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Unexpected Phenomena in the Mercury(II)−Chlorite Ion System: Formation and Kinetic Role of the $HgClO_2^+$ Complex

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On the basis of time-resolved spectrophotometric measurements, the formation of a novel chlorito complex, $HgClO_2^+$, was confirmed under acidic condition in the mercury(II)−chlorite ion system. The complex formation occurs within the dead time of the stopped-flow instrument applied ($\tau_d \sim 1$ ms). The stability constant of $HgClO_2^+$ was determined from the initial part of the kinetic traces recorded at the characteristic 325 nm absorbance maximum of the complex: $K = 41.7 \pm 1.9\ M^{-1}$, $\epsilon_{325} = 727 \pm 24\ M^{-1}\ cm^{-1}$ ($I = 1.0$ M ($NaClO_4$), 25.0 °C). An intense formation of chlorine dioxide was observed which is due to mercury(II)-catalyzed decomposition of chlorite ion. At longer reaction times, when most of the chlorite ion is consumed, the concentration of chlorine dioxide abruptly drops to its final value. This unique feature of the reaction is attributed to an autocatalytic redox cycle which is initiated by an electron transfer step between the coordinated chlorite ion and chlorine dioxide. The proposed mechanism postulates the formation of a Cl(II) intermediate which rapidly oxidizes both ClO_2^- and ClO_2.

Introduction

Chlorite ion[1] is well-known for its complex redox chemistry in acidic aqueous solution. It was shown before that different types of interactions may exist between chlorine(III) and metal ions.[2−15] Besides a kinetically inert complex,[7,15] $[(NH_3)_5Co(ClO_2)]^{2+}$, the formation of labile complexes was confirmed with U(VI),[2] Cu(II),[11] and Fe(III).[12] The uranyl complex is too weak and its properties could not be quantified. The stability constants and molar absorptivities of the other two species,[16] $CuClO_2^+$ and $FeClO_2^{2+}$, were determined on the basis of stopped-flow studies. While $Cu(ClO_2)^+$ is inert toward redox decomposition,[11] the formation of $FeClO_2^{2+}$ is the key reaction step in the redox cycle which leads to catalytic decomposition of chlorine(III).[12,13] The oxidation of low oxidation state metal ions by chlorine(III) typically shows complex stoichiometric and kinetic patterns.[3−6,8] Though chlorito complexes were not detected in these systems, it was assumed that some sort of association exists between the reactants and the reactions proceed via inner-sphere redox mechanisms.

Redox reactions of chlorite ion are often coupled with catalytic decomposition of this species producing chlorine dioxide which is stable under acidic condition.[17] As an exception, the disappearance of ClO_2 was found in acidic aqueous solution of chlorite ion, chlorine dioxide, and mercury(II).[18] This phenomenon was used to confirm the formation of chlorous acid as an intermediate in the oxidation of methanol with chlorate ion. On the basis of the chemical properties of oxychlorine species and Hg(II), the decay of ClO_2 is quite an unexpected phenomenon and indicates very unique features of the Hg(II)−ClO_2^-−ClO_2 system.

The observations imply that ClO_2 is involved in some sort of redox process and either oxidized to ClO_3^- or reduced to a lower oxidation state chlorine species. However, a direct involvement of Hg(II) in such a process can be excluded because it is not a strong enough oxidant to oxidize ClO_2 and it cannot be oxidized to a +III oxidation state either. This leads to the conclusion that the overall process proceeds through the formation of a so far unidentified intermediate which opens an efficient reaction path to remove ClO_2. In the present study, we report the formation of a novel chlorito complex, $HgClO_2^+$, and show that this species plays a significant role in the consumption of chlorine dioxide.

Experimental Section

Reagents. Acidic mercury(II) stock solution was prepared by adding analytical grade HgO (REANAL, Hungary) to 70% perchloric acid (Carlo Erba) in excess. The sludge was filtered after extensive stirring for 3−4 h. Excess liquid was removed by heating the mother liquor on a water bath and mercury(II) perchlorate was allowed to precipitate. The crystals were filtered off, washed with ethanol, and dissolved in dilute perchloric acid. The stock solution was purged with ozone for a brief period of time to remove any trace of Hg(I). Tests by adding concentrated NaCl solution to an aliquot of the stock solution were negative for Hg(I). Kinetic runs were identical regardless whether the samples were pretreated with ozone or not. Mercury(II) concentration was determined with an ICP-AES method by using a Spectroflame ICP instrument (Spectro GmbH, Germany). The acid content was determined by pH-metric titration with standardized NaOH solution, first converting Hg(II) into tetraiodo complex by adding excess KI to the sample. Sodium

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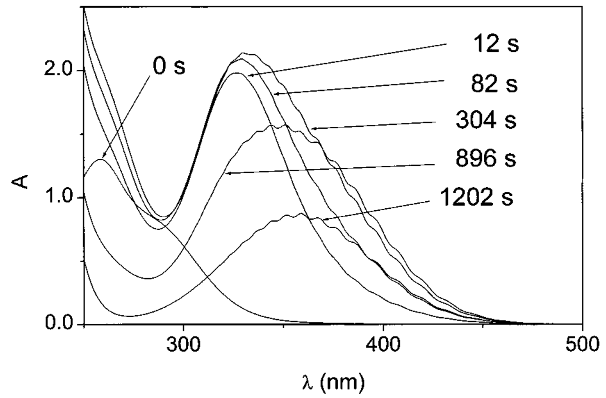

Figure 1. Characteristic spectral change as a function of time in the mercury(II)−chlorite ion reaction. $C_{Hg(II)}^0 = 0.015$ M; $C_{Cl(III)}^0 = 0.010$ M; $[H^+] = 0.025$ M; 25.0 °C; $I = 1.0$ M ($NaClO_4$).

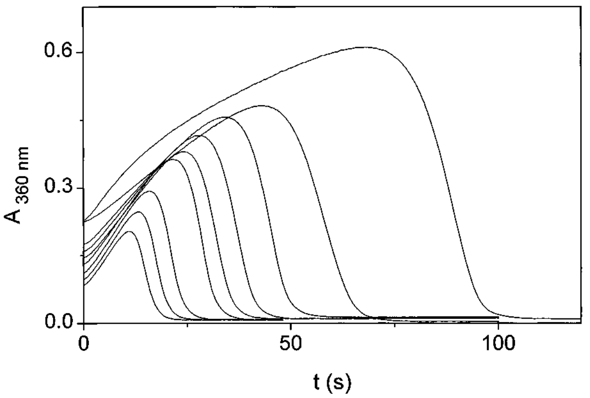

Figure 2. Stopped-flow traces as a function of acidity in the mercury(II)−chlorite ion reaction. $C_{Hg(II)}^0 = 0.030$ M; $C_{Cl(III)}^0 = 0.0050$ M; $[H^+] = 0.350, 0.300, 0.250, 0.200, 0.180, 0.160, 0.140, 0.120, 0.100$ M in the order of increasing absorbance at the maximum. 25.0 °C, $I = 1.0$ M ($NaClO_4$).

chlorite was obtained by purifying commercially available $NaClO_2$ (Fluka, 80% purity) as described earlier.[11] All other reagents were of the highest available purity. Reagent solutions and samples were prepared in doubly deionized and ultrafiltered water obtained from a MILLI-Q RG (Millipore) water purification system. Measurements were made at 25.0 ± 0.1 °C. The ionic strength was adjusted to 1.0 M with $NaClO_4$ prepared from perchloric acid and Na_2CO_3 (Reanal, Hungary).

Instrumentation and Methods. Potentiometric titrations were made with a Metrohm 721 NET Titrino system. Time-resolved spectral changes were monitored with either a HP-8543 diode array spectrophotometer equipped with an APL (Applied Photophysics) RX 2000 rapid mixer or an APL DX-17 MV sequential stopped-flow apparatus at 10 mm optical path. In the latter case, the spectra were generated from individual stopped-flow traces obtained at each 10 nm in the wavelength region studied by using the software package provided with the instrument. Fitting of the experimental data and kinetic model calculations was done with the program packages PSEQUAD[19] and SCIENTIST,[20] respectively.

Results and Discussion

In the first set of experiments, the spectra of various reaction mixtures of mercury(II), chlorite ion and chlorine dioxide were measured as a function of time by using conventional spectrophotometry. In order to prevent the precipitation of mercury hydroxide, all samples were acidified. The spectra of chlorine dioxide solutions containing mercury(II) did not change in a sealed spectrophotometric cell for several hours. Chlorine dioxide was also stable when chloride ion was added to the samples in 0.001−0.1 M concentration. When chlorite ion was added to a solution of mercury(II) and chlorine dioxide, a significant absorbance decay was observed at the characteristic absorbance band of ClO_2 ($\lambda_{max} = 360$ nm)[17] after an incubation period.

Upon mixing acidic solutions of mercury(II) and chlorite ion, first an intense absorbance increase was observed. The absorbance abruptly dropped to its final value at longer reaction times (Figure 1). One of the dominant absorbing species is chlorine dioxide in the near-UV−visible spectral region and, as a first approach, the observations correspond to the formation and subsequent decay of this species. The fine structure of the spectra and the absorbance maximum of the final spectrum at around 360 nm corroborates this assumption. Under certain conditions all chlorine dioxide, produced in the initial phase, was depleted and the reaction mixture became colorless. In other cases, the decay did not go to completion and some ClO_2 remained in the reaction mixture. Apparently, the actual course of the reaction strongly depends on the acidity, the concentrations, and concentration ratios of the reagents. When $[H^+]$ was increased, the transient amount of ClO_2 was decreased and the reaction became faster. However, as it was confirmed by stopped flow measurements, the kinetic pattern was basically the same under all conditions applied (Figure 2). The formation of chlorine dioxide is partly due to acid-catalyzed decomposition of chlorine(III) in this system. The stoichiometry and kinetics of the corresponding reactions are well established and were reported earlier.[21] Mercury(II) also catalyzes the decomposition because the initial absorbance change at the characteristic ClO_2 band became much faster by addition of Hg(II) to the samples. Subsequent decay of the absorbance implies that chlorine dioxide, which is otherwise inactive in acidic solution and in the absence of reducing agents, is an intermediate in this system.

An inspection of Figure 1 reveals that the absorbance maximum was shifted to higher wavelengths during the reaction until it reached 360 nm. Immediately after mixing the reactants, the absorbance maximum was observed at 325 nm and the characteristic fine structure of ClO_2 was not seen in the spectra. The 325 nm band cannot be assigned to Hg(II), ClO_2^-, or ClO_2, and the observations clearly confirm the formation of a novel species in the initial phase of the reaction. According to stopped-flow measurements at 400 nm, chlorine dioxide formation is relatively slow and does not interfere with spectral measurements in the first few hundred milliseconds. At longer reaction times the absorbance of ClO_2 suppresses other spectral effects.

The formation of the new species, observed as an absorbance jump at the beginning of the kinetic traces, was too fast to be monitored by the stopped-flow method ($\tau_d \sim 1$ ms). The concentration and pH dependencies of the initial absorbance change were studied at 325 nm by using the average absorbance value from the first 5−100 ms section of each stopped-flow trace. Evaluation of the data by using the Job method[22] confirmed the formation of a new species with a 1:1 stoichiometry for ClO_2^- and Hg(II). We assigned the spectral effects to the formation of the mercury(II)−chlorito complex. Ligand substitution reactions of mercury(II) are typically diffusion controlled, and the extremely fast initial absorbance change lends support to this assumption. The data were evaluated on the basis of the following equilibrium model:

$$H^+ + ClO_2^- \rightleftharpoons HClO_2 \qquad K_p = \frac{[HClO_2]}{[H^+][ClO_2^-]} \qquad (1)$$

$$Hg^{2+} + ClO_2^- \rightleftharpoons HgClO_2^+ \qquad K = \frac{[HgClO_2^+]}{[Hg^{2+}][ClO_2^-]} \quad (2)$$

The contribution of mercury(II), chlorite ion and chlorous acid to the measured absorbance is negligible at 325 nm. Provided that the acidity is constant, mercury(II) is in large excess over chlorite ion and the chlorito complex is the only absorbing species in the initial phase, the following expression applies:

$$A = \epsilon_{HgClO_2^+}[HgClO_2^+] = \epsilon_{HgClO_2^+}\frac{K'C_{Hg(II)}}{1 + K'C_{Hg(II)}}C_{Cl(III)} \quad (3)$$

where $\epsilon_{HgClO_2^-}$, K', $C_{Hg(II)}$, and $C_{Cl(III)}$ are the molar absorptivity of the complex, the pH-dependent apparent stability constant, and the total initial concentrations of mercury(II) and chlorite ion, respectively. After rearrangement, eq 3 yields

$$\frac{1}{A} = \frac{1}{\epsilon_{HgClO_2^+}C_{Cl(III)}} + \frac{1}{K'\epsilon_{HgClO_2^+}C_{Cl(III)}}\frac{1}{C_{Hg(II)}} \quad (4)$$

The data are plotted according to eq 4 in Figure 3. In the final calculations, K_p was fixed at the value reported earlier,[11] $\log K_p = 1.72$, and all experimental data were fitted simultaneously on the basis of eq 3. The results are $K = 41.7 \pm 1.9$ M^{-1} and $\epsilon_{HgClO_2^+}$ (at 325 nm) $= 727 \pm 24$ M^{-1} cm^{-1}.

Available stability constants for the chlorito complexes are collected in Table 1. As shown, mercury(II) forms about 3 and 40 times more stable complex than iron(III) and copper(II), respectively. The interpretation of these differences is not straightforward. An essential question is whether chlorite ion is coordinated via oxygen or chlorine atoms to the metal center. Structural data or, in the case of iron(III), a well-defined spectrum is not available for chlorito complexes because redox decomposition and coupled side reactions prevent thorough characterization of these species. Thus, the considerations regarding the coordination mode(s) of ClO_2^- need to be based on the comparison of the equilibrium constants.

Provided that O-coordination occurs, simple electrostatic considerations would predict the Fe(III) > Cu(II) ~ Hg(II) stability order. The deviation from this trend is a strong indication that other factors are also important. The "irregular" stability order can be justified by taking into account the hard−soft character of the metal ions. A specific interaction between the soft mercury(II) ion and the relatively soft chlorine atom may stabilize the $HgClO_2^+$ complex. Such a preference of Hg(II) toward a soft donor atom is well established in the case of mercury(II)−sulfito complexes.[23] In contrast, the soft−soft stabilization effect is very unlikely with iron(III) and copper(II) which are typical hard metal ions. Thus, the coordination mode of the ligand is not necessarily uniform in all chlorito complexes. The Cl-coordination seems to be favorable in the case of the soft mercury(II) while the O-coordination is expected to prevail in the other two complexes. These considerations are fully supported by the X-ray structure of the inert $[(NH_3)_5Co(ClO_2)][Pd(CN)_4]\cdot H_2O$ complex in which chlorite ion is coordinated to the hard cobalt(III) center via an oxygen atom.[15]

The kinetic profiles show distinct variation as a function of reagent concentration and pH. At relatively high ClO_2^- concentration, the stopped-flow traces at 360 nm feature a plateau before the absorbance decreases to its final value (Figure 4). In excess Hg(II), the absorbance increases at a growing rate in the initial phase indicating autocatalytic generation of ClO_2 (Figure 4, inset). This feature disappears on decreasing the [Hg(II)]/[Cl(III)] ratio. Concentration profiles for the $HgClO_2^+$ complex and ClO_2 were calculated from time-resolved spectra as shown in Figure 5. A comparison of these kinetic traces reveals that most likely the chlorito complex controls the reaction sequence which leads to the decay of chlorine dioxide. At constant $C_{Hg(II)}$ and pH, the actual concentration of $HgClO_2^+$ is determined by $C_{Cl(III)}$. Thus, after instantaneous formation of the complex, the concentrations of $C_{Cl(III)}$ and $[HgClO_2^+]$ decrease simultaneously. When chlorite ion is used up, the chlorito complex disappears and, as consequence, the depletion of chlorine dioxide also ceases. We propose the following kinetic model for the interpretation of the results:

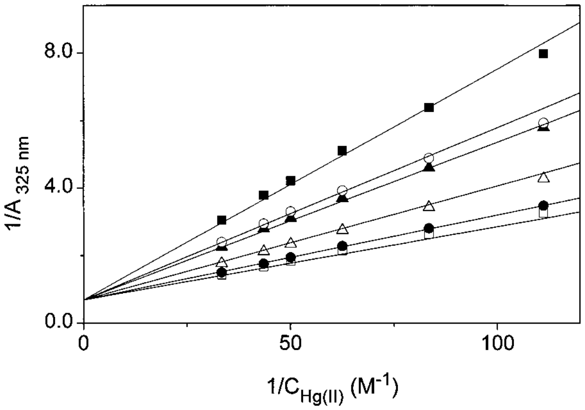

Figure 3. Plot of the absorbance according to eq 4 as a function of acidity at constant chlorite ion concentration. $C_{Cl(III)}^0 = 0.0020$ M; $[H^+] = 0.006$ M (●), 0.010 M (○), 0.020 M (▲), 0.035 M (△), 0.040 M (■), 0.060 M (□); 25.0 °C, $I = 1.0$ M ($NaClO_4$).

TABLE 1: Equilibrium Constants for the Reactions of ClO_2^- (1.0 M $NaClO_4$; 25.0 °C)

reaction	K	ref
$H^+ + ClO_2^- = HClO_2$	52.5	11
	36.3	14[a]
$Cu^{2+} + ClO_2^- = CuClO_2^+$	1.04	11
$Fe^{3+} + ClO_2^- = FeClO_2^{2+}$	13.8	12
	13.2	14[a]
$Hg^{2+} + ClO_2^- = HgClO_2^+$	41.7 ± 1.9	this work

[a] At 5.0 °C.

$$H^+ + ClO_2^- \rightleftharpoons HClO_2 \qquad \text{fast} \qquad (R1)$$

$$Hg^{2+} + ClO_2^- \rightleftharpoons HgClO_2^+ \qquad \text{fast} \qquad (R2)$$

$$ClO_2^- \rightarrow ClO_2 + ClO_3^- + Cl^- \qquad \text{slow initiation} \qquad (R3)$$

$$HgClO_2^+ + ClO_2 \rightarrow Hg^{2+} + ClO_3^- + Cl(II) \qquad \text{rate det} \qquad (R4)$$

$$ClO_2^- + Cl(II) + H^+ \rightarrow ClO_2 + HOCl \qquad \text{fast} \qquad (R5)$$

$$ClO_2 + Cl(II) \rightarrow ClO_3^- + HOCl \qquad \text{fast} \qquad (R6)$$

$$ClO_2^- + HOCl \rightarrow ClO_2 + Cl^- \ (+ ClO_3^-) \qquad \text{fast} \qquad (R7)$$

The concentration of the $HgClO_2^+$ complex, a key intermediate in this system, is controlled by (R1) and (R2) which are fast preequilibria. According to the model, chlorine dioxide is initially produced by relatively slow acid-catalyzed decomposition of chlorite ion, (R3). This reaction triggers the autocatalytic cycle and has marginal kinetic importance at longer reaction

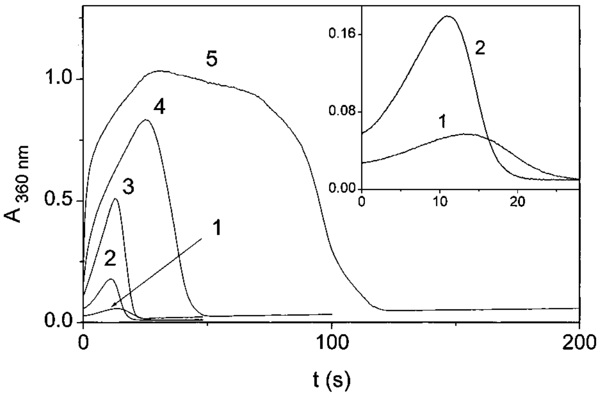

Figure 4. Stopped-flow traces as a function of chlorite ion concentration in the mercury(II)−chlorite ion reaction. $C_{\mathrm{Hg(II)}}^0 = 0.030$ M; $[\mathrm{H}^+] = 0.350$ M; $C_{\mathrm{Cl(III)}}^0 = 0.0020$ M (1), 0.0050 M (2), 0.010 M (3), 0.015 M (4), 0.020 M (5); 25.0 °C, $I = 1.0$ M ($NaClO_4$). Inset: Enlarged initial sections of traces 1 and 2.

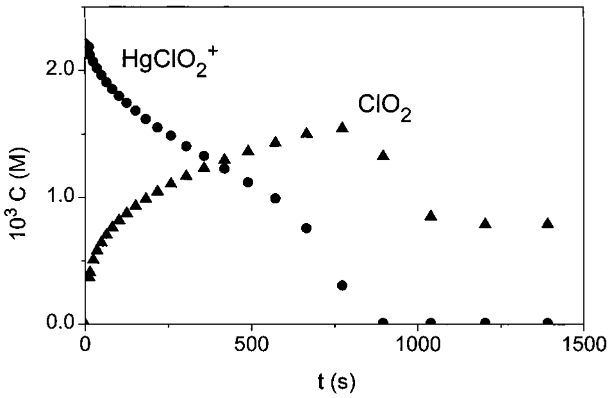

Figure 5. Kinetic profiles for $HgClO_2^+$ (●) and ClO_2 (▲) in the mercury(II)−chlorite ion reaction. $C_{\mathrm{Hg(II)}}^0 = 0.015$ M; $C_{\mathrm{Cl(III)}}^0 = 0.010$ M; $[\mathrm{H}^+] = 0.025$ M; 25.0 °C, $I = 1.0$ M ($NaClO_4$).

times. The consumption of ClO_2 occurs only when mercury(II) and chlorite ion are simultaneously present in the reaction mixture. This strongly suggests that chlorine dioxide reacts directly with the chlorito complex in the rate-determining step, (R4). Precipitation was not observed either during the reaction or when excess chloride ion was added to the reaction mixtures confirming that mercury(I) does not form in the redox process. It follows that direct involvement of Hg(II) in any redox step can be excluded and the electron transfer probably occurs between the coordinated chlorite ion and ClO_2. The model predicts the formation of a Cl(II) intermediate in step R4. The formation of Cl(II) was proposed in a few redox reactions of chlorite ion before,[4,8,13] but direct experimental evidence is not available to confirm the exact composition of this species. It can be ClO which is expected to react very rapidly with ClO_2^- (R5) and/or with other species in the system. According to pulse radiolysis studies, the lifetime of ClO is on the order of several 10 μs in aqueous solution and the second-order decay of ClO is catalyzed by ClO_2^-.[24] The product of this reaction is ClO_3^-, implying that ClO is also capable of oxidizing chlorine dioxide in a fast reaction step, (R6). The shapes of the kinetic traces are determined by the competition of chlorite ion and chlorine dioxide for the same reactive intermediate The sharp decay of ClO_2 at the end of the reaction strongly suggests that (R6) is faster than (R5). Such a competition between ClO_2^- and ClO_2 was postulated in the mechanism for the reduction of bromate ion by chlorous acid.[25] Under acidic condition, step R7 is fast and the main products are chloride ion and chlorine dioxide when chlorite ion is present in excess over hypochlorous acid.[26,27]

In model calculations, kinetic traces were simulated by assuming the simplest rate expressions for the individual steps and ignoring the pH dependence of the reaction. When an appropriate set of rate constants was selected, the calculations predicted that the ClO_2 concentration goes through a maximum as a function of time. The noted autoinhibition could also be reproduced and, similarly to the experimental observations, the maximum amount of ClO_2 increased with increasing $[ClO_2^-]$. The model appears to be less satisfactory for reproducing the exact shape of the kinetic curves. (The kinetic model and simulated kinetic traces are given in the Supporting Information.)

Quantitative evaluation of the mechanism would require thorough kinetic description of the component reactions. The complexity of reaction R7 is well documented and its kinetics and stoichiometry have been extensively studied before.[26,27] However, earlier proposed mechanisms are valid only for the slightly acidic neutral pH region and cannot be used for the conditions applied in the present study. It is open to question whether sufficient experimental information can be collected for the concentration and pH dependencies of the reaction rates and stoichiometries of steps R5, R6, and R7. Further complications may arise due to the formation of chloride ion. It forms relatively stable complexes with mercury(II) and may deactivate the catalyst.

In spite of the limitations, the proposed model provides appropriate qualitative interpretation of the results and consistent with the experimental observations. The autocatalytic nature of the overall reaction can be interpreted on the basis of the (R4)−(R6) reaction sequence. In these reaction steps, more ClO_2 is formed than consumed and (R4) becomes faster as the reaction proceeds. Because $[HgClO_2^+]$ is proportional to the total concentration of chlorite ion, eventually the autocatalytic effect is offset by the consumption of ClO_2^- in step R7. The abrupt decay of ClO_2 at the end of the reaction implies that Cl(II) oxidizes chlorine dioxide much faster than chlorite ion. Thus, as $[ClO_2^-]$ decreases the consumption of ClO_2 in step R4 becomes superior compared to its production in (R5) and (R7). Provided that sufficient kinetic information becomes available for the component reactions, the results presented here can serve as a basis to develop a detailed mechanism for the Hg(II)−ClO_2^-−ClO_2 reaction.

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Supporting Information Available: The simplified kinetic model and a figure with simulated kinetic traces. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Chlorite ion and chlorous acid are in fast equilibrium, and their concentration ratio is determined by the pH. The two species will not be distinguished in this paper and will be referred to as either chlorite ion or chlorine(III).

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