High Performance Liquid Chromatography Study on the Kinetics and Mechanism of Chlorite-Thiosulfate Reaction in Slightly Alkaline Medium

6 AUTHORS, INCLUDING:

Li Xu
University of Pécs
8 PUBLICATIONS **41** CITATIONS

SEE PROFILE

Attila K Horváth
University of Pécs
54 PUBLICATIONS **534** CITATIONS

SEE PROFILE

Chen Ji
China University of Mining Technology
9 PUBLICATIONS **35** CITATIONS

SEE PROFILE

Qingyu Gao
China University of Mining Technology
**80** PUBLICATIONS **413** CITATIONS

SEE PROFILE

High Performance Liquid Chromatography Study on the Kinetics and Mechanism of Chlorite−Thiosulfate Reaction in Slightly Alkaline Medium

Li Xu,[†] Attila K. Horváth,*,[‡] Ying Hu,[†] Chen Ji,[†] Yuemin Zhao,[†] and Qingyu Gao*,[†]

[†]College of Chemical Engineering, China University Mining and Technology, Xuzhou, 221116, People's Republic of China
[‡]Department of Inorganic Chemistry, University of Pécs, Ifjúság útja 6., H-7624 Hungary

ABSTRACT: Chlorite−thiosulfate reaction was studied by high performance liquid chromatography under slightly alkaline solution by monitoring the concentration of thiosulfate and tetrathionate simultaneously during the course of reaction. It is demonstrated that various polythionates are formed and the composition of polythionates mainly depends on pH. Initial rate studies have revealed that the formal kinetic order of hydrogen ion is unambiguously unity but that of chlorite ion is significantly larger, while that of thiosulfate is lower than one. A 10-step kinetic model is proposed with seven fitted and three fixed parameters by simultaneous evaluation of kinetic data taking all the important characteristics of the measured kinetic curves into account. It is also enlightened that higher formal kinetic order of chlorite and lower kinetic order of thiosulfate than unity is an inherent feature of the system and may explain the systematic deviation between the measured and the calculated data encountered in previous studies.
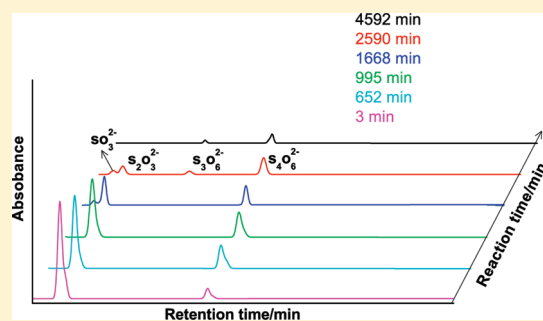
■ INTRODUCTION

Chlorite−thiosulfate reaction exhibits the most exotic dynamical feature, such as autocatalysis under batch conditions,[1] bistability, oscillations[1] or complex periodic and aperiodic (chaotic) behavior[2,3] in a continuously stirred tank reactor (CSTR) and appearance of different kinds of reaction-diffusion patterns (chemical waves and chemical reaction fronts) in unstirred system.[4−7] So far, no attempt has been made to unravel the detailed mechanism of this reaction due to its complexity. The main intermediates such as hypochlorous acid, tetrathionate, and chlorine dioxide react not only with the reactants, but also with each other, making the mechanism particularly complicated. To unravel the kinetics and mechanism of the chlorite−thiosulfate reaction it is therefore highly recommended to elucidate the kinetics of the subsystems of the parent reaction. A comprehensive survey of literature has revealed that kinetics and mechanisms of several conceivable subsystems of the chlorite−thiosulfate reaction[8,9] have already been investigated such as the hypochlorous acid−chlorite,[10−12] hypochlorous acid−thiosulfate,[13] hypochlorous acid−tetrathionate,[14,15] thiosulfate−chlorine dioxide,[16] tetrathionate−chlorine dioxide,[17] tetrathionate−chlorite,[9,18−22] sulfite−chlorine dioxide,[23] and the alkaline decomposition of tetrathionate[24−26] since the last 20 years and many kinetic models have been proposed involving series of different halogen- and sulfur-containing intermediates. But until now, no detailed kinetic model has yet been available for explanation of the appearance of oscillations, chaos, and patterns in the parent reaction.

To resolve the problems mentioned above first it is crucial to establish the main species involved in the reaction under conditions studied with supporting direct experimental evidence. It is also important to show how the concentration of these species varies with pH and with change of the initial concentration of the reactants as well. Survey of literature (see above) clearly indicates that the chlorite−thiosulfate reaction is an extremely complex chemical system therefore it is also necessary first to simplify somewhat this reaction with regard to the conditions studied. A promising opportunity for doing this is to keep the pH at alkaline conditions because it is well-known that chlorine dioxide is not formed under such experimental conditions.[8] Therefore, further reactions of chlorine dioxide can also be neglected. Although at these experimental circumstances no exotic phenomenon can be observed, we believe that a reliable kinetic model obtained by this method may serve as a solid starting point to be extended with additional reactions occurring at acidic conditions. This systematic extension may lead to a proposal of such an extensive kinetic model that is capable of a good description of all the exotic phenomena listed briefly in the introduction.

High performance liquid chromatography (HPLC) can be used to monitor the concentrations of the reactants as well as those of the long-lived intermediates directly. A necessary requirement to perform kinetic studies by HPLC is that the whole course of reaction as well as the lifetime of long-lived

intermediates cannot be effected by the separation process. Moreover, the reaction monitored has to be slow enough not to change the concentration of reactants, long-lived intermediates, and products during data acquisition. If these conditions are fulfilled then the data collected will be more informative compared to those ones that contain signals of (often linear) combination of concentrations belonging to several species (absorbance, potentials, etc.). Our latest results have clearly demonstrated that HPLC method is a convenient tool to study the kinetics and mechanisms of different complex systems.[27,28]

In the present work we are going to investigate the chlorite—thiosulfate reaction at different pHs and concentration ratio of reactants using HPLC while avoiding the overlapping UV—vis spectra of species involved in the reaction. Our aim is to find intermediates during the course of reaction at different pHs and to establish a kinetic model at the experimental conditions applied. Preliminary experiments have shown that studying the chlorite—thiosulfate reaction by HPLC meets the necessary requirements of performing good quality data acquisition under the conditions applied (pH $\geq$ 8.5). We also found that a further decrease in pH may cause at least two undesired side effects. On the one hand, application of lower pHs results in an increase of reaction rate to such an extent that concentration of thiosulfate and tetrathionate ions changes during the separation process and on the other hand chlorine dioxide may form in significant amount due to the well-known hypochlorous acid—chlorite reaction opening up the possibility of further side reactions. Therefore, measurements below pH = 8.5 were only useful for qualitative detection of the main intermediates of the system (focusing mainly on the formation of sulfur-containing intermediates) and have not been used for simultaneous evaluation.

■ MATERIALS AND INSTRUMENTATION

Materials and Methods. Commercially available reagents ($K_2S_4O_6$, $Na_2S_2O_3$, Na_2SO_3) were of the highest purity and were used without further purification. Sodium chlorite (technical grade) was purified as described earlier at -18 °C.[10] The chlorite content was checked by standard iodometric titration and its purity was found to be better than 97.5%. No chloride and no alkaline impurities could be detected in the purified $NaClO_2$. Potassium trithionate ($K_2S_3O_6$) and potassium pentathionate ($K_2S_5O_6$) were used as standards and prepared according to the method given elsewhere.[29,30] Their purity was checked and found to be better than 98.5%. All solutions were prepared by deionized water from a Milli-Q system having a specific conductivity of 18.2 $M\Omega^{-1}$ cm^{-1}. Thiosulfate stock solution (0.01 M) was standardized by iodometric titration once a week. The pH of the solutions was regulated by either phosphate or carbonate buffer between 6.0 and 10.5 while keeping the total concentration of the buffer components at 15.0 mM.

Mobile phase and running buffer solutions for HPLC separation were diluted solutions of phosphate or carbonate with additives such as tetrapropyl-ammonium hydroxide (TPAOH) and tetrabutyl-ammonium hydroxide (TBAOH) to improve selectivity and resolution. These species were also found not to affect the reaction.[31,32]

The different reacting solutions were initiated by introducing appropriate quantities of the reactants into the buffer solutions and were conducted in a batch reactor keeping the temperature constant at 25.0 $\pm$ 0.1 °C. Additional experiments were carried
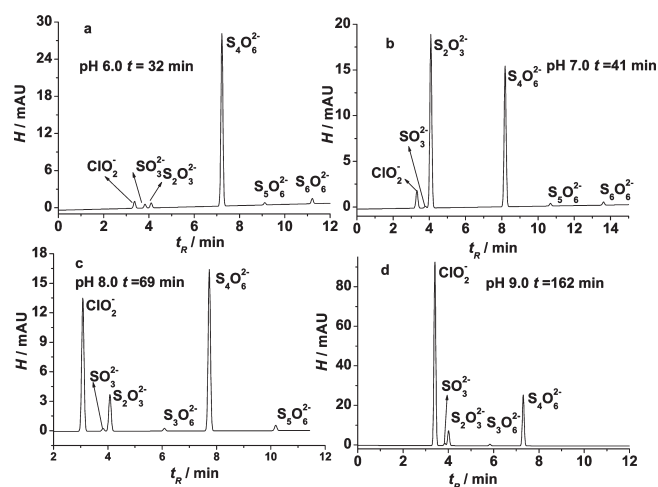

Figure 1. Typical chromatograms of the species in the $ClO_2^- - S_2O_3^{2-}$ reaction system at different pHs. (a) $[ClO_2^-]_0/[S_2O_3^{2-}]_0 = 1$; (b) $[ClO_2^-]_0/[S_2O_3^{2-}]_0 = 1$; (c) $[ClO_2^-]_0/[S_2O_3^{2-}]_0 = 10$; (d) $[ClO_2^-]_0/[S_2O_3^{2-}]_0 = 40$.

out in absence of oxygen and it was found that dissolved oxygen from air influences neither the determination of components nor the kinetics of the reaction under our experimental conditions. The concentration range of the reactants for the kinetic runs was 0.5—3.0 mM and 7.0—70.0 mM in case of thiosulfate and chlorite, respectively.

Instrumentation. The chromatographic system used in this study consists of a Model P680 pump with four pistons (Dionex Summit), a Model 7725 injection-valve equipped with a 20.0 μL sample loop (Rneodyne), a Phenomenex Ginimi C18 separation column (250 $\times$ 4.6 mm, 5 μm) and a Model UVD 170 UV detector. The mobile phase was prepared by mixing acetonitrile and 7.0 mM TPAOH solution according to a volumetric ratio of 15—85% ($v_{acetonitrile}/v_{TPAOHsolution}$) for pH = 6.0—9.0 with phosphate buffer, and 12—88% ($v_{acetonitrile}/v_{TPAOHsolution}$) for pH = 9.5—10.5 with carbonate buffer. The flow of mobile phase was kept constant at 1.0 cm^3/min. The samples were acquired by taking 5 μL of the solution and injecting it into the HPLC analytical column. Chromatograms were monitored at 230 nm and were recorded by Chameleon workstation. Before injection sample solutions were filtered through a 0.45 μm filter membrane.

Data Treatment. To determine the concentration of each species from the chromatograms, it is necessary to establish calibration curves that describe relationship between the concentration of species to be analyzed and the area of each peak. The integrated areas of peaks representing thiosulfate and tetrathionate are found to possess excellent linear correlation with their concentrations, where the correlation coefficient was always above 0.99. The reaction at pH = 6.0—8.0 was found to be slow enough to provide qualitative information about the intermediates and the products formed during the reaction, but was not so slow to provide detailed kinetic information. Therefore, these data were only used to identify intermediates and products. Majority of the kinetic runs at pH = 8.5—10.5 were maintained with excess of chlorite. At least 10—15 data points were collected in a typical kinetic run.

We used concentration—time data of thiosulfate and tetrathionate in each kinetic run for simultaneous data evaluation by ZiTa[33] program package. To obtain the kinetic model and the
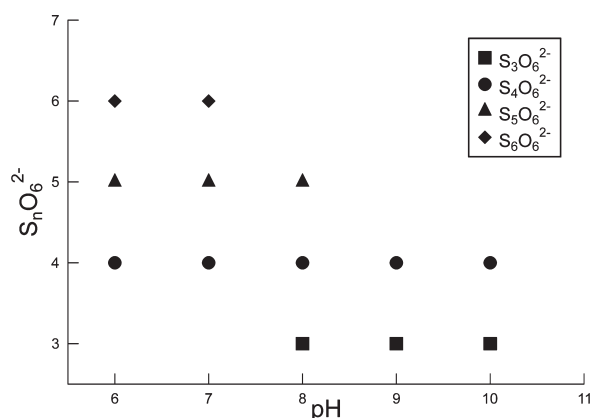
1854

dx.doi.org/10.1021/jp110909y |J. Phys. Chem. A 2011, 115, 1853–1860

Figure 2. pH dependence of the number of sulfur atoms (n) in different polythionates during the course of the $ClO_2^- - S_2O_3^{2-}$ reaction. $S_3O_6^{2-}$ (■), $S_4O_6^{2-}$ (●), $S_5O_6^{2-}$ (▲) and $S_6O_6^{2-}$ (◆).

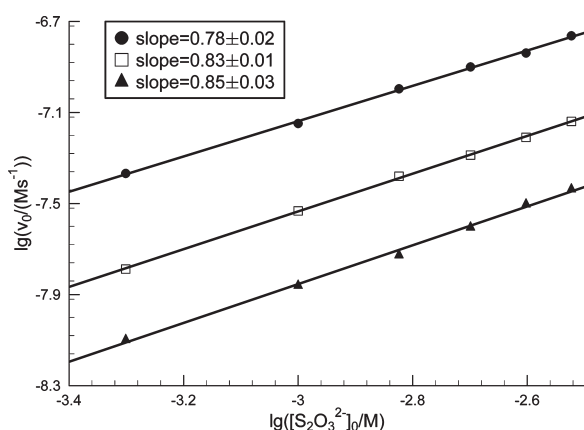**Figure 3.** Plots of the logarithm of the initial rate expressed by the comsumption of thiosulfate ion ($v_0 = -d[S_2O_3^{2-}]/dt$ at $t = 0$ s) against $lg([S_2O_3^{2-}]_0/M)$, $[ClO_2^-]_0 = 0.02$ M, pH = 9.29 (●), 9.64 (□), 9.98 (▲).

rate coefficients relative fitting procedure has been chosen to minimize the average deviation between measured and calculated concentrations. Altogether more than 2700 experimental points from 124 kinetic series were used for simultaneous evaluation. Our quantitative criterion for an acceptable fit was that the average deviation for relative fit approach 5%, which is close to the experimentally achievable limit of error of concentration determination under present experimental circumstances.

■ RESULTS

Identification of Species at Different pH. To identify species formed during the course of reaction, five experiments were monitored between pH = 6.0–10.0. Seven sulfur containing species exist in the reaction system, including sulfite, thiosulfate, trithionate, tetrathionate, pentathionate, hexathionate, and sulfate. Some species, such as thiosulfate, sulfite, trithionate, tetrathionate, and pentathionate, were identified by comparing their retention time to that of standard solutions; hexathionate was identified by comparing its HPLC retention factor with that of found in the literature.[31,32] Figure 1 shows the chromatograms of species at different pHs and at an appropriate reaction time. It obviously shows that thiosulfate and its oxidation products were
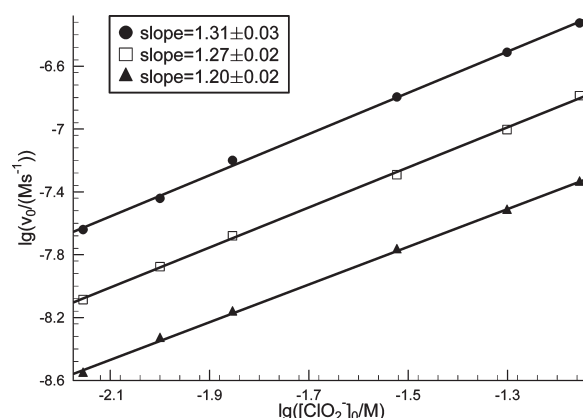

Figure 4. Plots of the logarithm of the initial rate expressed by the consumption of thiosulfate ion ($v_0 = -d[S_2O_3^{2-}]/dt$ at $t = 0$ s) against $lg([ClO_2^-]_0/M)$ at different pHs. $[S_2O_3^{2-}]_0 = 1.0$ mM. pH = 9.29 (●), 9.64 (□), 10.11 (▲).

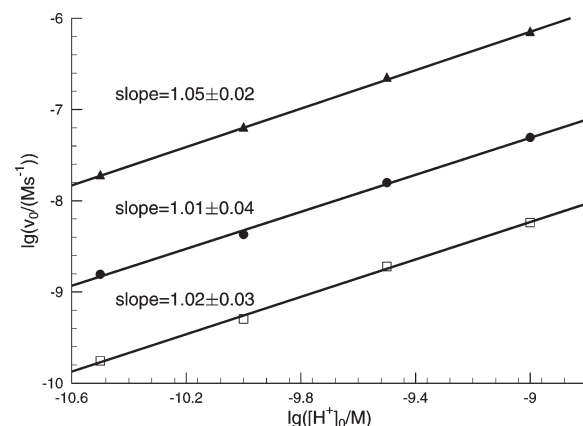**Figure 5.** Plots of the logarithm of the initial rate expressed by the consumption of thiosulfate ion ($v_0 = -d[S_2O_3^{2-}]/dt$ at $t = 0$ s) against $lg([H^+]_0/M)$ at different initial ratios of the reactants and at $[S_2O_3^{2-}]_0 = 0.5$ mM. $[ClO_2^-]_0/[S_2O_3^{2-}]_0 = 35$ (●), 40 (□), 45 (▲). Note that the curves belong to the markers (□) and (▲) are shifted along the Y-axis by −1 and +1, respectively, for better visibility.

baseline separated in a relatively short period of time. Therefore, the method was found to be suitable for kinetic studies and species analysis. Figure 2 depicts the different polythionates detected between pH = 6.0–10.0. The mean number of sulfur atoms in the polythionates (n) decreases with increasing pH. The effect of pH is therefore a key factor of the formation of polythionates according to our experiments. Tetrathionate was detected at pH = 6.0–10.0, but higher polythionates were only detected at lower pHs. This result is consistent with recent reports on similar reaction systems.[13,34] It is also interesting to note that $S_3O_6^{2-}$ cannot be detected below pH = 8.0 although it is more stable than tetrathionate in nonalkaline solution. We shall see that this observation can readily be explained by the kinetic model proposed (see, later). Pentathionate and hexathionate could be observed at pH 6.0 and 7.0, and hexathionate cannot be accumulated in detectable amounts due to its well-known decomposition in alkaline media.[35] In very weak alkaline solutions (pH < 9.0), pentathionate is fairly stable toward degradation. If, however, pH slightly increases pentathionate is no longer stable and

Table 1. Fitted and Fixed Rate Coefficients of the Proposed Kinetic Model[a]

step	rate equation	parameter
R1	$k_1[S_2O_3^{2-}][ClO_2][H^+]$	$k_1 = (1.54 \pm 0.02) \times 10^6 \ M^{-2} s^{-1}$
R2	$k_2[S_2O_3ClO^-]$	$k_2 \geq 0.1 \ s^{-1}$
R3	$k_3[S_2O_3ClO^-][ClO_2]$	$k_3/k_2 = 1380 \pm 150 \ M^{-1}$
R4	$(k_4 + (k_4')/(K_{HOCl})[H^+])[S_2O_3^{2-}][OCl^-]$	$k_4/k_8 = 0.881 \pm 0.087, k_4'/k_8' = 1.096 \pm 0.091$
R5	$k_5[SO_3^{2-}][ClO_2][H^+]$	$k_5 = (6.72 \pm 0.19) \times 10^6 \ M^{-2} \ s^{-1}$
R6	$k_6[S_2O_3^{2-}][S_2O_3Cl^-]$	$k_6/k_7 = 604 \pm 24$
R7	$k_7[ClO_2^-][S_2O_3Cl^-]$	$k_7 \geq 0.1 \ M^{-1} \ s^{-1}$
R8	$(k_8 + (k_8')/(K_{HOCl})[H^+])[SO_3^{2-}][OCl^-]$	$k_8 = 2.3 \times 10^4 \ M^{-1} \ s^{-1}, k_8' = 7.6 \times 10^8 \ M^{-1} \ s^{-1}$
R9	$k_9[S_4O_6^{2-}][SO_3^{2-}]$	$k_9 = 0.996 \pm 0.030 \ M^{-1} \ s^{-1}$
R10	$k_{10}[S_4O_6^{2-}][OH^-]$	$k_{10} = (1.07 \pm 0.04) \times 10^{-2} \ M^{-1} \ s^{-1}$

[a] No error indicates that the value in question was fixed during the fitting procedure.

decomposes[36] according to

$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \qquad (1)$$
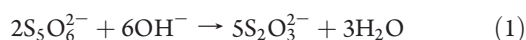
therefore, pentathionate cannot be observed when pH > 8.0.

Initial Rate Studies. Figure 3 shows log—log plot of the initial rate, defined by consumption of thiosulfate, against the concentration of thiosulfate at three different pHs. As seen linear correlation is obtained but the slope is markedly less than unity in all cases therefore we concluded that formal kinetic order of thiosulfate is less than one. Similar treatment of the initial rate against the initial concentration of chlorite yields that the formal kinetic order of chlorite is significantly higher than one at three different pHs as Figure 4 depicts. Thus, it is also clear that the kinetic order of chlorite is between 1 and 2. This result seems to be surprising since Nagypál et al.[8,9] reported clear first-order chlorite and thiosulfate dependences. We shall see later that the results reported here are inherent feature of the system that may explain the systematic deviations obtained from a rate equation being first order with respect to both thiosulfate and chlorite.[8,9] As Figure 5 shows, the formal kinetic order of the hydrogen ion is, however, clearly one independent of the concentration ratio of the reactants in agreement with earlier works.[8,9]

Proposed Kinetic Model. The detailed method to obtain the best fitting model was already published elsewhere.[21] Beside the reactants (thiosulfate and chlorite) and the products (tetrathionate, trithionate, sulfite) identified by HPLC we have also taken into account the following intermediates that were already proposed to participate in several subsystems of the chlorite—thiosulfate reaction: OCl^-, $S_2O_3ClO^-$, $S_2O_3Cl^-$. Considering all the conceivable mono- and bimolecular reactions between the species mentioned above, along with their H^+ and OH^- catalyzed pathways, we have started our fitting procedure by an initial kinetic model consisting of 84 different steps. The systematic fitting and reduction procedure led us to propose the following kinetic model to explain the main characteristics of the kinetic curves of the chlorite—thiosulfate reaction in alkaline medium:
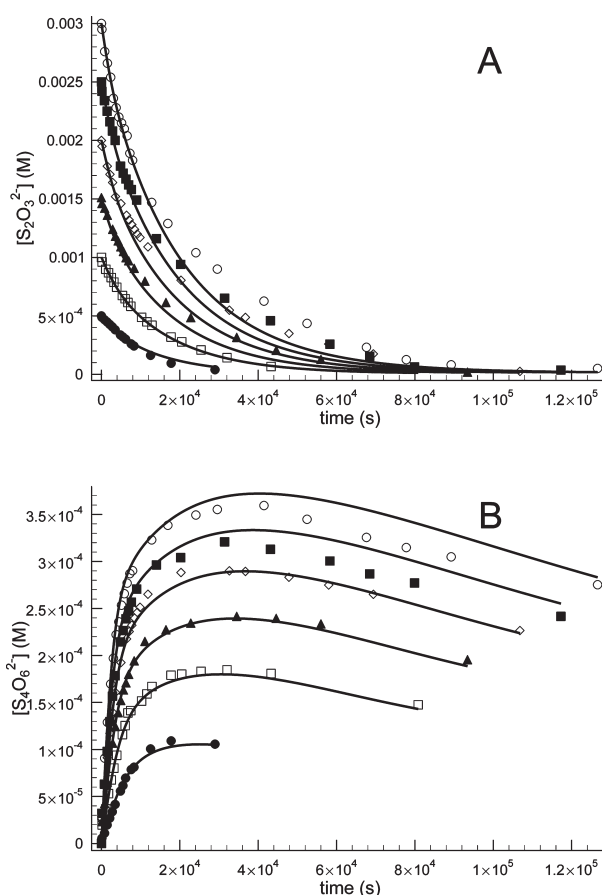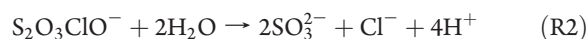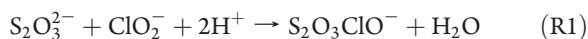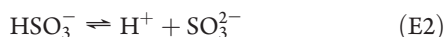
$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (E1)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \qquad (E2)$$

$$S_2O_3^{2-} + ClO_2^- + 2H^+ \rightarrow S_2O_3ClO^- + H_2O \qquad (R1)$$

$$S_2O_3ClO^- + 2H_2O \rightarrow 2SO_3^{2-} + Cl^- + 4H^+ \qquad (R2)$$

Figure 6. Measured (symbols) and calculated (solid lines) $[S_2O_3^{2-}]$—time curves (A) and $[S_4O_6^{2-}]$—time (B) at pH = 9.29 and at $[ClO_2^-]_0 = 0.02 \ M$. $[S_2O_3^{2-}]_0/mM = 0.5 \ (\bullet), 1.0 \ (\square), 1.5 \ (\blacktriangle), 2.0 \ (\diamond), 2.5 \ (\blacksquare), 3.0 \ (\circ)$.

$$S_2O_3ClO^- + ClO_2^- + 2H_2O \rightarrow 2SO_3^{2-} + 2OCl^- + 4H^+ \qquad (R3)$$

$$S_2O_3^{2-} + OCl^- + 2H^+ \rightarrow S_2O_3Cl^- + H_2O \qquad (R4)$$

$$SO_3^{2-} + ClO_2^- \rightarrow SO_4^{2-} + OCl^- \qquad (R5)$$
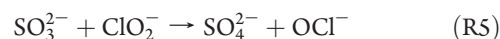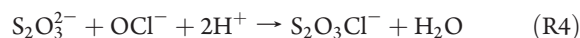
$$S_2O_3^{2-} + S_2O_3Cl^- \rightarrow S_4O_6^{2-} + Cl^- \qquad (R6)$$
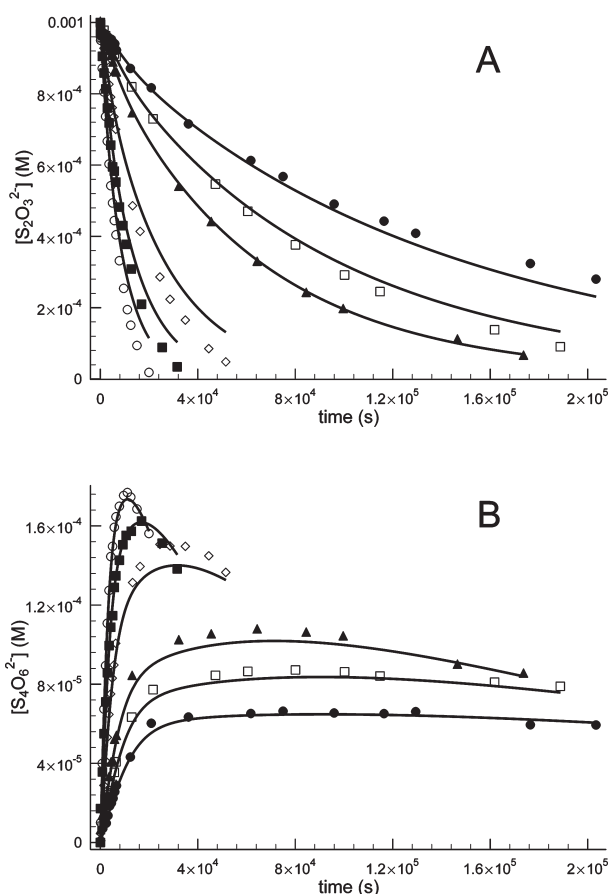
Figure 7. Measured (symbols) and calculated (solid lines) $[S_2O_3^{2-}]-$ time curves (A) and $[S_4O_6^{2-}]-$ time (B) at pH = 9.64 and at $[S_2O_3^{2-}]_0 =$ 1.0 mM. $[ClO_2^-]_0/M = 0.007$ (●), 0.01 (□), 0.014 (▲), 0.03 (◇, 0.05 (■), 0.07 (○).
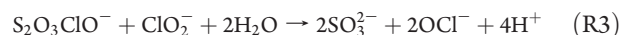

Figure 8. Measured (symbols) and calculated (solid lines) $[S_2O_3^{2-}]-$ time curves (A) and $[S_4O_6^{2-}]-$ time (B) at $[ClO_2^-]_0 = 0.0125$ M and at $[S_2O_3^{2-}]_0 = 0.5$ mM. pH = 9.0 (●), 9.5 (□), 10.0 (▲).

$$S_2O_3Cl^- + ClO_2^- + 2H_2O \rightarrow 2SO_3^{2-} + OCl^- + Cl^- + 4H^+ \quad (R7)$$
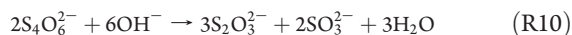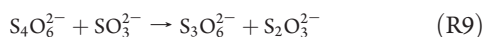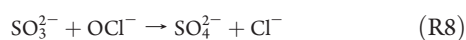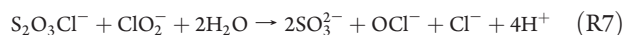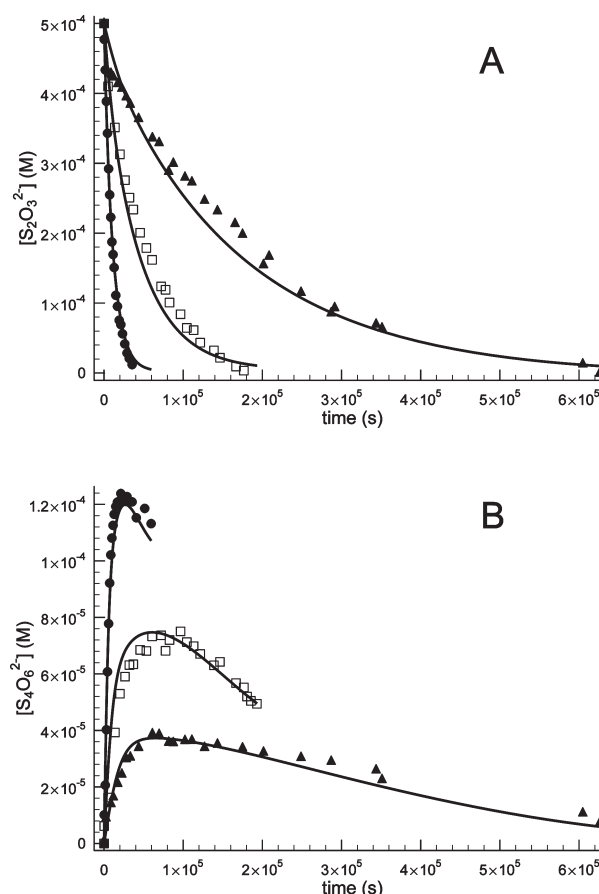
$$SO_3^{2-} + OCl^- \rightarrow SO_4^{2-} + Cl^- \quad (R8)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \quad (R9)$$

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (R10)$$

The rapid protonation and deprotonation processes E1 and E2 were taken into consideration with known equilibrium constants. They may be regarded as auxiliary processes necessary for interpreting the pH dependencies of some steps in terms of elementary reactions, but they are not central part of the proposed kinetic model. The average deviation of the simultaneous fit of all the kinetic curves was found to be 5.1% for the 124 concentration—time series in case of relative fitting procedure with seven fitted and three fixed parameters. The corresponding rate equations and the final results of all the kinetic parameters obtained can be seen in Table 1. Figures 6—8 indicate a sound agreement between the experimental and calculated data pairs suggesting that the proposed model is working properly within the concentration range studied.

Discussion. Step 1 was already proposed by Nagypál et al.[9] in which a short-lived intermediate $S_2O_3ClO^-$ was suggested to form. The rate coefficient of this process was found to be $4.7 \times 10^5 \, M^{-2} \, s^{-1}$, but it was also claimed that, although the agreement between the measured and the calculated curves was satisfactory, systematic deviation may be noticed in some part of the kinetic curves. Our calculation procedure yields an approximately three times higher value of $(1.54 \pm 0.02) \times 10^6 \, M^{-2} \, s^{-1}$ for k_1. In view of the fact that the accuracy of the measured points is at best 5—10%, reported by Nagypál and Epstein,[9] and the systematic deviation they encountered the agreement between their and our results sounds acceptable.

Step 2 is the first-order decomposition of $S_2O_3ClO^-$ that has never been proposed before. Our calculation indicated that this process must be fast, its rate coefficient must be higher than 0.1 s^{-1} meaning that the lifetime of this species has to be significantly less than 7 s, supporting the fact that this species is really a short-lived intermediate. The individual rate coefficient of this process cannot be determined from our experiments because k_2 is in total correlation with k_3, meaning that we were able to calculate only the ratio of k_3/k_2. It should also be noted that due to the rapid E2 equilibrium the product sulfite may equally be substituted with hydrogen-sulfite in the stoichiometric equation without any change in the calculated final result. Sulfite ion has been chosen because this is the main form of S(IV) at alkaline conditions.

Step 3 was also suggested by Nagypál and Epstein,[9] where the short-lived intermediate is oxidized by chlorite in a complex reaction to produce sulfite and hypochlorite ion. This reaction was also found to be fast, but only the ratio $k_3/k_2 = 1380 \pm 150 \, M^{-1}$ could

be calculated from our measurements as indicated above. We have also tried to include the reaction of thiosulfate and $S_2O_3ClO^-$

$$S_2O_3^{2-} + S_2O_3ClO^- \rightarrow S_4O_6^{2-} + OCl^- \qquad (2)$$
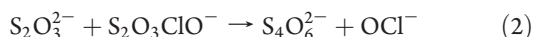
into the final model as suggested previously by Nagypál and Epstein[9] with no success. It has a serious consequence, namely tetrathionate is not directly formed from the intermediate $S_2O_3ClO^-$. As we shall see below, the thiosulfate–hypochlorite (hypochlorous acid) reaction is responsible for the production of tetrathionate. As one may easily notice sulfite and hypochlorite ions can readily be substituted in the stoichiometric equation with hydrogen-sulfite and hypochlorous acid, respectively, due to the rapid protolytic equilibria E1 and E2. The reason of choosing the deprotonated forms is simply the consequence of the fact that at alkaline conditions they are the dominant species of S(IV) and Cl(I). It should be emphasized again the final result does not change upon replacing the deprotonated forms with the protonated ones in the stoichiometric equation.

Step 4 is the initial step of the thiosulfate–hypochlorite reaction that was also proposed by Nagypál and Epstein,[9] although they were not able to determine the rate coefficient of this reaction from their measurements. We found that both hypochlorous acid and hypochlorite ion can react with thiosulfate ion, therefore, the rate of step R4 can be expressed as

$$v_4 = \left(k_4 + \frac{k_4'}{K_{HOCl}}[H^+]\right)[S_2O_3^{2-}][OCl^-] \qquad (3)$$

where K_{HOCl} is the acid dissociation constant of hypochlorous acid and k_4' is the rate coefficient of thiosulfate–hypochlorous acid reaction. Our calculation indicated that the ratio of rate of consumption of thiosulfate and sulfite can only be determined from our experiments. It means that the individual rate coefficients of k_4 and k_4' can be calculated if the rate coefficients of the corresponding reaction of hypochlorous acid and hypochlorite ion with sulfite are known from independent studies. In other words, mathematically, only the ratios of k_4/k_8 and k_4'/k_8' can be determined from our measurements as 0.881 ± 0.087 and 1.096 ± 0.091, respectively. Fortunately, both values (k_8 and k_8') were reported by Margerum's group[37] as $k_8 = 2.3 \times 10^4$ M^{-1} s^{-1} and $k_8' = 7.6 \times 10^8$ M^{-1} s^{-1}, therefore, we could calculate $k_4 = (2.03 \pm 0.20) \times 10^4$ M^{-1} s^{-1} and $k_4' = (8.33 \pm 0.69) \times 10^8$ M^{-1} s^{-1}. It means that the reaction between thiosulfate and hypochlorous acid is also very rapid and it is close to the diffusion control limit as expected. Comparison of k_4' with the rate coefficient of the initial step of the iodine–thiosulfate reaction[38] also supports the fact that hypochlorous acid is a more powerful oxidizing agent than iodine.

Step 5 was already studied independently by several research groups. Frerichs[39] et al. found that all forms of S(IV) react with chlorite and the rate coefficients were also given. Later, Huff Hartz et al.[40] showed that, in fact, sulfite is an inactive species to react with chlorite, only HSO_3^- and SO_2 can consume chlorite with a measurable rate. In alkaline conditions (pH > 9), only the reaction of HSO_3^- can be taken into consideration due to the fact that there is a six order magnitude difference between their rate coefficients determined by Huff Hartz et al.[40] Taking into account that pK_a of HSO_3^- is 6.3[40] and the rate coefficient between HSO_3^- and chlorite was found to be 5.5 M^{-1} s^{-1} one may easily calculate a value of 1.1×10^7 M^{-2} s^{-1} value for k_5 in v_5

$= k_5[H^+][SO_3^{2-}][ClO_2^-]$ rate equation. As seen, our calculation provided a value of $(6.72 \pm 0.19) \times 10^6$ M^{-2} s^{-1} for k_5, indicating a sound agreement between these values.

Step 6 was proposed by Nagypál and Epstein as well in their previous work.[9] We found this step to be essential since this is responsible for the formation of tetrathionate. Our calculations also indicated that this reaction has to be fast and its individual rate coefficient cannot be determined from the experiments. We could only calculate the ratio of k_6/k_7 to be 608 ± 24.

Step 7 was already found to be important in the chlorite–tetrathionate reaction.[21] In agreement with that study, our present experiments also support that this reaction is fast, indicating that $S_2O_3Cl^-$ is a short-lived intermediate. The calculations revealed that any value higher than 1 M^{-1} s^{-1} will lead to the same average deviation meaning that fixing k_7 in a reasonable value enables one to calculate k_6 as well. Chemically it means that the ratio of tetrathionate and sulfate formed in the reaction depends on the initial concentration ratio of the reactants.

Step 8 is the fast oxidation of sulfite by hypochlorite ion. The rate coefficient k_8 was found to be 2.3×10^4 M^{-1} s^{-1} by Fogelman et al.[37] It should also be noted that hypochlorous acid is more reactive to oxidize sulfite into sulfate and the rate coefficient of this reaction was also determined by Fogelman et al. as 7.6×10^8 M^{-1} s^{-1}.[37] We fixed these parameters throughout the fitting procedure. It also means that the rate equation of step R8 can be expressed by the following equation:

$$v_8 = \left(k_8 + \frac{k_8'}{K_{HOCl}}[H^+]\right)[SO_3^{2-}][OCl^-] \qquad (4)$$

where k_8' is the rate coefficient of the sulfite–hypochlorous reaction. As pointed out above it allowed us to determine the individual values of k_4 and k_4'.

Step 9 is the well-known sulfitolysis of tetrathionate. The reaction was first studied by Kurtenacker and Goldbach[41] and was reported to be applied for successful determination of polythionates.[42] The procedure was later modified by Iwasaki and Suzuki[43] to make it suitable for analyzing microamounts of polythionates. We have determined k_9 to be 0.996 ± 0.030 M^{-1} s^{-1} that agrees well with the value that could be estimated from the former study. This value is also in fairly good agreement with the value of 0.172 M^{-1} s^{-1} determined by Foerster and Centner at 0 °C without adjusting the ionic strength by supporting electrolyte.[44] More recently, Varga et al.[26] found this rate coefficient to be 0.545 M^{-1} s^{-1} that is in sound agreement with our recent findings.

Step 10 is the well-known alkaline decomposition of tetrathionate producing thiosulfate and sulfite eventually. Our value ($k_{10} = (1.07 \pm 0.04) \times 10^{-2}$ M^{-1} s^{-1}) determined here is in good agreement with that of found by Rolia and Chakrabarti[24] (0.0051 M^{-1} s^{-1}), however, it differs significantly from the results reported by Zhang et al.[25] and Varga et al.[26] due to the fact of applying higher ionic strength in the latter studies. As already pointed out by Breuer and Jeffrey,[45] positive kinetic salt effect results in a significant increase in the rate coefficient of the alkaline decomposition of tetrathionate with increasing ionic strength. One should also notice that steps 9 and 10 are responsible for the decay of tetrathionate at the later stages of the reaction. It is interesting to note, however, that as long as sulfite is present in the solution the main source of removal of tetrathionate is rather the sulfitolysis but not the alkaline

decomposition of tetrathionate. However, as the reaction proceeds, the concentration of sulfite is decreased and alkaline decomposition of tetrathionate starts to take over the role of sulfitolysis. It is also clear that a decrease in pH not only decreases the importance of alkaline decomposition of tetrathionate but the role of sulfitolysis as well, because around neutral pH, the well-known protolytic equilibrium E2 starts to be shifted to the left and the reactivity of HSO_3^- is significantly less toward tetrathionate. Because these are the only routes that lead to the formation of trithionate, it is now easily understood that no trithionate could be detected at slightly acidic conditions. Furthermore, at acidic solutions, HSO_3^- is no longer a long-lived intermediate in excess of chlorite due to increasing significance of step 5. It can also be seen that under these experimental conditions only a small amount of pentathionate is formed but this information is not enough to determine the rate coefficients of those further reactions where pentathionate can possibly be produced. The concentration of pentathionate may be enlarged at acidic conditions to determine the rate coefficients of different pathways leading to its formation, however, it would also mean a significant increase of the reaction rate well beyond the point where the reaction can safely be followed by HPLC method.

Formal Kinetics. It is also interesting to note that although no kinetic step being second order with respect to chlorite ion is involved in the proposed kinetic model, simplified evaluation of kinetic curves unambiguously indicated a formal kinetic order of chlorite significantly higher than 1. Furthermore, it is also expected to explain the markedly lower formal kinetic order of thiosulfate than unity as well. The reason may easily be understood if we take into consideration that $S_2O_3ClO^-$, $S_2O_3Cl^-$, and OCl^- are short-lived intermediates and we apply steady-state treatment for these species. Derivation leads to the following equations:

$$[S_2O_3ClO^-] = \frac{k_1[S_2O_3^{2-}][ClO_2^-][H^+]}{k_2 + k_3[ClO_2^-]} \quad (5)$$

$$[S_2O_3Cl^-] = \frac{\left(k_4 + \dfrac{k_4'}{K_{HOCl}}[H^+]\right)[S_2O_3^{2-}][OCl^-]}{k_6[S_2O_3^{2-}] + k_7[ClO_2^-]} \quad (6)$$

$$[OCl^-] = [ClO_2^-]\frac{\dfrac{2k_1k_3[S_2O_3^{2-}][ClO_2^-][H^+]}{k_2 + k_3[ClO_2^-]} + k_5[H^+][SO_3^{2-}]}{\dfrac{\left(k_4 + \dfrac{k_4'}{K_{HOCl}}[H^+]\right)k_6[S_2O_3^{2-}]^2}{k_6[S_2O_3^{2-}] + k_7[ClO_2^-]} + \left(k_8 + \dfrac{k_8'}{K_{HOCl}}[H^+]\right)[SO_3^{2-}]} \quad (7)$$

At the beginning stage of reaction the concentration of sulfite is very small therefore the second term of the nominator and the denominator in eq 7 can be neglected. Because evaluation of the kinetic orders of the reactants was carried out by initial rate studies, this assumption may be treated satisfactorily. At this condition, eqs 6 and 7 may be rewritten respectively as follows:

$$[S_2O_3Cl^-] = \frac{2k_1k_3[ClO_2^-]^2[H^+]}{(k_2 + k_3[ClO_2^-])k_6} \quad (8)$$

and

$$[OCl^-] = \frac{2k_1k_3[ClO_2^-]^2[H^+](k_6[S_2O_3^{2-}] + k_7[ClO_2^-])}{\left(k_4 + \dfrac{k_4'}{K_{HOCl}}[H^+]\right)k_6[S_2O_3^{2-}](k_2 + k_3[ClO_2^-])} \quad (9)$$

Consumption of thiosulfate can be expressed by the following equation,

$$-\frac{d[S_2O_3^{2-}]}{dt} = k_1[S_2O_3^{2-}][ClO_2^-][H^+] + \left(k_4 + \frac{k_4'}{K_{HOCl}}[H^+]\right)[S_2O_3^{2-}][OCl^-] + \\ + k_6[S_2O_3^{2-}][S_2O_3Cl^-] - k_9[S_4O_6^{2-}][SO_3^{2-}] - 3k_{10}[S_4O_6^{2-}][OH^-] \quad (10)$$

but the last two terms in eq 10 can also be treated as zero at the beginning stage of the reaction because concentrations of both products are negligible. Again, it should be stressed that this assumption is valid only at the early stage of reaction so the conclusions drawn are strictly applicable at these conditions but not for the whole course of reaction. Substituting eqs 8 and 9 into eq 10, we obtain the following expression:

$$-\frac{d[S_2O_3^{2-}]}{dt} = k_1[S_2O_3^{2-}][ClO_2^-][H^+] + \\ \frac{2k_1k_3[ClO_2^-][H^+]\left(2[S_2O_3^{2-}][ClO_2^-] + \dfrac{k_7}{k_6}[ClO_2^-]^2\right)}{k_2 + k_3[ClO_2^-]} \quad (11)$$

Analyzing eq 11 in large chlorite excess (i.e., $[ClO_2^-]_0 \gg [S_2O_3^{2-}]_0$), we arrive at

$$-\frac{d[S_2O_3^{2-}]}{dt} = 5k_1[S_2O_3^{2-}][ClO_2^-][H^+] + \frac{2k_1k_7}{k_6}[ClO_2^-]^2[H^+] \quad (12)$$

from which one can conclude the formal kinetic order of thiosulfate, chlorite, and hydrogen ion is between 0 and 1, between 1 and 2, and perfectly 1, respectively. These results are completely consistent with the information obtained from initial rate studies. Investigating the opposite case (i.e., excess of thiosulfate) reveals that eq 11 may be transformed to

$$-\frac{d[S_2O_3^{2-}]}{dt} = k_1[S_2O_3^{2-}][ClO_2^-][H^+] + \\ \frac{4k_1k_3}{k_2}[S_2O_3^{2-}][ClO_2^-]^2[H^+] \quad (13)$$

indicating that the formal kinetic order of thiosulfate and the hydrogen ion is perfectly one, while that of chlorite must as well lie between 1 and 2.

CONCLUSION

As expected, it is demonstrated that the HPLC method can be applied successfully to monitor the reaction between thiosulfate and chlorite ions in alkaline solution. Although it is also known that no exotic behavior appears at this pH range, we strongly believe that extension of this model with those various reactions which take place under acidic conditions may be a good candidate to simulate successfully several different nonlinear feature of the chlorite−thiosulfate reaction. This study, along with the knowledge of the greater stability of higher polythionates (including especially pentathionate and hexathionate) in acidic conditions, may therefore hint that further reactions of these compounds might have significant contribution to the overall dynamics of the parent reaction. It is therefore expected in the near future that the results presented here will inspire further detailed investigations on the oxidation reaction of higher polythionates as well.

AUTHOR INFORMATION

Corresponding Author

*E-mail: horvatha@gamma.ttk.pte.hu; gaoqy@cumt.edu.cn.

ACKNOWLEDGMENT

REFERENCES

(1) Orbán, M.; Kepper, P. D.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 431–433.

(2) Orbán, M.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 3907–3910.

(3) Maselko, J.; Epstein, I. R. *J. Chem. Phys.* **1984**, *80*, 3175–3178.

(4) Nagypál, I.; Bazsa, G.; Epstein, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 3635–3640.

(5) Szirovicza, L.; Nagypál, I.; Bárdi, I. *Int. J. Chem. Kinet.* **1991**, *23*, 99–101.

(6) Zhivotniko, V. V.; Koptyug, I. V.; Sagdeev, R. Z. *J. Phys. Chem. A* **2007**, *111*, 4122–4124.

(7) Koptyug, I. V.; Zhivotniko, V. V.; Sagdeev, R. Z. *J. Phys. Chem. B* **2008**, *112*, 1170–1176.

(8) Nagypál, I.; Epstein, I. R.; Kustin, K. *Int. J. Chem. Kinet.* **1986**, *18*, 345–353.

(9) Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1986**, *90*, 6285–6292.

(10) Peintler, G.; Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 2954–2958.

(11) Gordon, G.; Tachiyashiki, S. *Environ. Sci. Technol.* **1991**, *25*, 468–474.

(12) Kormányos, B.; Nagypál, I.; Peintler, G.; Horváth, A. K. *Inorg. Chem.* **2008**, *47*, 7914–7920.

(13) Varga, D.; Horváth, A. K.; Nagypál, I. *J. Phys. Chem. B* **2006**, *110*, 2467–2470.

(14) Horváth, A. K.; Nagypál, I. *Int. J. Chem. Kinet.* **2000**, *32*, 395–402.

(15) Varga, D.; Horváth, A. K. *J. Phys. Chem. A* **2009**, *113*, 13907–13912.

(16) Horváth, A. K.; Nagypál, I. *J. Phys. Chem. A* **1998**, *102*, 7267–7272.

(17) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *J. Phys. Chem. A* **2003**, *107*, 10063–10068.

(18) Horváth, A. K.; Nagypál, I.; Peintler, G.; Epstein, I. R. *J. Am. Chem. Soc.* **2004**, *126*, 6246–6247.

(19) Horváth, A. K. *J. Phys. Chem. A* **2005**, *109*, 5124–5128.

(20) Szalai, I.; Gauffre, F.; Labrot, V.; Boissonade, J.; Kepper, P. D. *J. Phys. Chem. A* **2005**, *109*, 7843–7849.

(21) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *Inorg. Chem.* **2006**, *45*, 9877–9883.

(22) Peintler, G.; Csekő, G.; Petz, A.; Horváth, A. K. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2356–2364.

(23) Horváth, A. K.; Nagypál, I. *J. Phys. Chem. A* **2006**, *110*, 4753–4758.

(24) Rolia, E.; Chakrabarti, C. L. *Environ. Sci. Technol.* **1982**, *16*, 852–857.

(25) Zhang, H.; Dreisinger, D. B. *Hydrometallurgy* **2002**, *66*, 56–65.

(26) Varga, D.; Horváth, A. K. *Inorg. Chem.* **2007**, *46*, 7654–7661.

(27) Gao, Q.; Wang, G.; Sun, Y.; Epstein, I. R. *J. Phys. Chem. A* **2008**, *112*, 5771–5773.

(28) Lu, Y.; Gao, Q.; Xu, L.; Zhao, Y.; Epstein, I. R. *Inorg. Chem.* **2010**, *49*, 6026–6034.

(29) Voslar, M.; Matejka, P.; Schreiber, I. *Inorg. Chem.* **2006**, *45*, 2824–2834.

(30) Kelly, D. P.; Wood, A. P. *Methods Enzymol.* **1994**, *243*, 34–61.

(31) Miura, Y.; Saitoh, A.; Koh, T. *J. Chromatogr., A* **1997**, *770*, 157–164.

(32) Miura, Y.; Saitoh, A.; Kawaoi, A. *J. Chromatogr., A* **2000**, *884*, 81–87.

(33) Peintler, G. *ZiTa*, version 5.0; a comprehensive program package for fitting parameters of chemical reaction mechanism; Attila József University: Szeged, Hungary, 1989−1998.

(34) Varga, D.; Horváth, A. K. *J. Phys. Chem. A* **2009**, *113*, 9988–9996.

(35) Koh, T.; Taniguchi, K. *Anal. Chem.* **1974**, *46*, 1679–1683.

(36) Wagner, H.; Schreier, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1978**, *4*, 281–284.

(37) Fogelman, K. D.; Walker, D. W.; Margerum, D. W. *Inorg. Chem.* **1989**, *28*, 986–993.

(38) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1341–1348.

(39) Frerichs, G. A.; Mlnarik, T. M.; Grun, R. J.; Thompson, R. C. *J. Phys. Chem. A* **2001**, *105*, 829–837.

(40) Hartz, K. E. H.; Nicoson, J. S.; Wang, L.; Margerum, D. W. *Inorg. Chem.* **2003**, *42*, 78–87.

(41) Kurtenacker, A.; Goldbach, E. *Z. Anorg. Allg. Chem.* **1927**, *166*, 177–189.

(42) Goehring, M.; Feldmann, U.; Helbing, W. *Z. Anal. Chem.* **1949**, *129*, 346–352.

(43) Iwasaki, I.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 576–580.

(44) Foerster, F.; Centner, K. *Z. Anorg. Chem.* **1926**, *157*, 45–82.

(45) Breuer, P. L.; Jeffrey, M. I. *Hydrometallurgy* **2004**, *72*, 335–338.

1860

dx.doi.org/10.1021/jp110909y |*J. Phys. Chem. A* 2011, 115, 1853–1860