ultraviolet rays[19] and a marked thermal oxygen effervescency.[20] From these unusual facts and a new finding reported here, the authors imagine that certain structural defects associated with oxygen are present in calcium aluminate glasses and these are closely related with the abnormal characteristics of crystalline $12CaO{\cdot}7Al_2O_3$.

Finally the authors will point out a close similarity between $12CaO{\cdot}7Al_2O_3$ and ultramarine, which is known as a pigment.[21] Ultramarine has an idealized formula, $Na_8[Si_6Al_6O_{24}]S_2$, and its structure is composed of sodalite unit in which various kinds of sulfur-related species such as S_2^- or S_3^- are included.[21,22] The sulfur-related species are also replaced by an appropriate anion (e.g. Cl^- or SO_4^{2-})[22]. These characteristics are entirely analogous to those of $12CaO{\cdot}7Al_2O_3$. A marked difference in apparent color is simply due to that in including radical species, i.e., O_2^- ($\lambda_{max} \cong 250$ nm),[23] S_2^- (≅400),[21] or S_3^- (≅620).[21] Ultramarine is also known as an effective catalyst for a variety of reactions, e.g., dehydrogenation, dehydration, and hydrodesulfurization, and its activity is assumed to be due to the presence of sulfur-related paramagnetic species.[24,25] An analogous catalytic activity may be, therefore, expected for $12CaO{\cdot}7Al_2O_3$ including the superoxide radical ion O_2^-.

Acknowledgment. The authors thank Dr. S. Ito of this department for his helpful discussion on the compounds in the $CaO–Al_2O_3$ system and K. Yamazaki for his technical assistance.

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Kinetics and Mechanism of the Autocatalytic Reaction between Iodine and Chlorite Ion[†]

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The kinetics of oxidation of iodine by chlorite is much more complicated than previously found. The rate exhibits a minimum as a function of hydrogen ion concentration, the reaction being characteristically autocatalytic, mainly due to the fact that oxidation of iodine is even faster by hypochlorous acid and chlorine. An important feature of the reaction is the acceleration of the disproportionation of chlorite by the intermediates of the title reaction, leading to the formation of a significant amount of chlorine dioxide. The rate cannot be described by an overall equation, but all the findings can be quantitatively explained by a mechanism consisting of 13 elementary or quasi-elementary steps. The stoichiometry of the reaction is kinetically controlled. Formation and reactions of Cl_2O_2 seem to play a crucial role in the reaction and in other reactions involving chlorite.

Introduction

Recently a number of most unusual and interesting phenomena were observed in the reaction between chlorite and iodide ions. Under certain conditions the concentration of iodine exhibits two extrema, while in CSTR bistability and oscillatory behavior were found.[1] The reaction consists of three parts, which under certain conditions are distinctly separated. First, in a relatively slow autocatalytic reaction, iodide is oxidized into iodine, which is then oxidized in a fast reaction into iodine chloride. The hydrolytic disproportionation of iodine chloride leading to the partial regeneration of iodine is the third stage of the reaction.[2] The kinetics of the second reaction, by far the fastest reaction, has been studied by Grant et al.[3] However, their experiments were made in a rather narrow pH range, and the CSTR studies have been performed at much higher acidity than the experiments of the mechanistic study. Our experiments revealed that in acidic solution the oxidation of iodine by chlorite is autocatalytic, taking into consideration the acceleration of disproportionation of chlorite ion leading to the formation of chlorine dioxide, and that the stoichiometry of the reaction strongly depends on the ratio of the reactants and on the reaction conditions. Since the reduction of chlorite into chloride ion obviously takes place in several steps, to elucidate the kinetics of the title reaction it is a rerequisite to study the hypochlorous acid–iodine and the chlorine–iodine systems. The detailed kinetic studies made it possible to give a quantitative account of all the experimental findings.

Experimental Section

Commercial grade $NaClO_2$ was recrystallized from water. Freshly prepared 0.10 M sodium chlorite stock solutions contained 0.001 M sodium hydroxide to maintain an alkaline pH, which retards decomposition.

Iodine monochloride was made by treating iodine with condensed chlorine according to the method of Cornog and Karges.[4] A 0.1 M ICl stock solution was prepared in 10 M $HClO_4$.

Chlorine monoxide dissolved in carbon tetrachloride was prepared by bubbling chlorine into a slurry of dry carbon tetrachloride and mercuric oxide. Stock solutions of HOCl were prepared by shaking the cold chlorine monoxide solution with cold aqueous solutions of 0.02 M perchloric acid. Concentrations of HOCl were determined by iodometric titration.

Stoichiometric and kinetic experiments were carried out with reaction mixtures buffered at pH ranging from 1.83 to 3.7. $H_3PO_4–KH_2PO_4$ buffer (0.2 M) was added into iodine stock solutions. Due to mixing, the final buffer concentration was 0.1 M in the reaction mixture. Measurements of pH were made, after mixing, with a Radelkis pH meter. In the case of some kinetic experiments the hydrogen ion concentrations were adjusted with $HClO_4$.

For rapid mixing a homemade stopped-flow apparatus, the mixing time of which is about 5 ms, was used. The reservoirs, the pushing syringes, and the 0.2-cm cell were thermostated to 25.0 °C. A Hitachi 193 spectrophotometer and storage oscilloscope were used for monitoring each change in absorbance at 460 nm ($\epsilon_{I_2} = 740$ cm^{-1} M^{-1}) and 360 nm ($\epsilon_{ClO_2} = 1050$ cm^{-1} M^{-1}).

Results and Discussion

Stoichiometry. In an excess of chlorite, iodine is quantitatively oxidized into iodate. According to Grant et al.[3] the stoichiometry is given by eq I. However, in acidic solutions the fate of chlorite

$$5ClO_2^- + 2I_2 + 2H_2O = 5Cl^- + 4IO_3^- + 4H^+ \qquad (I)$$

[†] Dedicated to Professor Viktor Gutmann on the occasion of his 65th birthday.

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Table I. Amount of Chlorine Dioxide Produced in the Chlorite–Iodine Reaction[a]

$10^4[I_2]_0$, M	$10^4[ClO_2]$, M	$[ClO_2]/[I_2]_0$	$10^4[I_2]_0$, M	$10^4[ClO_2]$, M	$[ClO_2]/[I_2]_0$
3.6	19.1	5.32	2.47	13.7	5.56
3.37	18.7	5.54	2.25	13.1	5.84
3.15	17.6	5.60	1.80	10.6	5.89
2.93	16.2	5.52	0.450	2.67	5.93
2.70	15.2	5.62	0.225	1.34	5.96

[a] $[ClO_2^-]_0 = 0.010$ M; pH = 2.0; $T = 25$ °C.

Table II. Relative Amount of Iodine Reacted in the Fast First Stage of the Iodine–Chlorite Reaction[a]

$10^4[ClO_2^-]_0$, M	$\Delta[I_2]/[ClO_2^-]_0$			
	pH 1.83	pH 2.0	pH 3.0	pH 3.7
0.5	1.03	1.25		
0.6	1.01	1.20	1.24	
1.0	0.780	0.940	1.09	1.20
1.2	0.761	0.925	1.01	1.12
2.0	0.655	0.725	0.850	0.955
3.0	0.580	0.601	0.742	
4.0	0.503	0.522	0.653	0.827
6.0	0.430	0.428	0.543	0.733
8.0	0.376	0.389	0.462	
10.0	0.341	0.350		
12.0	0.320	0.328		

[a] $\Delta[I_2] = [I_2]_0 - [I_2]_{min}$; $[I_2]_0 = 4.7 \times 10^{-4}$ M.

ion is not so unambiguous: chlorine dioxide is formed as well as chloride ion, and the stoichiometry of the reaction strongly depends on the initial conditions. The disproportionation of chlorite ion was not taken into consideration in the description of chlorite oscillators since its rate is negligible in comparison to the rate of the other redox reactions. However, this is true for the spontaneous disproportionation only. The intermediates of the redox reactions can greatly increase the rate of the disproportionation reaction to such an extent that its rate becomes commensurable with the rate of the main reaction. As can be seen from the data of Table I, when iodine is oxidized by chlorite at pH 2, the amount of chlorine dioxide increases with increasing concentration of iodine; however, the relative amount of chlorine dioxide ($[ClO_2]/[I_2]_0$) increases with decreasing initial concentration of iodine, that is with increasing excess of chlorite ion, and approaches a limiting value. This value indicates that at a high excess of chlorite ion the limiting stoichiometry can be given by

$$I_2 + 10ClO_2^- + 4H^+ = 2IO_3^- + 6ClO_2 + 4Cl^- + 2H_2O \quad \text{(II)}$$

This stoichiometry is supported by titration of 10 mL of 0.01 M sodium chlorite solution by 0.001 M iodine solution, the pH of which was adjusted to 2. The iodine solution was added in 1-mL portions, and the ClO_2 formed was expelled from the solution, after each portion was added, by bubbling nitrogen through the solution. The color of iodine persisted only after the eleventh portion was added.

If chlorite is not in excess, the reaction takes place in two stages. In this case one has to distinguish the stoichiometry of the two stages. The amounts of iodine reacted as a function of chlorite ion concentration at four different pH values are given in Table II. The data indicate that in this first fast stage of the reaction iodine is oxidized to species in the +1 oxidation state (HOI, ICl):

$$ClO_2^- + 2I_2 + H^+ + H_2O = ICl + 3HOI \quad \text{(III)}$$

In acidic solutions in the presence of chloride ion the formation of ICl_2^- can be spectrophotometrically observed at 343 nm.[5] The slow second stage of the reaction is the disproportionation of the +1 iodine-containing species to iodine and iodate. The ratio $\Delta[I_2]/[ClO_2^-]_0$ decreases with increasing initial concentration of chlorite and with increasing hydrogen ion concentration. However,

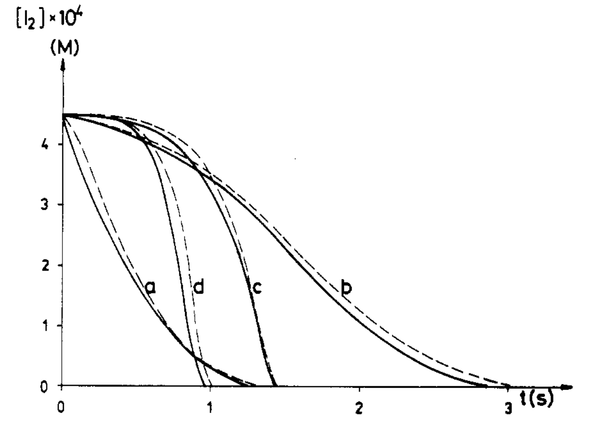

Figure 1. Measured (—) and calculated (– –) iodine concentration as a function of time in the iodine–chlorite reaction at different hydrogen ion concentrations. $[ClO_2^-]_0 = 2.0 \times 10^{-3}$ M; $[H^+] = 2.0 \times 10^{-4}$ (a), 0.01 (b), 0.10 (c), and 0.2 (d) M.

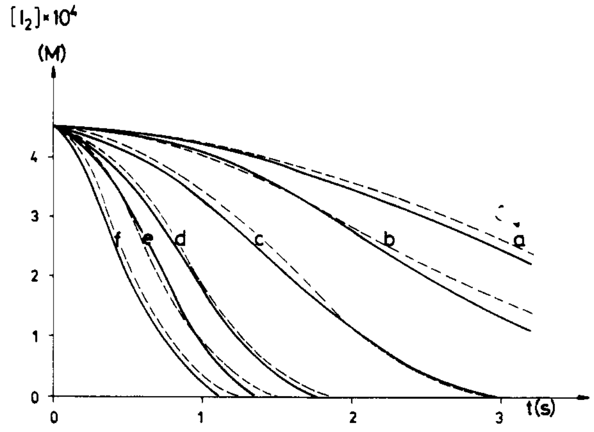

Figure 2. Effect of initial chlorite concentration on the measured (—) and calculated (– –) iodine vs. time curves (pH 2.0). $[ClO_2^-]_0 = 4.5 \times 10^{-4}$ (a), 1.0×10^{-3} (b), 2.0×10^{-3} (c), 5.0×10^{-3} (d), 1.0×10^{-2} (e), and 2.0×10^{-2} (f) M.

the limiting stoichiometry corresponding to eq III is not reached. These findings can be easily explained by the following three reactions:

$$I_2 + ClO_2^- + H^+ + H_2O = 2HOI + HOCl \quad \text{(IIIa)}$$

$$I_2 + HOCl = ICl + HOI \quad \text{(IIIb)}$$

$$HOCl + 2ClO_2^- + H^+ = 2ClO_2 + Cl^- + H_2O \quad \text{(IIIc)}$$

The weight of eq IIIc obviously decreases with decreasing chlorite ion concentration and increasing pH in accordance with the data of Table II. All in all, the title reaction does not have an unique stoichoimetry; the quality and quantity of the products is determined by the kinetics of the rather complex reaction.

Kinetics. According to Grant et al.[3] the overall rate of the chlorite oxidation of iodine is as follows:

$$-\frac{1}{2}\frac{d[I_2]}{dt} = \left(k_1[ClO_2^-] + k_2\frac{[ClO_2^-]}{[H^+]} + k_3\right)[I_2] \quad \text{(IV)}$$

The hydrogen ion dependence of the rate, however, is much more complicated. As is evident from the plots of iodine concentration vs. time of Figure 1, the rate does not monotonically decrease with increasing hydrogen ion concentration but exhibits a minimum at about pH 2. Furthermore, below pH 3 the disappearance of iodine is characteristically autocatalytic. It is noteworthy that the oscillatory behavior has been found earlier by Dateo et al.[1] only below pH 2.

The autocatalytic character of the reaction is suppressed by increasing the concentration of chlorite (Figure 2). This effect has been found by us in more acidic solutions too.

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(5) Cason, D. L.; Neumann, H. M. *J. Am. Chem. Soc.* **1961**, *83*, 1822.

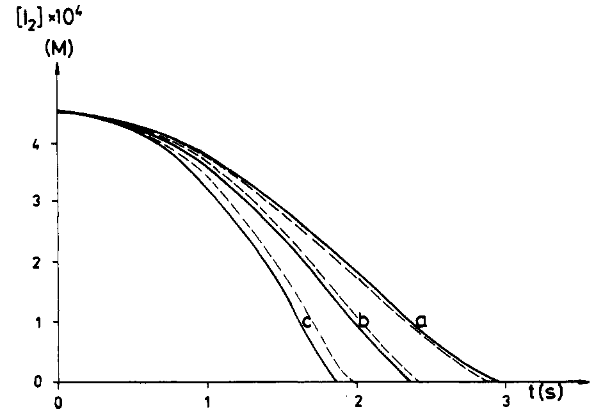

Figure 3. Effect of initial chloride concentration on the measured (—) and calculated (- -) iodine vs. time curves in the iodine–chlorite reaction (pH 2.0) $[ClO_2^-]_0 = 2.0 \times 10^{-3}$ M; $[Cl^-]_0 = 1.0 \times 10^{-3}$ (a), 5.0×10^{-3} (b), and 2.0×10^{-2} (c) M.

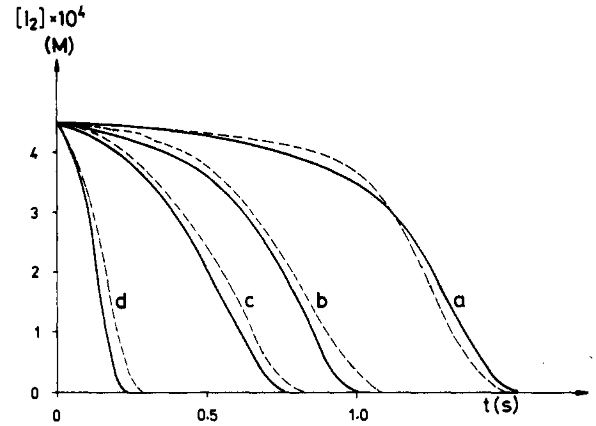

Figure 4. Effect of initial iodine chloride concentration on the measured (—) and calculated (- -) iodine vs. time curves in the iodine–chlorite reaction. $[H^+] = 0.10$ M; $[ClO_2^-]_0 = 2.0 \times 10^{-3}$ M; $[ICl]_0 = 0$ (a), 1.0×10^{-5} (b), 5.0×10^{-5} (c), and 5.0×10^{-4} (d) M.

To elucidate the autocatalytic nature of the reaction, the effect of the products on the rate has been studied. Iodate has no effect at all. Above pH 3 chloride ion has no effect either; however, in more acidic solution it significantly decreases the length of the induction period, and this effect is proportional to the chloride concentration (Figure 3). We conjectured that the effect of chloride is due to the formation of iodine chloride; therefore, the effect of ICl on the rate has also been studied. As shown by the curves of Figure 4, the inducation period is greatly shortened by rather small amounts of iodine chloride. (I(+1) is present under the experimental conditions in the form of ICl, ICl_2^-, and HOI, respectively.)

According to the data of Table I, chlorine dioxide is formed in the reaction. The formation of chlorine dioxide is significant below pH 3. The effect of chlorite concentration on the rate of the chlorine dioxide formation is shown by the curves of Figure 5. These curves also indicate autocatalytic reaction. Chloride ion and iodine chloride act as catalysts in the formation of chlorine dioxide too.

Both the autocatalytic nature of the reaction and the formation of chlorine dioxide require the study of the kinetics of the reaction between hypochlorous acid and iodine.

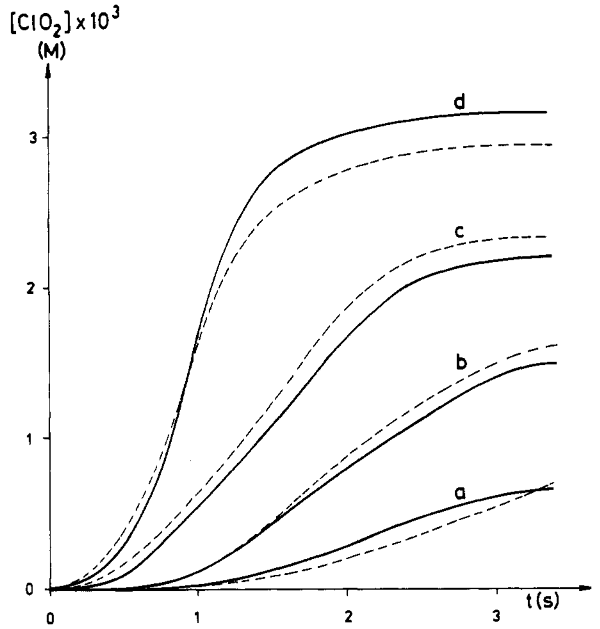

Figure 5. Formation of chlorine dioxide in the iodine–chlorite reaction (pH 2.0) $[I_2]_0 = 4.5 \times 10^{-4}$ M; $[ClO_2^-]_0 = 2.0 \times 10^{-3}$ (a), 5.0×10^{-3} (b), 1.0×10^{-2} (c), and 2.0×10^{-2} (d) M.

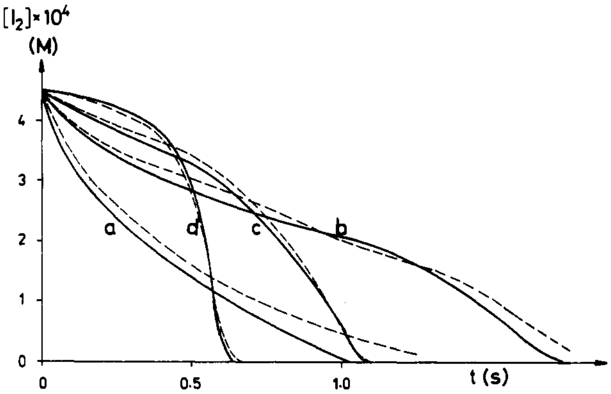

Figure 6. Measured (—) and calculated (- -) iodine concentration as a function of time in the iodine–hypochlorous acid reaction at different hydrogen ion concentrations. $[HOCl]_0 = 1.5 \times 10^{-3}$ M; $[H^+] = 2.0 \times 10^{-4}$ (a), 4.0×10^{-3} (b), 1.0×10^{-2} (c), and 0.10 (d) M.

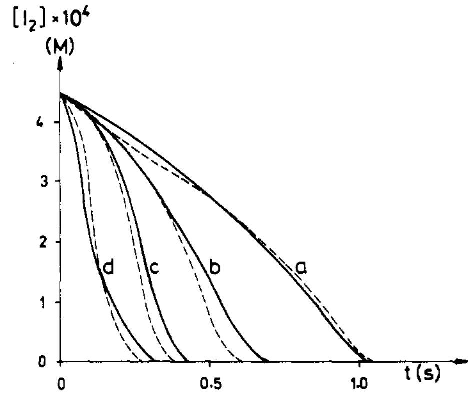

Figure 7. Effect of initial chloride concentration on the measured (—) and calculated (- -) kinetic curves in the iodine–hypochlorous acid reaction (pH 2.0). $[HOCl]_0 = 1.5 \times 10^{-3}$ M; $[Cl^-]_0 = 0$ (a), 5.0×10^{-4} (b), 1.0×10^{-3} (c), and 5.0×10^{-3} (d) M.

Kinetics of the Hypochlorous Acid–Iodine Reaction. When iodine is in excess, there is a minimum on the iodine concentration vs. time curve just as in case of the chlorite–iodine system under the same conditions. According to the kinetic curves of Figure 6, there are some similarities in the kinetics of the two reactions. The rate exhibits a minimum as a function of hydrogen ion concentration, although the minimum is slightly shifted, and the autocatalytic character of the reaction is noticeable above this hydrogen ion concentration. The rate increases with increasing concentration of hypochlorous acid, and the rate-increasing effect of chloride ions exceeds their effect observed in the case of chlorite ion oxidation of iodine (Figure 7).

To complete the kinetic studies, we have made some experiments on the rate of the reaction between chlorine and iodine, since in this system there are a number of possibilities for the formation

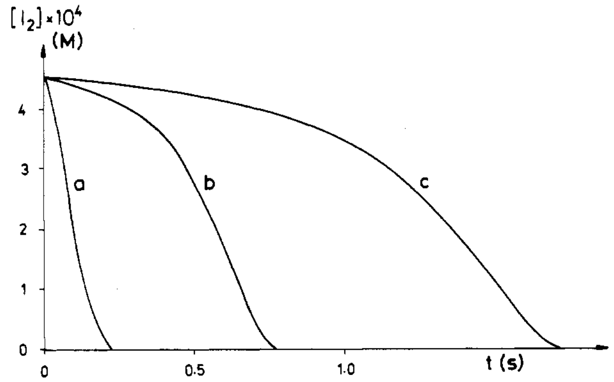

Figure 8. Comparison of the rates of reaction of iodine with chlorine (a), hypochlorous acid (b), and chlorite (c). $[H^+] = 5.0 \times 10^{-2}$ M; $[ClO_2^-]_0 = [HOCl]_0 = [Cl_2]_0 = 2.0 \times 10^{-3}$ M; $[NaClO_4] = 5 \times 10^{-2}$ M.

of elementary chlorine. This reaction is very rapid, and if iodine is in excess, the fast disappearance of iodine is followed by its much slower partial regeneration. As shown by the curves of Figure 8, under the same conditions the rate of the oxidation of iodine increases in the following order of reactants: $Cl_2 > HOCl > ClO_2^-$. In fact, the reaction with chlorine is even faster than indicated by curve a of Figure 8. In 0.05 M perchloric acid chlorine is partially hydrolyzed into HOCl and Cl^-. When the pH is low enough to prevent the hydrolysis of chlorine, the rate is so high that the rate constant could not be determined by our stopped-flow instrument. However, the rate of the partial regeneration of iodine is independent of the three different oxidants.

Mechanism. Contrary to the work of Grant et al.[3] the dependence of the rate of the reaction on the concentration of iodine, chlorite ion, and hydrogen ion cannot be described by the three-term rate equation (eq IV). It is plausible to find first a mechanism for the obviously much simpler hypochlorous acid oxidation of iodine and then to expand this set of equations to give an account of the behavior of the chlorite–iodine system.

Mechanism of the Hypochlorous Acid Oxidation of Iodine. The kinetic curves suggest that there is an autocatalytic and a nonautocatalytic path in the reaction. The rate of the nonautocatalytic path decreases with increasing hydrogen ion concentration; therefore, it becomes dominant only above pH 3, and its role below pH 2 is restricted to the initiation of the reaction. The rate of the autocatalytic route, however, increases with increasing hydrogen ion concentration, and below pH 2 the contribution of the nonautocatalytic route becomes negligible.

The reaction starts with the hydrolysis of iodine:

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \qquad (1)$$

The iodide ion is rapidly oxidized by HOCl:

$$I^- + HOCl \rightarrow ICl + OH^- \qquad (2)$$

Iodine chloride is reversibly hydrolyzed:

$$ICl + H_2O \rightleftarrows HOI + Cl^- + H^+ \qquad (3)$$

HOI formed in the hydrolysis of either iodine or iodine chloride is then oxidized by HOCl:

$$HOI + HOCl \rightarrow HIO_2 + Cl^- + H^+ \qquad (4)$$

$$HIO_2 + HOCl \rightarrow IO_3^- + Cl^- + 2H^+ \qquad (5)$$

The autocatalysts is caused by the shift of reaction 3 to the left-hand side below pH 2 and the reaction between ICl and HOCl to give chlorine

$$ICl + HOCl \rightarrow HOI + Cl_2 \qquad (6)$$

which then reacts extremely fast with iodine

$$Cl_2 + I_2 \rightarrow 2ICl \qquad (7)$$

The rate constants of (1) were determined by a relaxation study by Eigen and Kustin,[6] but unfortunately there is not direct and independent information available on the rate constants of reactions 2–7. Good agreement between all the experimentally found and calculated kinetic curves were obtained when the rate constants summarized in Table III were assumed. Although this is only one of the possible mechanisms, it seems remarkable that even the very unusual double-inflexion curves of Figure 6 (curves b and c) are quite well described by it. In these experiments the oxidation of HOI is relatively slow; therefore, HOI accumulates and decreases the rate of hydrolysis and consequently the rate of the nonautocatalytic reaction decreases. However, the increase of the concentration of HOI increases the rate of the formation of ICl, which accelerates the autocatalytic cycle. This double effect results in a second inflexion on the curves if 2 < pH < 3.

Table III. Component Reactions and Rate Constants Used in the Calculations

no.	reaction	k_i	k_{-i}
1	$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$	3 s^{-1}	3×10^{12} M^{-2} s^{-1}
2	$I^- + HOCl \rightarrow ICl + OH^-$	2×10^8 M^{-1} s^{-1}	
3	$ICl + H_2O \rightleftarrows HOI + Cl^- + H^+$	100 s^{-1}	1×10^6 M^{-2} s^{-1}
4	$HOI + HOCl \rightarrow HIO_2 + Cl^- + H^+$	2×10^3 M^{-1} s^{-1}	
5	$HIO_2 + HOCl \rightarrow IO_3^- + Cl^- + 2H^+$	1×10^3 M^{-1} s^{-1}	
6	$ICl + HOCl \rightarrow HOI + Cl_2$	3×10^4 M^{-1} s^{-1}	
7	$I_2 + Cl_2 \rightarrow 2ICl$	2×10^6 M^{-1} s^{-1}	
8	$HOI + ClO_2^- \rightarrow HOCl + IO_2^-$	4×10^4 M^{-1} s^{-1}	
9	$HIO_2 + ClO_2^- \rightarrow IO_3^- + HOCl$	500 M^{-1} s^{-1}	
10	$HOCl + ClO_2^- + H^+ \rightarrow Cl_2O_2 + H_2O$	1×10^4 M^{-2} s^{-1}	
11	$Cl_2 + ClO_2^- \rightarrow Cl_2O_2 + Cl^-$	2×10^3 M^{-1} s^{-1}	
12	$Cl_2O_2 + ClO_2^- \rightarrow 2ClO_2 + Cl^-$	1×10^4 M^{-1} s^{-1}	
13	$Cl_2O_2 + I_2 + 2H_2O \rightarrow 2HOCl + 2HOI$	1×10^5 M^{-1} s^{-1}	

Mechanism of the Chlorite Oxidation of Iodine. The shape of the kinetic curves indicates that just as in the case of the hypochlorous acid oxidation a "simple" and an autocatalytic path should be distinguished.

The first step is the hydrolysis of iodine; however, while in the case of hypochlorous acid iodide is oxidized, chlorite reacts with hypoiodous acid:

$$HOI + ClO_2^- \rightarrow HOCl + IO_2^- \qquad (8)$$

Iodite is oxidized further to iodate:

$$HIO_2 + ClO_2^- \rightarrow IO_3^- + HOCl \qquad (9)$$

Grant et al.[3] considered but discarded the idea that in the chlorite oxidation of iodine reactions 1 and 8 play any significant role. They argued that decreasing the concentration of iodide by adding iodate to the reaction mixture should increase the rate, but no such effect was found. Furthermore, they stated that the rate of the reaction of HOI with iodide is faster than that with chlorite. Both arguments are fallacious. First, the rate of the Dushman reaction strongly depends on the concentrations of iodide and hydrogen ions. Under the experimental conditions the rate of this reaction is so small that iodate should not influence the rate of the chlorite oxidation of iodine. Secondly, the rate constants k_{-1} and k_8 differ by many orders of magnitude indeed, but since the concentration of chlorite is much bigger than that of iodide the role of reaction 8 can be very important. Grant et al.[3] assumed the formation and reactions of the species $IClO_2$, although except for the analogy with Cl_2O_2 and I_2O_2, there is no chemical evidence to justify it. The facts that, according to our experiments, there is no spectrophotometrically observable interaction between ClO_2 and iodine either in acidic aqueous or in carbon tetrachloride solution and that leaving out all the reactions in which $IClO_2$ is

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(6) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.

involved from the Epstein–Kustin[7] mechanism of the chlorite–iodide reaction does not impair the agreement between the calculated and found periodic character of the reaction in CSTR, but even improves it, indicate that $IClO_2$ does not play a significant role. Both the autocatalytic character of the reaction and the formation of chlorine dioxide can be quantitatively described by considering the formation and reactions of Cl_2O_2, a firmly established intermediate of redox reactions involving oxyanions of chlorine.[8]

Chlorine and hypochlorous acid formed in reactions 6, 8, and 9 react with chlorite ion:

$$ClO_2^- + HOCl + H^+ \rightarrow Cl_2O_2 + H_2O \qquad (10)$$

$$ClO_2^- + Cl_2 \rightarrow Cl_2O_2 + Cl^- \qquad (11)$$

An approximation on the rate constants of (10) and (11) can be made from a kinetic study by Emmenegger and Gordon.[9] Under the given experimental conditions the most likely source of ClO_2 is the reaction of Cl_2O_2 with chlorite ion:

$$Cl_2O_2 + ClO_2^- \rightarrow 2ClO_2 + Cl^- \qquad (12)$$

The autocatalysis observed in the decrease of iodine concentration can be accounted for by the plausible reaction between Cl_2O_2 and iodine:

$$Cl_2O_2 + I_2 + 2H_2O \rightarrow 2HOCl + 2HOI \qquad (13)$$

Table III summarizes the reactions and the corresponding rate constants used in the calculation of the kinetic curves by the Gear algorithm. Most of the numerical values for the rate constants are hypothetical, but all of them are chemically reasonable. No distinction was made in the calculations between IO_2^- and HIO_2, as well as between ClO_2^- and $HClO_2$. In Figures 1–7 the calculated curves are shown as dashed lines. The agreement of the measured and calculated kinetic curves obtained for fairly broad ranges of reactant concentrations clearly indicates that the suggested mechanism is a likely one. We do believe that the formation and redox reactions of Cl_2O_2 play a crucial role in general in the unusual kinetics of reactions involving chlorite ion.

Registry No. I_2, 7553-56-2; ClO_2^-, 14998-27-7; HOCl, 7790-92-3.

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Complex Formation of Amino Polyphosphonates. 1. Potentiometric and Nuclear Magnetic Resonance Studies of Nitrilotris(methylenephosphonato) Complexes of the Alkaline-Earth-Metal Ions

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The complex formation equilibria of nitrilotris(methylenephosphonic acid) (NTMP, H_6L) with the alkaline-earth-metal ions (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) have been studied potentiometrically at 25.0 °C and at an ionic strength of 0.1 M (KNO_3). The successive protonation constants of ligand NTMP, K_n, were determined as $\log K_1 = 12.7 \pm 0.1$, $\log K_2 = 7.15 \pm 0.02$, $\log K_3 = 5.88 \pm 0.02$, $\log K_4 = 4.62 \pm 0.02$, and $\log K_5 = 1.4 \pm 0.1$. The first protonation constant K_1 was confirmed by the ^{31}P NMR chemical shift of the ligand. The complex formation constants were obtained as $\log K_{ML}$ = 7.52, 7.86, 6.52, and 6.34 (±0.02) for Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively. The first protonation constants of the complexes reveal quite large values and are in the reverse order of K_{ML} ($\log K_{MHL}$ = 9.42, 8.80, 9.41, and 9.72 (±0.02) for Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively). The second and third protonation constants are nearly equal for the four metal ions ($\log K_{MH_2L}$ = 6.10–6.16, $\log K_{MH_3L}$ = 4.8–5.1). The ^{31}P NMR spectra of the complexes have been measured in aqueous solution under the same conditions as used in the potentiometric studies. The chemical shifts of each species of H_nL and MH_mL were evaluated on the basis of the formation constants obtained potentiometrically. The ^1H and ^{13}C NMR spectra are also reported. The results of potentiometric and nuclear magnetic resonance studies suggest strongly that the first protonation of a metal complex occurs on the nitrogen atom of the ligand, with the M–N bond ruptured.

Introduction

The properties of amino polyphosphonates (APP) were first reported as early as 1949 by Schwarzenbach[1] concurrently with those of amino polycarboxylates (APC). The protonation and complex formation of alkaline-earth and transition metals with ethylenediaminetetrakis(methylenephosphonic acid) (EDTMP) and nitrilotris(methylenephosphonic acid) (NTMP) have been studied by Martell et al.[2-4] Rizkalla and Zaki[5-7] have reported the results for EDTMP and Irani et al.[8,9] and Nikitina et al.[10] for NTMP. These results show very large discrepancies. Martell[3,4] has noted that the results reported before 1976 contain a considerable degree of inaccuracy because the reagents were not pure. Other properties of NTMP and EDTMP complexes have been studied mainly by Dyatlova et al.[10,11] and other Russian investigators.[12]

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