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Effect of Chloride Ion on the Kinetics and Mechanism of the Reaction between Chlorite Ion and Hypochlorous Acid

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The effect of chloride ion on the chlorine dioxide formation in the ClO_2^-−HOCl reaction was studied by following $\cdot ClO_2$ concentration spectrophotometrically at pH 5−6 in 0.5 M sodium acetate. On the basis of the earlier experimental data collected without initially added chloride and on new experiments, the earlier kinetic model was modified and extended to interpret the two series of experiments together. It was found that the chloride ion significantly increases the initial rate of $\cdot ClO_2$ formation. At the same time, the $\cdot ClO_2$ yield is increased in HOCl but decreased in ClO_2^- excess by the increase of the chloride ion concentration. The two-step hydrolysis of dissolved chlorine through $Cl_2 + H_2O \rightleftharpoons Cl_2OH^- + H^+$ and $Cl_2OH^- \rightleftharpoons HOCl + Cl^-$ and the increased reactivity of Cl_2OH^- compared to HOCl are proposed to explain these phenomena. It is reinforced that the hydrolysis of the transient Cl_2O_2 takes place through a HOCl-catalyzed step instead of the spontaneous hydrolysis. A seven-step kinetic model with six rate parameters (constants and/or ratio of constants) is proposed on the basis of the rigorous least-squares fitting of the parameters simultaneously to 129 absorbance versus time curves measured up to ∼90% conversion. The advantage of this method of evaluation is briefly outlined.

Introduction

The reaction of chlorite ion with hypochlorous acid and (at lower pH) with dissolved chlorine has important practical applications in water and wastewater treatment[1] and in pulp bleaching.[2] Beside the practical aspects, the kinetics and mechanism of the reaction is important from theoretical point of view; it has central role in the dynamics of the systematically designed chlorite-driven chemical oscillators.[3–5] The stoichiometry, kinetics, and mechanism of the ClO_2^-−HOCl reaction have therefore been the focus of interest for decades.[6–10]

Hypochlorous acid is one of the intermediates formed from chlorite ion. Therefore the products of the reaction between chlorite and hypochlorous acid (i.e., chlorine dioxide and chlorate ion) always appear in the redox reactions of chlorite ion in slightly acidic solution. The chlorate is usually a final product, but the fate of chlorine dioxide depends on the stoichiometric ratio of the reactants. It is usually a final product in chlorite excess and an intermediate in excess of the reducer because chlorine dioxide is also a strong oxidizing agent. Because of its high absorbance at 360 nm compared to other oxyhalogen species, measuring the $\cdot ClO_2$ concentration may therefore be regarded as a convenient tool for kinetic study of the redox reactions of chlorite ion. The kinetics and mehanism of the decomposition of chlorous acid[11] and the supercatalytic tetrathionate−chlorite reaction have recently been studied and interpreted in our laboratory, using the principle outlined.[12,13] The kinetic model and the appropriate rate constants for the chlorite-hypochlorous acid reaction published by Peintler et al.[14] were used as auxiliary

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data in these studies. The model suggested previously has six steps with four independent constants:

$$\mathrm{ClO_2^- + HOCl + H^+ \rightarrow Cl_2O_2 + H_2O}; \quad k_1 = 1.12\times10^6\ \mathrm{M^{-2}\ s^{-1}} \quad (1)$$

$$\mathrm{Cl_2O_2 + ClO_2^- \rightarrow 2{\cdot}ClO_2 + Cl^-}; \quad k_2: \text{see below} \quad (2)$$

$$\mathrm{2HOCl + ClO_2^- \rightarrow ClO_3^- + Cl_2 + H_2O}; \quad k_3 = 2.1\times10^3\ \mathrm{M^{-2}s^{-1}} \quad (3)$$

$$\mathrm{ClO_2^- + Cl_2 \rightarrow Cl_2O_2 + Cl^-}; \quad k_4: \text{see below} \quad (4)$$

$$\mathrm{Cl_2O_2 + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+}; \quad k_5 > 10\ \mathrm{s^{-1}}\text{(fixed)} \quad (5)$$

$$\mathrm{Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+}$$

$$v_6 = k_{f6}[\mathrm{Cl_2}] = k_{b6}[\mathrm{HOCl}][\mathrm{Cl^-}][\mathrm{H^+}] \quad (6)$$

The forward and reverse rate constants for eq 6 (k_{f6} = 11 $\mathrm{s^{-1}}$ and $k_{b6} = 1.8 \times 10^4\ \mathrm{M^{-2}\ s^{-1}}$) were taken from the work of Eigen and Kustin.[15]

Cl_2O_2 and Cl_2 are reactive intermediates, and both are involved in two different further reactions. Therefore, the ratio of these rate constants of the two pathways could only be calculated. Using the above kinetic model, $k_2/k_5 = 5.4 \times 10^4\ \mathrm{M^{-1}}$ and $k_4/k_{f6} = 3.7 \times 10^3\ \mathrm{M^{-1}}$ were calculated beside k_1 and k_3 by rigorous fitting of the parameters to the 87 experimental curves simultaneously. It should be mentioned that the third order eq 1 may be replaced by

$$\mathrm{HClO_2 + HOCl \rightarrow Cl_2O_2 + H_2O}$$

$$v_1 = k_1'[\mathrm{HClO_2}][\mathrm{HOCl}];$$

$$k_1' = K_\mathrm{d} \times k_1; \qquad K_\mathrm{d} = \frac{[\mathrm{H^+}][\mathrm{ClO_2^-}]}{[\mathrm{HClO_2}]}$$

In other words, it is hypothetically assumed that the reactive species is in fact chlorous acid instead of the chlorite ion.

To our best knowledge, it was the first attempt of the rigorous, simultaneous fitting of all experimental curves to calculate rate constants of a complex kinetic system. The general interest of the ClO_2^-−HOCl reaction and the slow spreading of the rigorous, simultaneous evaluation of the kinetic experiments explains that this publication has received more than 60 independent citations. The general approach of the evaluation of the kinetic experiments is still the fitting of the individual curves and to analyze the parameters calculated as a function of the initial concentrations, in spite of the significant advances in computing power. We have recently proved, however, that the individual evaluation of the kinetic curves may lead to inherent pitfalls in complex kinetic systems.[16]

The last two decades have witnessed the publication of several new aspects on the kinetics and mechanism of the ClO_2^-−HOCl reaction. These new results make the reinvestigation of the system necessary to modify and to extend the basic core of the kinetic model proposed 20 years ago. We shall mainly focus on five important issues: the interpretation of the third order process[17] (eq 3), the formation of chlorate[18] from Cl_2O_2, the unusually high yield[19] of $\cdot ClO_2$, the effect of chloride ion,[20] and the further reaction of $\cdot ClO_2$ with hypochlorite ion.[21]

The second order dependence of the rate on [HOCl] in eq 3 was originally explained by assuming a weak hydrogen-bonded association between ClO_2^- and HOCl, followed by its reaction with HOCl. Beach and Margerum,[22] however, have determined the equilibrium as well as the forward rate constant of the formation of Cl_2O in aqueous solution of HOCl.

$$\mathrm{2HOCl \rightleftharpoons Cl_2O + H_2O} \quad (7)$$

The equilibrium constant, the forward rate constants for the uncatalyzed, and acetic acid catalyzed pathways are 1.15 × $10^{-2}\ \mathrm{M^{-1}}$, 0.12 $\mathrm{M^{-1}\ s^{-1}}$, and 280 $\mathrm{M^{-2}\ s^{-1}}$, respectively. Fábián and Gordon[17] proposed an alternative interpretation of the second order dependence of [HOCl] in eq 3 by assuming that the reactive intermediate is Cl_2O instead of a hydrogen-bonded association. Their interpretation seems to be more plausible than ours, but it has no effect on the fitting because eq 7 is in fact a fast preequilibrium through the acetic acid catalyzed pathway. In other words, k_3 may be replaced by $k'_3 = k_3 \times 0.0115$ if eq 3 is replaced by the reaction of chlorite with dichlorine oxide.

Gordon and Takiyashiki[18] studied the reaction in 0.1 M phosphate buffer at pH 6−10, where the main product is chlorate. They proposed fast preequilibrium instead of the irreversible eq 1, and the step

$$\mathrm{Cl_2O_2 + HOCl \rightarrow ClO_3^- + Cl_2 + H^+} \quad (8)$$

instead of the spontaneous, first-order hydrolysis of Cl_2O_2 (eq 5).

Jia et al.[19] investigated the process in phosphate buffer at pH 5.5−7.5 and in 1:1 acetate/acetic acid buffer at 1.0 M ($NaClO_4$) ionic strength and at large chlorite excess, where the pseudofirst order condition applies. According to them, the reactive species is the chlorite ion and the Cl_2O_2 is formed through a general acid-catalyzed pathway, as follows:

$$\mathrm{HOCl + ClO_2^- \rightleftharpoons HOClOClO^-} \quad (9)$$

$$\mathrm{HOClOClO^- + HA \rightarrow Cl_2O_2 + H_2O + A^-} \quad (10)$$

They assumed that further reactions of Cl_2O_2 are eq 2, and the OH^- and A^- assisted formation of ClO_3^- and Cl^-

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instead of the spontaneous hydrolysis (eq 5). Moreover, they found that acetate ion accelerates the formation of $\cdot ClO_2$ enormously. It was interpreted by a steady-state formation and further reactions of acetyl hypochlorite. They found moreover, that in some cases, when HOCl was the limiting reagent, greater than 100% of $\cdot ClO_2$ was formed even if the

$$HOCl + 2ClO_2^- + H^+ \rightarrow 2\cdot ClO_2 + H_2O + Cl^- \qquad (11)$$

stoichiometry was assumed. This finding was interpreted by partial transformation of the excess ClO_2^- into HOCl according to the step

$$Cl_2O_2 + ClO_2^- + H_2O \rightarrow 2HOCl + ClO_3^- \qquad (12)$$

Later on, we have also found it to be a crucial step in the kinetic model of the decomposition of chlorous acid.[11]

It was found that the—in principle sluggish—chloride ion is also an active species in many steps of the redox reactions of the chlorite ion.[11-13] Nicoson and Margerum have also studied the kinetics and mechanism of the reaction of chlorine with chlorite ion in presence of chloride ion and in acetic acid/acetate buffer.[20] The background chloride ion concentration was—in general—1 M, but it was replaced by acetate ion in some experiments up to 0.5 M. The chloride ion did not appear on the reagent side of the proposed mechanism. Its effect was interpreted through the

$$Cl_2 + Cl^- \rightleftharpoons Cl_3^- \qquad (13)$$

and eq 6 equilibrium.

Csordás et al.[21] investigated the interaction between chlorine dioxide and hypochlorite ion at pH 6.5−10.5 and at 1.0 M ($NaClO_4$) ionic strength. Their interesting result is that hypochlorite reacts with chlorine dioxide at lower pH according to the

$$ClO^- + 2\cdot ClO_2 \rightarrow 2ClO_3^- + Cl^- + 2H^+ \qquad (14)$$

stoichiometry, and catalyzes the decomposition of $\cdot ClO_2$

$$2\cdot ClO_2 + H_2O = ClO_3^- + ClO_2^- + 2H^+ \qquad (15)$$

above pH 9. Finally, in a longer period, ClO_2^- reacts with OCl^-, producing Cl^- and ClO_3^-, that is, eventually the stoichiometry given in eq 14 will be established at high pH, too.

Yin and Ni have thoroughly studied many practical aspects of $\cdot ClO_2$ generation.[23-25] They found that the initial rate significantly increases if chloride is added to the initial solution. At 2:1 $[ClO_2^-]_0/[HOCl]_0$ concentration ratio the initial rate is given by the equation

$$\frac{d[\cdot ClO_2]}{dt} = (k_1 + k'_1[Cl^-])[ClO_2^-][HOCl][H^+] \qquad (16)$$

with $k_1 = 1.2 \times 10^{6}\ M^{-2}\ s^{-1}$ and $k'_1 = 1.1 \times 10^{9}\ M^{-3}\ s^{-1}$ at 25 °C, $I = 0.2$ M NaAc. According to these data, 0.001 M initial chloride concentration increases the initial rate by a factor of 2. Another important finding of the authors is that no chlorine dioxide is formed in 4.5 M sulfuric acid in the absence of added chloride ion.[25]

In the light of new results, we were prompted to carry out new experiments on the system in presence of chloride ion and re-evaluate the earlier and new experiments together. Our aim is to check the newly proposed steps and to reveal the effect of chloride ion on the ClO_2^-−HOCl reaction not only under pseudofirst order condition or at fixed initial concentration ratio of the reactant but also in a wide ratio of the reagent concentrations. At the same time, the whole set of kinetic curves are evaluated simultaneously, instead of the usual simplified calculation.

Experimental Section

Reagents. Commercially available (Sigma-Aldrich) sodium chlorite was purified and recrystallized as described previously.[14] The chlorite content of the purified compound was checked by standard iodometric titration and found to be 99.5%. No chloride impurities could be detected in the purified sodium chlorite. The hypochlorous acid solution was freshly prepared by dissolving chlorine gas in a slurry of yellow HgO in distilled water and distilling the solution from the HgO. All other chemicals (sodium chloride, sodium acetate, acetic acid) were of the highest purity commercially available. The stock solutions were freshly prepared for each series of experiments.

Methods

All kinetic runs were carried out in 0.5 M sodium acetate, with the pH of solutions regulated between 5 and 6 by adding the necessary amount of acetic acid ($pK_d^{HAc} = 4.55$). The temperature was adjusted to 25.0 ± 0.1 °C. Solutions for the kinetic runs were prepared in a 10 mm quartz cuvette equipped with Teflon stopper and a magnetic stirrer. The last component (HOCl stock solution in 0.5 M NaAC) was introduced from a fast delivery pipet just before the cuvette was closed. The total volume of the solution was 3.2 cm^3 to minimize the air above the solution. By this setup, less than 0.5% of the $\cdot ClO_2$ evolved could escape from the solution.

The reaction was followed by Zeiss S10 diode-array UV−vis spectrophotometer at the visible range. Absorbance measured at 360 nm was used to evaluate the kinetic traces, where chlorine dioxide has a strong absorption maximum ($\varepsilon_{\cdot ClO_2} = 1250\ M^{-1}\ cm^{-1}$), but weak absorbances of hypochlorous acid ($\varepsilon_{HOCl} = 7.0\ M^{-1}\ cm^{-1}$) and chlorite ($\varepsilon_{ClO_2^-} = 2.0\ M^{-1}\ cm^{-1}$) were also taken into consideration during the calculation process. Twenty-one experimental curves were recorded at $[ClO_2^-] = 4.74$ mM and $[HOCl] = 0.15$ mM, at three pH values (5.25, 5.55, 5.95), and at each pH at seven different chloride concentrations in the range of 0.0−10.00 mM. In an other series of experiments, the pH values and the chloride concentrations were the same but HOCl was in excess, that is, $[ClO_2^-] = 0.568$ mM, $[HOCl] = 3.00$ mM.

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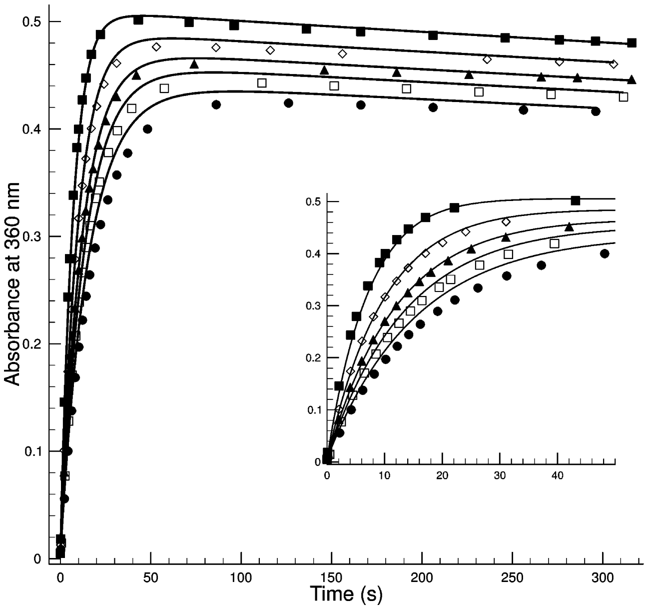

Figure 1. Measured (symbols) and calculated (solid lines) absorbances as a function of the initial chloride concentration in HOCl excess. $[HOCl]_0 = 3.00$ mM, $[ClO_2^-]_0 = 0.568$ mM, pH 5.55; $[Cl^-]_0$ (mM) = 0 (•), 1.0 (□), 2.0 (▲), 4.0 (◆), 8.0 (■). To see the trends better, the inset shows the measured and calculated absorbances at the beginning of the reaction.

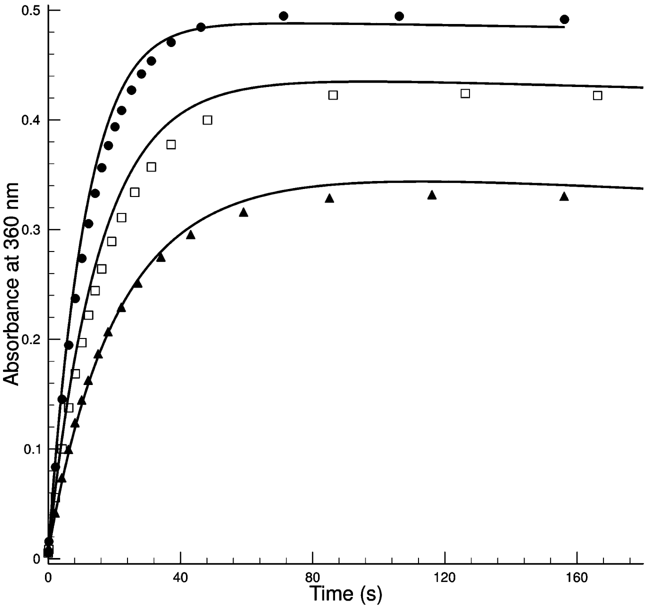

Figure 3. Measured (symbols) and calculated (solid lines) absorbances at different pH in HOCl excess. $[HOCl]_0 = 3.00$ mM, $[ClO_2^-]_0 = 0.568$ mM, $[Cl^-]_0 = 4.0$ mM, pH 5.95 (▲), 5.55 (□), 5.25 (•).

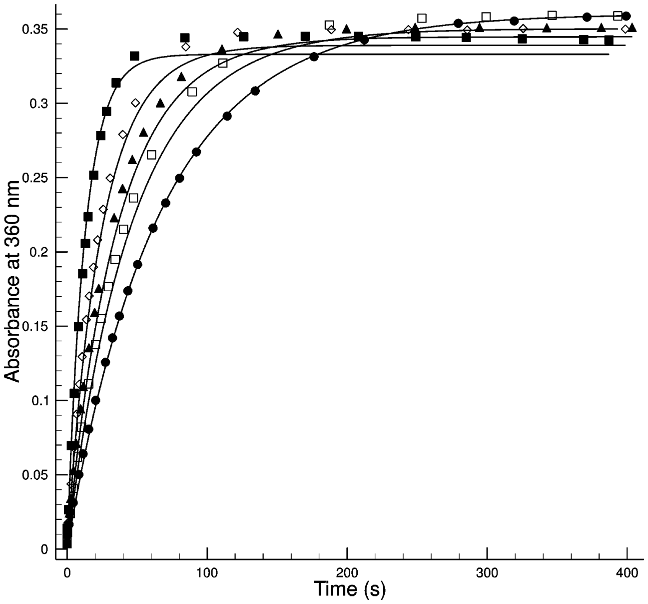

Figure 2. Measured (symbols) and calculated (solid lines) absorbances at different initial chloride concentrations in ClO_2^- excess. $[HOCl]_0 = 0.15$ mM, $[ClO_2^-]_0 = 4.74$ mM, pH 5.25; $[Cl^-]_0$ (mM) = 0 (•), 1.0 (□), 2.0 (▲), 4.0 (◆), 10.0 (■).

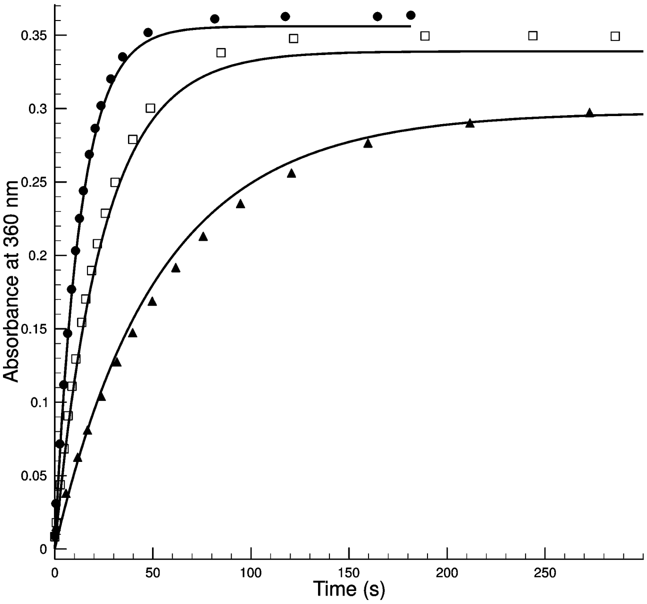

Figure 4. Measured (symbols) and calculated (solid lines) absorbances at different pH in ClO_2^- excess. $[HOCl]_0 = 0.15$ mM, $[ClO_2^-]_0 = 4.74$ mM, $[Cl^-]_0 = 4.0$ mM, pH 5.95 (▲), 5.55 (□), 5.25 (•).

Results

The new experimental results are illustrated in Figures 1–4. It is seen in Figure 1 that the increasing initial chloride concentration significantly increases the rate and the yield of $\cdot ClO_2$ formation in HOCl excess. Note, that after reaching the maximum, $[\cdot ClO_2]$ slightly decreases. The maximum absorbance, assuming

$$HOCl + 2ClO_2^- + H^+ \rightarrow 2\cdot ClO_2 + Cl^- + H_2O \quad (17)$$

stoichiometry, would be 0.73 at 360 nm, and the actual maximum is only 70% of that. Figure 2 illustrates again the significant increasing effect of the initial chloride concentration on the rate of the $\cdot ClO_2$ formation. It is seen moreover that, contrary to Figure 1, the $\cdot ClO_2$ yield slightly decreases with increasing initial chloride concentration. Note that the maximum absorbance under the given concentration would be 0.384, and the experimental curves are approaching this value at $[Cl^-]_0 = 0$ M only. Figures 3–4 show that the increase of pH shifts the reaction in the direction of formation of ClO_3^- instead of $\cdot ClO_2$.

Building up the Kinetic Model. The experimental data were evaluated by the program package *ZiTa*.[26] The earliest version of this program was also used to evaluate those 87 experimental curves that were used to set up the model given by eqs 1−6 in the Introduction. That model was in perfect harmony with the experimental findings, including the initial rates, the changing stoichiometry, and reaction order with the change of the $[HOCl]_0/[ClO_2^-]_0$ concentration ratio and pH (Figures 1−4 in ref 14). The earliest version of the program package was not able to take into account the slight pH change in buffered solution. Besides, it could fit only concentrations and it was assumed that $\cdot ClO_2$ is the only absorbing species at 360 nm. The newest version of the program is able to evaluate practically all types of kinetic experiments, taking into account the possible fast equilibria and preequilibria, the stoichiometric constraint, and any measured experimental data that can be calculated from the concentrations, without any constraint on the number of experiments and experimental points.

As a first step, the earlier data were evaluated by fitting the relative deviation of the measured and calculated absorbances, taking into account the weak absorbance of the reactants at 360 nm and the following fast equilibria:

$$HAc \rightleftharpoons H^+ + Ac^-; \quad pK_d^{HAc} = 4.55 \tag{18}$$

$$HOCl \rightleftharpoons H^+ + OCl^-; \quad pK_d^{HOCl} = 7.40 \tag{19}$$

and

$$HClO_2 \rightleftharpoons H^+ + ClO_2^-; \quad pK_d^{HClO_2} = 1.74 \tag{20}$$

Besides, the earlier model was slightly modified by replacing eq 1 with eq 20 and

$$HClO_2 + HOCl \rightarrow Cl_2O_2 + H_2O \tag{21}$$

Eq 3 was replaced by the preequilibrium

$$2HOCl \rightleftharpoons Cl_2O + H_2O \tag{22}$$

and by the reaction

$$Cl_2O + ClO_2^- \rightarrow Cl_2 + ClO_3^- \tag{23}$$

The function to be minimized by fitting the rate constants is defined as

$$s = \sum_{i=1}^{N} \sum_{j=1}^{p_i} [(A_{ij}^e - A_{ij}^c)/A_{i,\max}^e]^2$$

where N is the number of experimental curves (87), p_i = the number of measured absorbance in the ith experimental curve, A_{ij}^e and A_{ij}^c are the experimentally measured and the calculated absorbances at the jth point of the ith experimental curve, and $A_{i,\max}^e$ is the maximum change of absorbance in experiment i. The weighing of the curves by the reciprocal of the maximum of the measured absorbance is important because this value changed by more than 1 order of magnitude. The weighing means that all of the curves have similar influence on the average deviation, which may be interpreted in this way as percentage. The model provided practically the same average deviation, which was calculated by the earliest version of *ZiTa*.

As a next step of the evaluation, we included those experiments from the present work in which no chloride was added to the initial solutions. The average deviation slightly decreased, which justifies the possibility of simultaneous evaluation of the earlier and present experiments. Then, we systematically checked the role of the steps suggested since the publication of the model eqs 1–6.

It turned out that the eq 1 is not reversible. More specifically, the rate in reverse direction is much slower than the further transformation of Cl_2O_2. However, the replacement of the spontaneous hydrolysis of Cl_2O_2 (eq 5) by eq 8 significantly improved the fitting. Note that eq 8 along with eq 6 is in fact a HOCl-catalyzed hydrolytic disproportionation of Cl_2O_2 because the fast hydrolysis of Cl_2 produces HOCl back. Including

$$2\cdot ClO_2 + OCl^- + H_2O \rightarrow 2ClO_3^- + Cl^- + 2H^+ \tag{24}$$

stoichiometry with a rate equation to be first order with respect of both chlorine dioxide and hypochlorite ion, according to Csordás et al.,[21] is also justified by the improvement of the fitting.

The next step of building up the model was to include all of the new experiments. The number of directly measured data were reduced to have approximately the same number of data from the new as from the earlier experiments. Then, we started a systematic search for the Cl^--catalyzed steps. As the presence of initial chloride increases the role of chlorine, its possible further reactions were also systematically checked. It turned out that replacing eq 4 by

$$Cl_2 + HClO_2 \rightarrow Cl_2O_2 + Cl^- + H^+ \tag{25}$$

significantly decreases the average deviation. If both processes (eqs 4 and 25) are taken into account, then the further improvement is less than 4%, that is, keeping eq 4 in the model is not justified on computational basis. Two further steps were found to be sufficient to describe all of the earlier and present experiments, namely:

$$ClO_2^- + HOCl \rightarrow ClO_3^- + Cl^- + H^+$$

$$v = k[HOCl][ClO_2^-][Cl^-]$$

and

$$HOCl + HClO_2 \rightarrow Cl_2O_2 + H_2O$$

$$v = k[HOCl][HClO_2][Cl^-]$$

The average deviation between the measured and calculated absorbances at 1782 experimental points of 129 curves is 3.43%. The proposed kinetic model contains the protonation equilibria 18−20 with the given data and the following steps:

$$2HOCl \overset{fast}{\rightleftharpoons} Cl_2O + H_2O; \quad K_{eq} = 0.0115\ M^{-1} \tag{E1}$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+; \quad K_{eq} = 6.1 \times 10^{-4}\ M^2 \tag{E2}$$

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$$HOCl + HClO_2 \rightarrow Cl_2O_2 + H_2O$$

$$v_1 = k_{r1}[HOCl][HClO_2] + k'_{r1}[HOCl][HClO_2][Cl^-] \quad (R1)$$

$$Cl_2 + HClO_2 \rightarrow Cl_2O_2 + Cl^- + H^+$$

$$v_2 = k_{r2}[Cl_2][HClO_2] \quad (R2)$$

$$Cl_2O_2 + ClO_2^- \rightarrow 2\cdot ClO_2 + Cl^-$$

$$v_3 = k_{r3}[Cl_2O_2][ClO_2^-] \quad (R3)$$

$$Cl_2O_2 + HOCl \rightarrow Cl_2 + ClO_3^- + H^+$$

$$v_4 = k_{r4}[Cl_2O_2][HOCl] \quad (R4)$$

$$C1_2O + ClO_2^- \rightarrow C1_2 + C1O_3^-$$

$$v_5 = k_{r5}[Cl_2O][ClO_2^-] \quad (R5)$$

$$ClO_2^- + HOCl \rightarrow ClO_3^- + Cl^- + H^+$$

$$v_6 = k_{r6}[ClO_2^-][HOCl][Cl^-] \quad (R6)$$

$$\cdot ClO_2 + OCl^- \rightarrow \cdot Cl_2O_3^-$$

$$v_7 = k_{r7}[\cdot ClO_2][OCl^-] \quad (R7)$$

$$\cdot ClO_2 + \cdot Cl_2O_3^- + H_2O \xrightarrow{\text{fast}} Cl^- + 2H^+ + 2ClO_3^-$$

The rate constants calculated are collected in Table 1. The increase of the average deviation (column 2) if the given step is omitted, and the others are fitted characterizes the importance of the step in the model. Note, that if k_3 is zero then this calculation becomes pointless, because no $\cdot ClO_2$ is formed at all. Equilibrium E1 was taken to be fast, because it is catalyzed by HAc and H^+.[22]

Discussion

It is interesting that the model contains two different initial steps (k_{r1} and k_{r5}) between the species present in the reactant solutions in absence of added chloride. In chlorite excess k'_{r1} dominates and drives the reaction almost exclusively. The presence of chloride opens three more initial steps (k_{r1}, k_{r2}, and k_{r6}). k'_{r1} and k_{r2} are responsible for the increasing initial rate and k_{r6} for the decreasing yield of $\cdot ClO_2$ in chlorite excess. Cl_2O_2 is a reactive intermediate; it is formed in three and consumed in two steps. As usual, only the ratio of the rate constants of the consuming steps can be calculated. k_{r4} was fixed at 10^4 M^{-1} s^{-1} but any value above 10^3 M^{-1} s^{-1} leads to the same k_{r3}/k_{r4} ratio. Cl_2 is also a reactive intermediate, taking place in E2 and R2 processes, which is why the k_{r2}/k_{f6} ratio is given in the Table. k_{r7} is responsible for the slight decrease of $\cdot ClO_2$ illustrated in Figure 1. Without k_{r7}, the visible decrease of $\cdot ClO_2$ in Figure 1 would be fitted by a horizontal line. The most interesting steps are the chloride-catalyzed ones (k'_{r1} and k_{r6}). Both are appearing when HOCl is one of the reactant. For the interpretation of the chloride catalysis, we should start from the plausible assumption of Eigen and Kustin, that the hydrolysis of chlorine in fact is a two-step process, namely:

Table 1. Rate Constants of the Kinetic Model[a]

rate constant	average deviation (%)	literature
$k_{r1} = (1.91 \pm 0.01) \times 10^4$ M^{-1} s^{-1}	22.8	2.3×10^4 (ref 24), 10^5 (ref 17)
$k'_{r1} = (7.8 \pm 0.4) \times 10^6$ M^{-2} s^{-1}	8.5	2.1×10^7 (ref 24)
$k_{r2}/k_{f6} = (6.6 \pm 0.2) \times 10^4$ M^{-1}	11.4	
$k_{r3}/k_{r4} = 41 \pm 2$		
$k_{r4} = 10^4$ M^{-1} s^{-1} (fixed)	5.0	
$k_{r5} = (1.4 \pm 0.1) \times 10^5$ M^{-1} s^{-1}	7.9	
$k_{r6} = (1.8 \pm 0.1) \times 10^2$ M^{-2} s^{-1}	5.3	
$k_{r7} = 3.5 \pm 0.3$ M^{-1} s^{-1}	4.2	0.91 (ref 21)

[a] Note that the second column contains the average deviation in percent if the given step is omitted from the model.

$$Cl_2 + H_2O \rightleftharpoons Cl_2OH^- + H^+ \quad (R8)$$

$$Cl_2OH^- \rightleftharpoons HOCl + Cl^- \quad (R9)$$

It is easy to realize that if $k_{f6} = k_{r8} = 11$ s^{-1}, $k_{b6} = k_{-r9} = 1.8 \times 10^{4}$ M^{-1} s^{-1} and $k_{-r8} = k_{r9} > 10^{5}$ then the result is equivalent with process E2 from equilibrium and kinetic aspects too, but an intermediate with very low concentration appears in the system. Assuming Cl_2OH^- to be the reacting species, the third-order $v'_1 = k'_1$ $[HClO_2][HOCl][Cl^-]$ equation can be replaced by $v'_1 = k'_1 K_{eq}^{R9}$ $[HClO_2][Cl_2OH^-]$. Similar transformation applies for k_{r6}. It seems to be a reasonable assumption that these equilibria and the increased reactivity of Cl_2OH^- are responsible for the appearance of chloride catalysis in this and in many other redox reactions of the oxychlorine species. As chloride ion is one of the product of the reaction, it is in fact an autocatalyst. The difference between the rate of the uncatalyzed and autocatalyzed path is not very high, thus the typical autocatalytic feature of the product formation does not appear on the experimental curves. Numerical calculations showed, however, that it may appear at higher (>0.1 M) initial concentrations in stopped-flow time scale. It should be stressed again that all the effects of the chloride ion are due to the shift of eq 6, which is decomposed to eqs R8 and R9 introducing Cl_2OH^-.

Four comparable data is found in Table 1 from the literature. Taking into account the basically different experimental conditions, the agreements are satisfactory. Many other thermodynamically and stoichiometrically conceivable kinetic steps were checked. None of them decreased the average deviation by more than 5% and seven of them decreased it in between 1−5%. When all the seven reactions were added to the model, the least-squares fit improved to 2.98%, and rate constants for the following three processes could be calculated with acceptable standard error:

$$Cl_2O_2 + HClO_2 \rightarrow 2\cdot ClO_2 + H^+ + Cl^-;$$

$$k_{r10} = (1.5 \pm 0.1) \times 10^9\ M^{-1}s^{-1} \quad (R10)$$

$$ClO_2^- + Cl_2 \rightarrow Cl^- + Cl_2O_2;$$

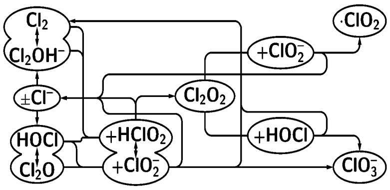
$$k_{r11} = (1.3 \pm 0.1) \times 10^5\ M^{-1}\ s^{-1} \quad (R11)$$

$$ClO_2^- + Cl_2O_2 + H_2O \rightarrow 2HOCl + ClO_3^-;$$

$$k_{r12} = (1.2 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1} \quad (R12)$$

Note, however, that reactive intermediates (Cl_2 or Cl_2O_2) are involved in all the three steps, thus the data calculated

Scheme 1



are in fact $k_{r10}/k_{r4} = 1.5 \times 10^5$; $k_{r12}/k_{r4} = 1.2$ and $k_{r11}/k_{f6} = 1.2 \times 10^4$ M^{-1}. As the inclusion of three further steps decreases the average deviation by 13% only, and the elimination of any of the remaining steps in the proposed model increases it by at least 22% (R7, Table 1), the above steps are not part of the proposed mechanism. They should be regarded as tentative steps meaning that their effect cannot be excluded, but they may play decisive role only under basically different conditions. It should be mentioned that eq R12 is responsible for the unusually high yield (>100%) of $\cdot ClO_2$. No direct experimental evidence is found in our data for this phenomenon; however, the inclusion of step R12 into the model decreases the average deviation from 3.43 to 3.30%. Furthermore, it should be noted that neither the spontaneous nor the OH $^-$ assisted hydrolysis of Cl_2O_2 can be included into the model by least-squares fitting. Scheme 1 provides a visual representation of the model proposed that may help to comprehend it more easily.

The model presented does not contain any general acid catalyzed path. As the acetate concentration, therefore the [H$^+$]/[HAc] concentration ratio was kept constant in all of our experiments, they do not provide any basis to distinguish between the specific and general acid catalysis. We will continue our efforts to unravel the role of the general and specific acid catalysis in as wide ratio of initial concentrations as was used before and in this work.

It is assumed in the model that in all the processes of Cl_2O_2 formation one of the reactive species is $HClO_2$. This assumption is in accord with the general tendency that the protonated oxyhalogen species are much more reactive than the corresponding ions due to the decrease of the bond-order of one of the halogen-oxygen bonds by protonation. This principle was the basis of working out an algorithm to design 24 new propagating acidity fronts.[27] As it is mentioned in the Introduction, Jia et al.[19] assumed ClO_2^- to be the reactive species in the rate-determining step (eq 9). It should be noted that our results do not exclude this possibility. If we assume that the transient $OClOClOH^-$ reacts with an acid directly and through a chloride catalyzed path

$$ClO_2^- + HOCl \overset{\text{fast}}{\rightleftharpoons} OClOClOH^- \qquad (R13)$$

$$OClOClOH^- + H^+ \rightarrow Cl_2O_2 + H_2O \qquad (R14)$$

$$v_{14} = k_{r14}[OClOClOH^-][H^+] + k'_{r14}[OClOClOH^-][H^+][Cl^-]$$

then the rate equations of eq R1 may be transformed into a kinetically equivalent steps as follows:

$$v_1 = v_{14} = \frac{K_{eq}^{R13} k_{r14}}{K_d^{HClO_2}}[HOCl][HClO_2] + \frac{K_{eq}^{R13} k'_{r14}}{K_d^{HClO_2}}[HOCl][HClO_2][Cl^-] \qquad (R15)$$

that is,

$$k_{r1} = \frac{K_{eq}^{R13} k_{r14}}{K_d^{HClO_2}}; \quad k'_{r1} = \frac{K_{eq}^{R13} k'_{r14}}{K_d^{HClO_2}}$$

It means that − on a computational basis − no unequivocal answer can be given to the question whether $HClO_2$ or ClO_2^- is the reactive species in the decisive initial steps. Taking into account the plausible interpretation of the chloride catalysis through Cl_2OH^- and the well-known increased reactivity of the protonated oxyhalogen species, we are inclined to suggest that $HClO_2$ reacts in the first, rate-determining steps. Further work is in progress in our laboratory to answer the yet open questions.

Conclusion

The practically and theoretically important, therefore thoroughly studied ClO_2^-−HOCl reaction was reinvestigated to revise our earlier mechanism and supplement it with the chloride ion concentration dependence of the $\cdot ClO_2$ formation in the pH range 5−6 in a wide concentration range and at an ionic strength of 0.5 M sodium acetate. An improved version of our program package, which is able to take into account the fast pre-equilibria and any measured parameter that can be calculated from the concentrations without restriction concerning the number of experiments and experimental points was used in the rigorous least-squares fitting of the kinetic parameters. A systematic search for the best fitting model revealed that the presence of chloride ion profoundly increases the initial rate and the yield of $\cdot ClO_2$ in HOCl excess. It turned out, moreover that − in presence of chloride, which increases the Cl_2 concentration − $HClO_2$ takes over the role of ClO_2^- in the reaction with chlorine. All of these features are explained by taking into account that the hydrolysis of chlorine is in fact a two-step equilibrium involving Cl_2OH^- in low concentration.

The questions still open regarding the kinetic model of the reaction are briefly outlined. It should be stressed again, that the presented results are due to the practically unlimited possibilities of our program *ZiTa*. Its use prevents us from being trapped in the possible pitfalls, which may inherently occur if the kinetic curves are analyzed individually.

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