance units/second, equal to 0.17 using a band-pass of 20 nm, 5.7×10^{-2} with a band-pass of 10 nm and 5.3×10^{-2} with a band-pass of 5 nm. (b) With the monochromator set at 380 nm, and a band-pass of 10 nm, no increase in absorbance could be detected in 13 s. Since the smallest change in absorbance that we can detect is approximately 3×10^{-3} , we conclude that the rate under these conditions is less than 2.3 \times 10⁻⁴ absorbance units/s. (c) When the reaction was monitored in the Beckman spectrophotometer equipped with a less intense lamp and using a band-pass of 0.1 nm, the rate measured was 1.5×10^{-4} absorbance units/s at 360 nm. In view of these results we decided to perform our stopped-flow experiments using a band-pass of 10 nm with the monochromator set at 380 nm.

In a typical kinetics experiment on the Cl(III)-Br₂ reaction, the initial chlorine(III) concentration was approximately 1×10^{-2} M and that of bromine 3×10^{-4} M. Therefore, the bromide ion concentration produced was 6×10^{-4} M. With these concentrations the reaction between chlorine(III) and bromide ion is too slow, even in 1 M perchloric acid, to produce a significant decrease in the chlorine(III) concentration during the time scale of our stopped-flow experiments. However, it is fast enough to modify the shape of the decay curves. At $[H^+] = 9.77 \times 10^{-4} \text{ M}$ (Figure 3) the absorbance increases exponentially and the end of the reaction is clearly discernible; when $[H^+] = 0.583$ M the absorbance increases exponentially at the beginning and linearly at the later stages of the reaction, which we ascribe to chlorine dioxide



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Figure 3. Result obtained when sodium chlorite and bromine were reacted in the stopped-flow spectrophotometer: $[H^+] = 9.77 \times 10^{-4}$ M, initial bromine concentration is 2.56×10^{-4} M and sodium chlorite concentration 1.20×10^{-2} M; circles = experimental points, solid line = calculated.



Figure 4. Effect of bromide ion on the rate constant. The rate constant, $k(Br^{-})$, pertains to a given bromide concentration, and k_{max} is the rate constant when no sodium bromide is added. Data obtained at $[H^+] =$ 1.58×10^{-3} M (circles) and 4.47×10^{-3} M (squares). Initial sodium chlorite concentration is 1.16×10^{-2} M and bromine concentration 2.0 $\times 10^{-4}$ M.

production by the Cl(III)-Br- reaction and decomposition of chlorous acid. We found that exponential curves were obtained as long as the hydrogen ion concentration was 0.3 M or lower. Therefore, we set $[H^+] = 0.3$ M as the upper limit in our study of the kinetics of the chlorine(III)-bromine reaction.

Rate Studies. The kinetics results reported below were obtained at 25 °C in the presence of excess sodium chlorite, usually at 15-fold excess. Unless otherwise specified, the ionic strength of the solution was adjusted to 0.66 ± 0.01 M with sodium perchlorate. Experiments carried out with excess bromine were plagued by irreproducibility, probably due to the high volatility of bromine.

A typical result obtained with excess chlorite ion is shown in Figure 3. The curve can be described by an exponential function, implying that the reaction is first order with respect to bromine. A value of the pseudo-first-order rate constant was obtained by using a least-squares fit to the function $\ln (A_{\infty} - A_t)$ plotted against time, where A_t is the absorbance at time t and A_{∞} is the absorbance after no further reaction is observed. The pseudo-first-order rate constant k was determined at six concentrations of chlorine(III) in the range 1×10^{-3} to 4.4×10^{-2} M. A plot of k against [Cl(III)] is linear, indicating that the reaction is first order with respect to chlorine(III), and the slope of the line gives a value of the pseudo-second-order rate constant.

The ionic strength of the solution was varied either by diluting the buffer or by adding sodium perchlorate. The pseudo-first-order rate constant determined at constant chlorine(III) and bromine concentrations was independent of the ionic strength in the range 1.64×10^{-2} to 0.503 M, and decreased by ~20% upon increasing the ionic strength to 1.06 M. We interpret these results as evidence that at least one of the species involved in the rate-determining step is uncharged.

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Figure 5. Plot of the reciprocal of the pseudo-first-order rate constant against [Br⁻]: [H⁺] = 1.58×10^{-3} M and initial sodium chlorite concentration: 1.16×10^{-2} M. A linear least-squares fit of the points obtained at [Br⁻] < 1.77×10^{-2} M yields slope = (14.1 ± 0.5) M⁻¹ s; intercept = $(3.20 \pm 0.18) \times 10^{-2}$ s.



Figure 6. As in Figure 5, but with $[H^+] = 4.47 \times 10^{-3}$ M. A least-squares fit yields slope = (20.8 ± 0.2) M⁻¹ s; intercept = $(1.8 \pm 0.5) \times 10^{-2}$ s.

Addition of sodium bromide decreases the reaction rate. Figure 4 shows the results obtained at two hydrogen ion concentrations $(1.58 \times 10^{-3} \text{ and } 4.47 \times 10^{-3} \text{ M})$; k(Br) is the rate constant at a bromide ion concentration [Br] and k_{max} is the rate constant when no sodium bromide is added. (We use the term k_{max} and not k(0), rate constant at zero bromide concentration, because bromide is a product of the reaction and the condition [Br] = 0 is experimentally unattainable.)

Figures 5 and 6 show plots of the reciprocal of the pseudofirst-order rate constant as a function of the bromide ion concentration. The curvature of the plot at $[H^+] = 1.58 \times 10^{-3} \text{ M}$ (Figure 5) can be explained by assuming that both Br₂ and Br₃⁻ react with chlorine(III), with bromine reacting faster. No curvature is observed in the plot at $[H^+] = 4.47 \times 10^{-3} \text{ M}$ (Figure 6), indicating that reaction with Br₃⁻ is not important, up to a bromide ion concentration of $5.00 \times 10^{-2} \text{ M}$. Reaction with tribromide ion at $[H^+] = 4.47 \times 10^{-3} \text{ M}$ can be detected if the bromide ion concentration is sufficiently large, as indicated by the results presented in Figure 7, where the rate constant measured at $[Br^-] = 0.530 \text{ M}$ has been included.

To establish the rate law, the effect of the hydrogen ion concentration is considered next. Before doing so, we point out an interesting feature of Figure 3. Namely, the absorbance at the start of the reaction is too large to be due to bromine and chlorine(III). From the intercept of a plot of $\ln (A_{\infty} - A_i)$ against time we find that the absorbance at t = 0 is 0.229; for comparison, the absorbance of the mixture Cl(III) + Br₂ before reaction is calculated to be 0.045. Since the dead time of our stopped-flow apparatus is 3 ms¹⁴ the absorbance at t = 0 corresponds to the



Figure 7. As in Figure 6, but including higher bromide ion concentrations.



Figure 8. Spectra of chlorine dioxide and of the intermediate(s) formed in the fast reaction preceding the rate-determining step: O, absorbance of chlorine dioxide at the end of the reaction; *, absorbance of the intermediate(s) formed in the fast step. Initial bromine concentration is $(2.6 \pm 0.10) \times 10^{-4}$ M, and sodium chlorite concentration $(1.20 \pm 0.02) \times 10^{-2}$ M. [H⁺] = 1.58×10^{-3} M.

absorbance 3 ms after the start of the experiment. Therefore, we conclude that a fast reaction is taking place before the rate-determining step.

In order to gain insight into the nature of the intermediate(s) formed in the fast step, two types of experiments were performed: (1) kinetics determination of the spectrum of the intermediate(s), (2) measurement of the order of the reaction with respect to chlorine(III) in the presence of sodium bromide at a concentration of 0.25 M.

The spectrum of the intermediate(s) formed in the fast step was determined by monitoring the reaction at different wavelengths, using a band-pass of 10 nm. From the intercept of the plot of $\ln (A_{\infty} - A_i)$ against time we obtain the absorbance at t = 0, which corresponds to the absorbance of the intermediate(s) plus the absorbance of the excess chlorine(III). The absorbance at the end of the reaction is A_{∞} . It corresponds to the absorbance of chlorine dioxide plus that of the chlorine(III). The spectra of the intermediate(s) and of chlorine dioxide determined between 360 and 450 nm are presented in Figure 8. No significant difference between the two spectra can be detected and, within experimental error, the rate constant obtained was independent of the wavelength used to monitor the reaction.

Figure 9 shows the results obtained in the determination of the order with respect to chlorine(III) in the presence of sodium bromide. The points can be fitted by an equation describing saturation kinetics, implying the presence of a fast equilibrium prior to the rate-determining step.¹⁸ It should be noted that when no sodium bromide is added the reaction is first order with respect

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Figure 9. Plot of pseudo-second-order rate constant against sodium chlorite concentration. Rate constants were measured in the presence of 0.25 M sodium bromide at $[H^+] = 9.77 \times 10^{-4}$ M. The experimental points can be fitted by the equation $k_{app} = B_1[\text{NaClO}_2]/(1 + B_2[\text{Na-ClO}_2])$, with $B_1 = (8.21 \pm 1.04) \times 10^3$ M⁻² s⁻¹, and $B_2 = (29.2 \pm 4.4)$ M⁻¹; solid line : calculated.

to chlorine(III), indicating that under these conditions the fast step may be considered to be an irreversible reaction.

Based on the evidence presented in Figures 8 and 9 we propose that the fast reaction preceding the rate-determining step is

$$ClO_2^- + Br_2 \rightarrow BrClO_2 + Br^-$$
 (II)

Reaction II is analogous to those proposed in the chlorine(III)– Cl_2 and chlorine(III)– I_2 reactions.^{5,6,9} Thus, bromide ion influences the reaction rate by reacting with bromine to form Br_3^- and by displacing the equilibrium of reaction II toward the reactants.

An alternative explanation is that the fast step corresponds to the reaction $ClO_2^- + Br_2 \rightarrow ClO_2 + Br_2^-$. We decided against this interpretation in view of the known rate constants for the decay of $Br_2^{-.19}$ At pH 6-7 the reaction 2 $Br_2^- \rightarrow Br_3^- + Br^-$ has a rate constant of 3×10^9 M⁻¹ s⁻¹ (at higher acidities Br_2^- decays even faster). Using 1.0×10^{-2} and 3.0×10^{-4} M as values for the chlorine(III) and bromine initial concentrations we conclude that, in order to be competitive, the reaction between Cl(III) and Br_2 must have a rate constant of 9×10^7 M⁻¹ s⁻¹. This value is 4 orders of magnitude larger than the pseudo-second-order rate constant determined experimentally.

The variation of the pseudo-second-order rate constant with hydrogen ion concentration is shown in Figure 10. A possible interpretation of these results is that, in the range of acidities employed, only the reactivity of the chlorite ion can be determined. In terms of reaction sequence III-V

$$HClO_2 \rightleftharpoons ClO_2^- + H^+ = K_a$$
, fast (III)

$$ClO_2^- + Br_2 \rightarrow BrClO_2 + Br^- \quad k, \text{ fast} \quad (IV)$$

$$ClO_2^- + BrClO_2 \rightarrow 2ClO_2 + Br^- \quad k', \text{ slow} \quad (V)$$

the rate law is

$$\frac{1}{2} \frac{d[CIO_2]}{dt} = \frac{k'K_a[CI(III)][Br_2]}{K_a + [H^+]}$$
(1)

where $[Cl(III)] = [ClO_2^-] + [HClO_2]$ and $BrClO_2$ is formed irreversibly in step IV at low $[Br^-]$.

A test of this scheme is the kinetics determination of the dissociation constant of chlorous acid. Referring to Figure 10, we identify b with K_a ; the value obtained from the fit, $K_a = 1.23 \times 10^{-2}$ M, is about 4 times larger than the most reliable value reported in the literature.¹²

In view of this discrepancy, we propose that in the present reaction chlorite ion and chlorous acid have the same reactivity;



Figure 10. Variation of the pseudo-second-order rate constant with [H⁺]. The points can be fitted by the equation $k_{app} = a/(b + [H^+])$, with $a = (36.1 \pm 3.0) \text{ s}^{-1}$, and $b = (1.23 \pm 0.02) \times 10^{-2} \text{ M}$; solid line = calculated.

the hydrogen ion dependence of the rate constant is due to the difference in reactivity between the intermediates $BrClO_2$ and $BrClO_2H^+$.

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

$$\frac{1}{2} \frac{d[ClO_2]}{dt} = \frac{(c_1 + c_2[Br^-])[Br_2][Cl(III)]^2}{d[Cl(III)] + e[Br^-]}$$
(2)

In eq 2, c_1 and/or d are functions of $[H^+]$; c_2 and e may depend on $[Br^-]$ and $[H^+]$.

Under conditions where $d[Cl(III)] \gg e[Br^-]$ and $c_1 \gg c_2[Br^-]$ the rate law becomes

$$\frac{1}{2} \frac{d[ClO_2]}{dt} = (c_1/d)[Br_2][Cl(III)]$$
(3)

where (c_1/d) is the pseudo-second-order rate constant. It has a value of $(2.45 \pm 0.09) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at $[\text{H}^+] = 1.58 \times 10^{-3} \text{ M}$, and its variation with $[\text{H}^+]$ is of the form $a/(b + [\text{H}^+])$, as indicated by the results shown in Figure 10.

Mechanism

Bromine hydrolyzes to produce hypobromous acid according to the reaction 16,20

$$Br_2 + H_2O \rightleftharpoons BrOH + Br^- + H^+$$
 $K_h = 9 \times 10^{-9} M^2$

In devising a mechanism for the Cl(III)-Br₂ reaction we must consider the possibility that both Br_2 and BrOH react with chlorine(III). At pH 7.41 and an initial bromine concentration of 3×10^{-4} M, all the bromine is present as BrOH. Under these conditions the reaction is first order with respect to BrOH and the observed rate constant, 20.6 M⁻¹ s⁻¹, indicates that hypobromous acid is considerably less reactive than bromine. Additional evidence that reaction with BrOH is not important at [H⁺] $\geq 5.89 \times 10^{-5}$ M is (a) in the absence of added bromide ion, the equilibrium [BrOH] is not a linear function of the initial bromine concentration. Thus, if reaction with BrOH were important the reaction would not be first order with respect to bromine. Experimentally, however, we found that the reaction was first order with respect to bromine at all the acidities employed. (b) Changing the hydrogen ion concentration from 5.89 \times 10⁻⁵ M to 9.77 \times 10^{-4} M decreases the equilibrium [BrOH] by a factor of 4 but the rate constant is unchanged.

Table I presents a mechanism consistent with our results at $[H^+] \ge 5.89 \times 10^{-5}$ M and low bromide ion concentrations. In the presence of added sodium bromide reactions 2 and 3 (Table I) are reversible and reaction between Br_3^- and chlorine(III) must be considered. A full description of the interaction between Br_3^- and chlorine(III) requires study of the Cl(III)-Br₂ reaction at

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Reaction between Chlorine and Molecular Bromine

TABLE I: Mechanism^a Valid at Low Bromide Ion Concentration

1	$HClO_2 \rightleftharpoons H^+ + ClO_2^-$	K _a , fast
2	$Br_2 + ClO_2^- \rightarrow BrClO_2 + Br^-$	k_2 , fast
3	$Br_2 + HClO_2 \rightarrow BrClO_2H^+ + Br^-$	k_3 , fast
4	$BrClO_2H^+ \Rightarrow BrClO_2 + H^+$	K_4 , fast
5	$BrClO_2 + ClO_2^- \rightarrow 2ClO_2 + Br^-$	k_5 , slow
5a	$BrClO_2 + HClO_2 \rightarrow 2ClO_2 + Br^- + H^+$	k_5 , slow

^a The rate law derived from this mechanism is

 $[Br_2]_0 = [BrClO_2] + [BrClO_2H^+]$, and $[Cl(III)] = [ClO_2^-] +$ [HClO₂].

$$\frac{1}{2} \frac{d[ClO_2]}{dt} = \frac{k_5 K_4 [Cl(III)] [Br_2]_0}{K_4 + [H^+]}$$

high bromide concentrations. A complication arises from interference of the reaction between chlorine(III) and bromide ion, which becomes more important the higher the acidity. Therefore, we will limit ourselves to analyzing in detail only the results we have obtained at low bromide ion concentrations (no sodium bromide added).

The pseudo-first-order rate constant deduced from the rate law in Table I is given by

$$k_{\rm app} = \frac{k_5 K_4 [\rm Cl(III)]}{K_4 + [\rm H^+]} \tag{4}$$

Equation 4 predicts that, when no bromide ion is added initially, the pseudo-first-order rate constant is a linear function of the chlorine(III) concentration, a prediction verified by our experimental observations.

Figure 10 shows the variation of the pseudo-second-order rate constant, $k_{app}/[Cl(III)]$, with the hydrogen ion concentration. Comparing eq 4 with that shown in Figure 10, we obtain

$$a = k_5 K_4 = 36.1 \pm 3.0 \text{ s}^{-1}$$

 $b = K_4 = (1.23 \pm 0.02) \times 10^{-2} \text{ M}$

Therefore, we obtain $k_5 = (2.94 \pm 0.25) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, which is consistent with the value of the rate constant obtained experimentally in the range $[H^+] = 5.89 \times 10^{-5} - 9.77 \times 10^{-4} M.$

Minimum values for K_2 and K_3 can be deduced from the condition that reactions 2 and 3 are irreversible at low bromide ion concentration. The equilibrium constants K_2 and K_3 are related by the equation $K_2K_a = K_3K_4$. Typical initial concentrations of bromine and chlorine(III) in our experiments were 3.0×10^{-4} and 1.0×10^{-2} M, respectively; using these values we obtain $K_2 \ge 1.5$ and $K_3 \ge 0.33$.

A representative result obtained in our kinetics experiments is shown in Figure 3. The curve can be described by a single exponential, implying that the fast steps, reactions 2 and 3 in Table I, have gone to completion within 3 ms, the dead time of our stopped-flow spectrophotometer. This fact allows us to deduce minimum values for k_2 and k_3 . Taking a reaction to be complete after five lifetimes have elapsed, and using 1.0×10^{-2} M as the initial chlorine(III) concentration, we obtain $k_2 = k_3 > 1.7 \times 10^5$ $M^{-1} s^{-1}$.

A reviewer has pointed out that chloride ion, present in the Kodak sodium chlorite, can react with Br_2 to give Br_2Cl^- (K = 1.6 M^{-1}), which could influence the kinetics of the reaction. If a step involving Cl(III) and Br₂Cl⁻ significantly affected the kinetics, the pseudo-first-order rate constant determined with excess Cl(III) would not be a linear function of the initial concentration of chlorine(III). We find, however, that a plot of the pseudo-first-order rate constant against the initial concentration of chlorine(III) is linear in the range 1.0×10^{-3} to 4.4×10^{-2} M.

Discussion

The mechanism presented in Table I accounts for all our experimental observations in the absence of added bromide ion. The parameters derived from our results are summarized in Table II.

In analogy with the intermediates Cl₂O₂ and IClO₂,³⁻⁵ BrClO₂ is proposed as an intermediate in the Cl(III)-Br₂ reaction. The observed [H⁺] dependence for [H⁺] $\geq 5.89 \times 10^{-5}$ M is explained

TABLE II: Parameters Derived from the Mechanism of Table I

parameter	value	
k5	$(2.94 \pm 0.25) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	
K_4	$(1.23 \pm 0.02) \times 10^{-2} M$	
K_2	>1.5	
K_3	>0.33	
k_2	$>1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	
k_3	$>1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	

by postulating the existence of the less reactive intermediate $BrClO_2H^+$. In the range of acidities studied the reactivity of BrClO₂H⁺ cannot be determined. The rate constant measured at pH 7.41 is assigned to reaction between chlorite ion and BrOH.

From the rate data obtained at low bromide ion concentration (no sodium bromide added) and $[H^+] \ge 5.89 \times 10^{-5}$ M, we derive a value for the rate constant of the reactions of chlorite ion and chlorous acid with BrClO₂, $k_5 = (2.94 \pm 0.25) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, and we determine the acidity constant of the intermediate BrClO₂H⁺, $K_4 = (1.23 \pm 0.02) \times 10^{-2}$ M. The value derived for K_4 , the acidity constant of BrClO₂H⁺, is about 5 times as large as that for chlorous acid.¹² The presence of a bromine atom in BrClO₂H⁺ should make this species a stronger acid than HClO₂.

Most reactions involving oxidation of chlorine(III) to chlorine dioxide proceed by an outer-sphere electron-transfer mechanism, chlorous acid being less reactive than chlorite ion.²¹ We interpret the reactivity pattern $HClO_2 = ClO_2^-$ inferred from our rate data as evidence that the chlorine(III)-Br₂ reaction proceeds by an inner-sphere electron-transfer mechanism in which attack on the substrate is carried out by the nonbonding electrons of the chlorine atom in ClO_2^- and $HClO_2$.

Another reaction where an unusual reactivity pattern for the ClO_2^{-}/ClO_2 couple has been observed is the oxidation of chlorine(III) by permanganate ion. In this system chlorous acid reacts faster than chlorite ion, a result that has been interpreted in terms of hydrogen bonding between chlorous acid and permanganate ion.^{ĭ2}

We have considered the mechanism of decomposition of HClO₂, which is very susceptible to catalysis by chloride ions and trace amounts of iron, but it seems to follow a free-radical mechanism.²²⁻²⁴ Thus, this reaction is not a helpful model for the chlorine(III) oxidation-reduction reactions that we are considering in connection with chlorite-based oscillators.

Comparison among the mechanisms proposed for the reaction of chlorine(III) and chlorine,^{5,9} bromine (this work) and iodine⁶ reveals at least one similarity and some differences. The similarity is that in all three systems the results are consistent with the participation of $XClO_2$ -type intermediates (X = Cl, Br, I) formed by reaction VI. Further reactions of XClO₂ produce the final products.

$$ClO_2^-$$
 (or $HClO_2$) + $X_2 \rightarrow XClO_2 + X^-$ (+ H⁺) (VI)

Chlorine(III) oxidizes iodine to iodate ion and reduces bromine and chlorine to bromide and chloride ions, respectively. This difference in behavior can be understood in terms of the redox properties of the halogens.^{13,18}

Our results show that chlorine dioxide is the exclusive oxidation product in the reaction of chlorine(III) with bromine. In contrast, chlorine oxidizes chlorine(III) to chlorine dioxide and chlorate ion.^{5,7} A possible explanation of this difference is that chlorine is a stronger oxidizing agent than bromine.²⁵ An alternative interpretation is that chlorate ion is produced by reaction with hypochlorous acid formed by the hydrolysis of chlorine: Cl_2 + $H_2O \rightleftharpoons Cl^- + HOCl + H^+$. The latter argument is supported by the following observations. (1) The yield of chlorate ion increases with decreasing acidity,9 and decreases with addition of sodium chloride.⁵ Lowering the acid concentration displaces

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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 [HOCI]/[Cl₂] 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)-Cl₂ reaction, where the rate-determining step has not been identified.5,9

In the oxidation of iodine by chlorine(III) the reaction ClO₂⁻ $+ I_2 \rightarrow IClO_2 + I^-$ 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 BrClO₂, reaction 2 in Table I, is not rate-determining, and we derive a minimum value for its rate constant, $k_3 > 1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Since iodide ion is a better leaving group than bromide ion, we interpret the values of the rate constants for the formation of BrClO₂ and IClO₂ 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 BrClO₂ and IClO₂. However, we must bear in mind that chlorine is a better electron acceptor than bromine and iodine²⁵ 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 BrClO₂ 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 BrClO₂H⁺ 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 Ion¹

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The stoichiometry and kinetics of the reaction between chlorine(III) and bromide ion were studied spectrophotometrically at 25.0 \pm 0.5 °C and ionic strength 1.2 M (NaClO₄). The main products are Br₃⁻ and Cl⁻ when bromide ion is in excess, ClO₂ and Br₂ when chlorine(III) is in excess. With sufficient acid and excess bromide ion, the stoichiometry of the reaction is $HClO_2 + \delta Br^- + 3H^+ \rightarrow 2Br_3^- + Cl^- + 2H_2O$. The rate law for this reaction is $(1/2)d[Br_3^-]/dt = k[H^+][Br^-][Cl(III)]$ where $k = (9.51 \pm 0.14) \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$. When the reaction is carried out with [Cl(III)] > [Br⁻], the stoichiometry is difficult to define. In the range [Cl(III)] $\approx (1.50-2.00) \times 10^{-3}$ 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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⁽¹⁾ Part 35 in the series "Systematic Design of Chemical Oscillators." Part 34: ref 8.

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