# Kinetics and Mechanism of Alkaline Decomposition of the Pentathionate Ion by the Simultaneous Tracking of Different Sulfur Species by High-Performance Liquid Chromatography

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ABSTRACT: Alkaline decomposition of pentathionate has been investigated by high-performance liquid chromatography, which allows us to track different sulfur-containing species simultaneously in the presence of a carbonate/hydrogen carbonate buffer at 25.0 ± 0.1 °C and at a constant ionic strength. It has been shown that, besides the major product, thiosulfate, not only tetrathionate but also hexathionate appears in significant amounts during the course of the reaction. At higher pHs, both of them are unstable long-lived intermediates because of their well-known alkaline degradation, but a decrease of the pH increases their stability (especially that of tetrathionate), meaning that they may even become end products. On the basis of these observations, a 10-step kinetic model with five fitted and five fixed rate coefficients is suggested and discussed to take all of the most important characteristics of the decomposition into account. We have also demonstrated and discussed that the well-known thiosulfate-assisted rearrangement of pentathionate leading to hexathionate might only play a very minor role in the formation of hexathionate under our experimental conditions.
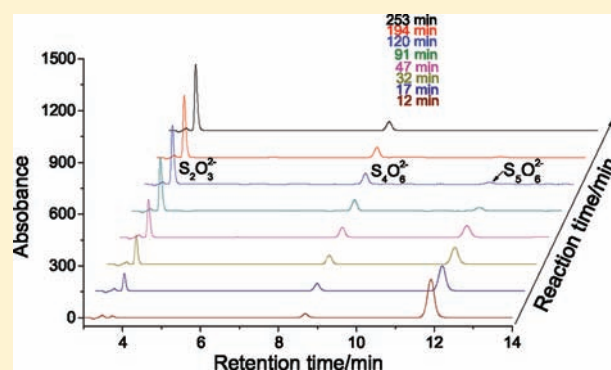
INTRODUCTION

The oxidation of thiosulfate by different oxidizing agents exhibits a wide variety of interesting nonlinear dynamical phenomena, such as autocatalysis under batch conditions,[1] bistability, and oscillations[1] or complex periodic and aperiodic behavior[2,3] as well as multistationary states[4] in a continuously stirred tank reactor and the appearance of different kinds of reaction—diffusion patterns (chemical waves and chemical reaction fronts) in an unstirred system.[5−8] During the oxidation process of thiosulfate, leading eventually to sulfate, a rich variety of sulfur-containing intermediates is expected to be involved.[9,10] These transient species may react further not only with the reactants but also with each other, making the reaction in question particularly complicated.[11] Using hydrogen peroxide, hypochlorous acid, and chlorite as oxidizing agents of thiosulfate, recent kinetic studies have clearly demonstrated that pentathionate is formed in detectable amounts[9,10,12] and may therefore contribute to the appearance of a rich variety of nonlinear phenomena.[3,6−8,13−15] Pentathionate is also known as an important intermediate in the redox transformations or metabolism of sulfur compounds in many environmental, industrial, and biological systems.[16] For instance, one of its notable applications is the formation of Cu_xS layers on the polyamide surface, markedly promoting the optoelectrical efficiency of transportation, where potassium pentathionate is used as a precursor of polymer sulfurization in acidic conditions as a result of its polysulfur chain.[17,18]

Lixiviation of noble metals from their ores by thiosulfate for the formation of their thiosulfate complexes seems to be a promising opportunity to replace that cyanidation process because of their relative nontoxicity. However, inevitably the formation of polythionates followed by their strong absorption on the ion-exchange site of the resin reduces the efficiency of this method.[19] It is, therefore, crucial to remove the polythionates from the leach prior to the ion-exchange process. Degradation of the polythionates in an alkaline medium seems to be a promising solution to this problem. The stability of the polythionates in an alkaline medium increases with decreasing length of the sulfur chain; the most stable polythionate is therefore trithionate.[20] The alkaline degradation of tetrathionate has been studied thoroughly by several research groups over several decades; therefore, comprehensive data are readily available at different experimental conditions.[21,22] Compared to tetrathionate, notably less is known about the alkaline degradation of pentathionate, although by now the involvement of this species in the oxidation reactions of thiosulfate has already been established.[9,10,12]

Christiansen et al. showed[23] that the rate of alkaline decomposition of pentathionate is linearly proportional to the concentration of pentathionate and hydroxide ions and observed a strong positive kinetic salt effect, as expected, just as a result of

the rate-determining step between likewise charged reactants. It was also shown that the rate of decomposition is independent of the thiosulfate concentration and a complex formula for the rate coefficient of the reaction was derived from their experiments at 20 °C:

$$\log\left(\frac{\mathrm{d}\ln c_{\mathrm{S_5O_6^{2-}}}}{\mathrm{d}t}\right) = -12.7 + 0.96\mathrm{pH}$$

$$+ 2.2\frac{\sqrt{I}}{1 + \sqrt{I}} \pm 0.1 \tag{1}$$

where I stands for the ionic strength. In agreement with an earlier finding,[24] they also found that thiosulfate is not the only product of the reaction; some tetrathionate and colloidal sulfur were formed as well. A couple of decades later Wagner and Schreier have reinvestigated[25] the decomposition and found that colloidal sulfur, formed during the course of the reaction, was later dissolved and the only product of the decomposition was thiosulfate. They claimed that sulfur and sulfite were the only intermediates of the reaction and did not even mention tetrathionate as a possible intermediate. A plausible mechanism was suggested to take their experimental observations into account in which the rate-determining step of the decomposition was the attack of OH^- on the γ-S atom of the sulfur chain followed by subsequent reactions of the intermediates to produce thiosulfate and sulfoxylic acid. They also proposed that the sulfur-chain-shortening sulfitolysis of pentathionate occurs via the same pathway; i.e., sulfite attacks the γ-S atom of the sulfur chain in the rate-determining step.[26] These discrepancies clearly indicate that the alkaline decomposition of pentathionate should be reinvestigated by recently available experimental and computational techniques to provide a more reliable kinetic model.

The classical methodologies for the kinetic study of chemical reactions involving sulfur species, like titration and UV spectrophotometry, have their limitation not to provide independent information about the concentration of the reactants, intermediates, and end products involved in the reaction. Fast separation of the sulfur species by using high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE), however, offers a convenient tool to monitor simultaneously the concentration of some sulfur-containing species during the course of the reaction.[9,10,27]

Successful application of these separation techniques requires that (i) the reaction to be monitored be slow compared to the separation process, (ii) the pH and other conditions used in the separation process not alter the reaction mechanism and not accelerate the rate of the reaction of interest, and (iii) the concentrations of relevant species be measurable within the linear range of detection. These conditions are expected to be fulfilled for studying the alkaline decomposition of pentathionate by HPLC and CE methods and allow us to determine quantitatively the concentrations of pentathionate, thiosulfate, and tetrathionate and to follow qualitatively that of hexathionate.

■ EXPERIMENTAL SECTION

Materials and Solutions. Commercially available reagents of the highest purity available were used without further purification such as potassium tetrathionate, sodium sulfite, sodium sulfate, sodium carbonate, and sodium hydrogen carbonate. Potassium trithionate was prepared as described previously[28] with slight modifications detailed elsewhere.[29] Its purity was found to be 98.5%. Potassium pentathionate

was prepared following the description reported by Kelly and Wood[28] in which thiosulfate reacts with concentrated hydrochloric acid in the presence of arsenic trioxide as the catalyst. Its purity was checked by HPLC (or CE) and by titration with $HgCl_2$ and found to be 98.37%. All solutions were prepared by Milli-Q distilled water, having a specific conductivity of 18.2 $M\Omega^{-1}$ cm^{-1}. A carbonate/hydrogen carbonate buffer was used to maintain the pH between 9.3 and 10.88, taking the pK_a of hydrogen carbonate as 10.3.[30] The ionic strength was maintained at 0.05 M using the appropriate concentration of the buffer components. The initial concentration of pentathionate was varied between 0.1 and 1.0 mM.

Methods and Instrumentation. The HPLC separation experiments were conducted on a Dionex-3 instrument equipped with a variable-wavelength detector. A C18 silicon column was used; the mobile phase consisted of a 0.0158 M carbonate buffer solution containing 7 mM tetra(n-butyl)ammonium hydroxide (TPAOH) as the ion-pair agent and acetonitrile. The separation performance was optimized to a ratio of 88:12 ($v_{\mathrm{water}}/v_{\mathrm{acetonitrile}}$).

The electrophoresis experiments were carried out on a P/ACE MDQ Capillary Electrophoresis System (Beckman Coulter Inc., Fullerton, CA) equipped with a diode-array detector. A fused-silica capillary of 75 μm inner diameter and 57 cm total length (50 cm to the detector) was used. Samples were injected using an autosampler in the hydrodynamic mode by overpressure (0.5 psi) for 5 s. A 32 Karat Software (Beckman Coulter Inc.) was used for data acquisition and analysis. Data were usually taken at 214 nm for most of the separations, while a shorter wavelength (190 nm) was necessary for the detection of trithionate and sulfite. The running buffers were composed of 5 mM KH_2PO_4 and 5 mM $(NH_4)_2SO_4$.

The reactions were initiated by introducing appropriate quantities of the reactants into the buffer solutions. A portion of the solution in the reactor was withdrawn at regular intervals with a syringe and injected into the HPLC system or with an autosampler for the CE system for analysis. All experiments, including the reaction and separation processes, were conducted at 25.0 ± 0.1 °C. Samples were filtered through a 0.45 μm membrane filter before HPLC injection.

Data Treatment. To determine the concentration of each species from the chromatograms, it is necessary to establish calibration curves that describe the relationship between the concentration of species to be analyzed and the area of each peak. The integrated areas of the peaks representing thiosulfate, tetrathionate, and pentathionate are found to possess excellent linear correlation with their concentrations, where the correlation coefficient was always above 0.99. Because we were not able to prepare pure hexathionate, its peak area on the chromatograms could not be converted into the concentration, meaning that hexathionate detection was only proven to be semiquantitative. Chromatographic data at 230 nm were used for most of the kinetic measurements, but for CE, both data of 190 and 214 nm were used for identification of the species. The experimental curves (concentration−time series of pentathionate, thiosulfate, and tetrathionate) were analyzed simultaneously with the program package *Zita*.[31] Altogether more than 1200 experimental points from 81 kinetic series were used for simultaneous data evaluation. Our quantitative criterion for an acceptable fit was that the average deviation for the relative fit approach 5%, which is close to the experimentally achievable limit of error of the concentration determination under the present experimental circumstances.

■ RESULTS

Identification of Sulfur-Containing Species. Our experiments by both HPLC and CE confirmed that four sulfur-containing species exist in detectable amounts during the course of the reaction. Figure 1 represents typical chromatograms and an electropherogram measured during the decomposition.
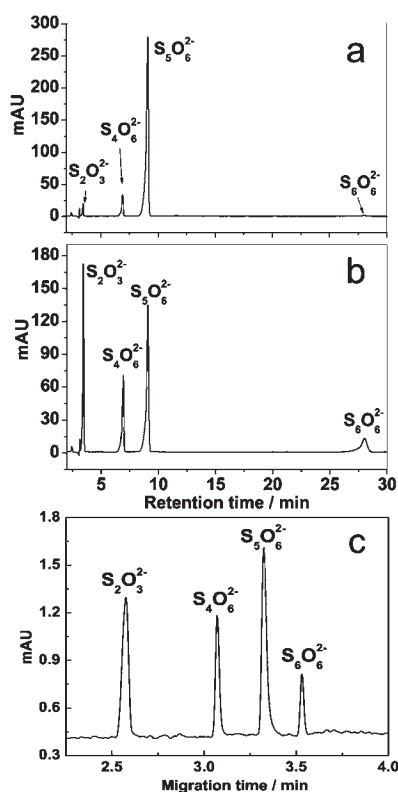
Figure 1. Detection of sulfur-containing species in the decomposition of pentathionate by HPLC and CE. Chromatograms: $[S_5O_6^{2-}]_0 =$ 0.5 mM, pH = 9.61, λ = 230 nm at (a) $t = 26$ min and (b) $t = 270$ min. Electropherogram: $[S_5O_6^{2-}]_0$ = 0.4 mM, pH = 9.80, λ = 214 nm at (c) $t = 80$ min.

Some species, such as pentathionate, thiosulfate, and tetrathionate, were identified by comparing their retention times to those of standard solutions; hexathionate was, however, identified by comparing its HPLC retention factor with that found in the literature.[32] Tetrathionate was relatively stable at lower pH, although at longer time scale under our experimental conditions, it is definitely an intermediate because of its well-known alkaline decomposition.[21,22] Hexathionate was also observed as an intermediate; it is, however, less stable in alkaline conditions than lower polythionates. Unfortunately, its detection was only semiquantitative because we could not convert its peak area to concentration because of the lack of pure hexathionate. The peak area—time curves for hexathionate were only used to confirm the proposed kinetic model qualitatively; i.e., hexahionate concentration—time curves have to go through a maximum. Thiosulfate was proven to be the major sulfur-containing end product of the reaction, but we also observed trace amounts of sulfate and sulfur precipitation. It is interesting to note that during the course of the reaction the amount of colloidal sulfur increased first, but later its amount decreased and, even in some experiments, it completely disappeared. It should also be mentioned that we did not detect sulfite and trithionate in our experimental circumstances, although their role in the alkaline decomposition of polythionates is confirmed.[21,22,25] Later, we shall see that this observation can be readily understood by our proposed kinetic model. Trace amounts of sulfate may be explained either by small impurities of pentathionate or by the oxidation of intermediate sulfite by dissolved oxygen during the

course of the reaction, although the sulfite concentration is low under our experimental conditions.
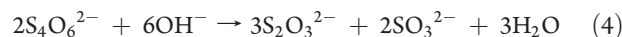
Stoichiometry. On the basis of our experiments, it is difficult to present the exact stoichiometry of the reaction. It is almost sure that one of the limiting stoichiometries has to be

$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \quad (2)$$
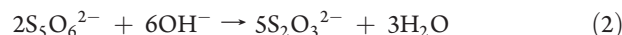
but we would like to emphasize that we did not reach this limiting stoichiometry under our experimental circumstances. It is expected, however, that if the pH is higher, then polythionates disappear from the reacting solution sooner and eventually only thiosulfate is expected to form. This idea was checked in separate experiments where the end product of the alkaline decomposition of pentathionate was checked at pH = 12.0—13.0 after completion. The result clearly showed that eq 2 is the limiting stoichiometry at strongly alkaline solutions. At experimental circumstances, where the kinetics of the alkaline decomposition was studied, we may consider several side reactions that affect the stoichiometry. Among them, the following process is the most plausible:

$$S_5O_6^{2-} \rightarrow S_4O_6^{2-} + S \quad (3)$$

It explains both the formation of the long-lived tetrathionate and that of colloidal sulfur. The disappearance of sulfur at the later stages of the reaction may be due to the formation of sulfite from the alkaline decomposition of tetrathionate

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (4)$$

followed by

$$S + SO_3^{2-} \rightarrow S_2O_3^{2-} \quad (5)$$

One may easily notice that eq 2 may easily be constructed by the following linear combination $[2(3) + (4) + 2(5)]$ of some steps of the proposed model, but eq 4 has significance only at high pHs.[21,22] At lower pHs, however, the stoichiometry of the alkaline decomposition of tetrathionate changes, meaning that different polythionates may appear to a detectable extent and colloidal sulfur may precipitate. These facts together support the difficulties of presenting an exact stoichiometry or limiting stoichiometries in the present case.
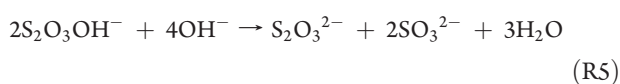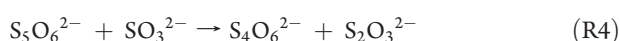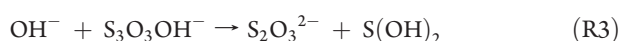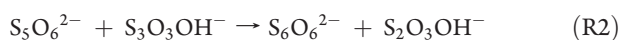
Initial Rate Studies. Figure 2 shows the logarithm of the initial rate of the decomposition (defined as $v_0 = -d[S_5O_6^{2-}]/dt$ at $t = 0$). It clearly confirms the earlier results reported by Christiansen and co-workers that formal kinetic orders of both pentathionate and hydroxide ions are definitely unity within the concentration studied.[23]

Proposed Kinetic Model. The approach we have chosen to analyze our data set has already been successfully applied in several cases of our previous works and the essence of this method has already been published elsewhere.[11,33] The most critical part of this method is to postulate the set of species (reactants, intermediates, and products) involved in the reactions. Besides the reactants (pentathionate and hydroxide ions), the products (thiosulfate and sulfur), and the intermediates identified by HPLC and/or CE methods (tetrathionate and hexathionate) and by the isotope trace labeling method[25] (sulfite), several other intermediates likely to participate in the reaction are postulated such as sulfoxylic acid, $S_2O_3OH^-$, $S_3O_3OH^-$, and $S_4O_3OH^-$. The next step is to find all of the conceivable reactions among all of these species. We then considered that all of these reactions have rate equations
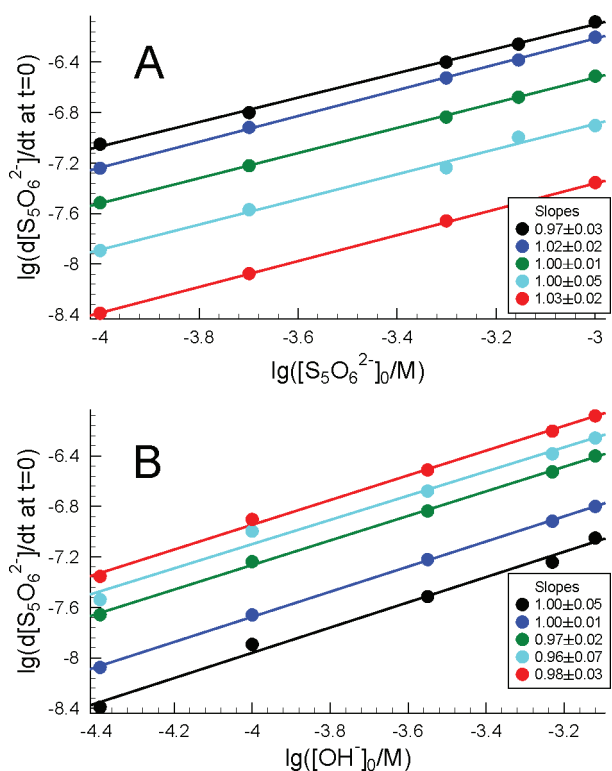
Figure 2. Plots of the logarithm of the initial rate of decomposition of pentathionate (symbols) against (A) $\log([S_5O_6^{2-}]_0/M)$ at pH = 9.30 (red), 9.61 (cyan), 10.01 (green), 10.45 (blue), and 10.77 (black) and against (B) $\log([OH^-]_0/M)$ at $[S_5O_6^{2-}]_0/mM$ = 0.1 (black), 0.2 (blue), 0.5 (green), 0.7 (cyan), and 1.0 (red). Solid lines were obtained by a least-squares linear fit.
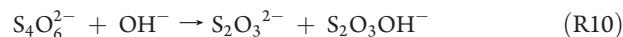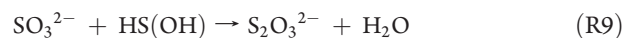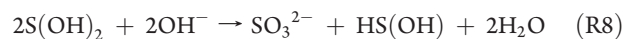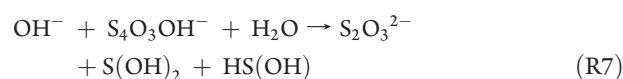
consisting of two terms: the first one is independent of $[OH^-]$, and the second one is proportional to $[OH^-]$. As a start, rate coefficients determined from independent studies were fixed and the rest of them were fitted during the evaluation procedure. The rate parameters, which became insensitive for the average deviation between the measured and calculated data, were omitted step by step, but the omission was only executed if the given parameter became insensitive again after its resensitization. In our interpretation, resensitization means that the rate coefficient of the given step was increased to change the value of the average deviation at least by 5%. The model reduction procedure led us to propose the following kinetic model for the decomposition of pentathionate:

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{E1}$$

$$S_5O_6^{2-} + OH^- \rightarrow S_2O_3^{2-} + S_3O_3OH^- \tag{R1}$$

$$S_5O_6^{2-} + S_3O_3OH^- \rightarrow S_6O_6^{2-} + S_2O_3OH^- \tag{R2}$$

$$OH^- + S_3O_3OH^- \rightarrow S_2O_3^{2-} + S(OH)_2 \tag{R3}$$

$$S_5O_6^{2-} + SO_3^{2-} \rightarrow S_4O_6^{2-} + S_2O_3^{2-} \tag{R4}$$

$$2S_2O_3OH^- + 4OH^- \rightarrow S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \tag{R5}$$

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

no.	rate equation	parameter
R1	$k_1[S_5O_6^{2-}][OH^-]$	0.513 ± 0.037 M^{-1} s^{-1}
R2	$k_2[S_5O_6^{2-}][S_3O_3OH^-]$	$k_2/k_3 = 3.15 \pm 0.56$
R3	$k_3[OH^-][S_3O_3OH^-]$	$\geq 10^3$ M^{-1} s^{-1}
R4	$k_4[S_5O_6^{2-}][SO_3^{2-}]$	$\geq 10^3$ M^{-1} s^{-1}
R5	$k_5[S_2O_3OH^-]^2$	$\geq 10^5$ M^{-1} s^{-1}
R6	$k_6[S_6O_6^{2-}][OH^-]$	1.08 ± 0.06 M^{-1} s^{-1}
R7	$k_7[OH^-][S_4O_3OH^-]$	$\geq 10^4$ M^{-1} s^{-1}
R8	$k_8[S(OH)_2]^2$	$\geq 10^5$ M^{-1} s^{-1}
R9	$k_9[SO_3^{2-}][HS(OH)]$	$k_9/k_4 = 7.17 \pm 0.69$
R10	$k_{10}[S_4O_6^{2-}][OH^-]$	$(4.0 \pm 0.2) \times 10^{-2}$ M^{-1} s^{-1}

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

$$S_6O_6^{2-} + OH^- \rightarrow S_2O_3^{2-} + S_4O_3OH^- \tag{R6}$$

$$OH^- + S_4O_3OH^- + H_2O \rightarrow S_2O_3^{2-} \\ + S(OH)_2 + HS(OH) \tag{R7}$$

$$2S(OH)_2 + 2OH^- \rightarrow SO_3^{2-} + HS(OH) + 2H_2O \tag{R8}$$

$$SO_3^{2-} + HS(OH) \rightarrow S_2O_3^{2-} + H_2O \tag{R9}$$

$$S_4O_6^{2-} + OH^- \rightarrow S_2O_3^{2-} + S_2O_3OH^- \tag{R10}$$

The rapid de- and reprotonation process (E1) was taken into account with a known equilibrium constant[30] to follow the small change in the pH during the course of decomposition (pK_{E1} = 10.3). Table 1 contains the fitted and fixed rate coefficients of the proposed model. The sound agreement between the measured and calculated concentrations (see Figures 3–6) and the 3.8% relative average deviation indicate that the proposed model is working properly within the concentration range used in the experiments.
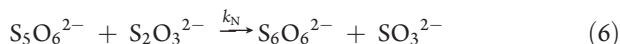
■ DISCUSSION

Step (R1) is the initiating rate-determining step of the alkaline decomposition of pentathionate that proceeds via scission of the inner S–S bond, yielding thiosulfate and $S_3O_3OH^-$. This step was already suggested by several research groups earlier.[23,25] In the molecular level, it is reasonably supported that the hydroxide ion attacks the γ-S atom of the sulfur chain of pentathionate. The formation of the adduct $S_5O_6OH^{3-}$ is probably followed by the heterolytic inner S–S bond cleavage, resulting in the nucleophilic displacement of thiosulfate by the hydroxide ion. Our fitting procedure has yielded a value of 0.513 ± 0.037 M^{-1} s^{-1} that is in reasonable agreement with the mean value that can be calculated from eq 1 at 20 °C as 0.19 ± 0.04 M^{-1} s^{-1} by substitution of the value of the ionic strength used in our experiments.

Step (R2) is a fast reaction that produces hexathionate and $S_2O_3OH^-$. This step has not been proposed before because no experiments were available previously, indicating that hexathionate was formed during the decomposition. Our calculation indicated that the individual rate coefficient of the reaction cannot be calculated from our experiments because k_2 is in total correlation with k_3, meaning that only the k_2/k_3 ratio could be
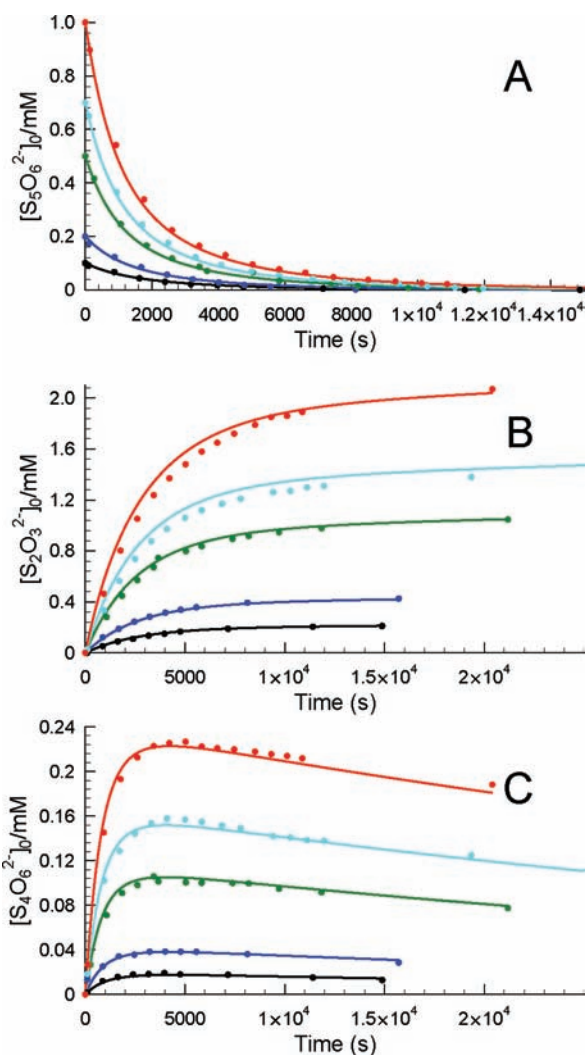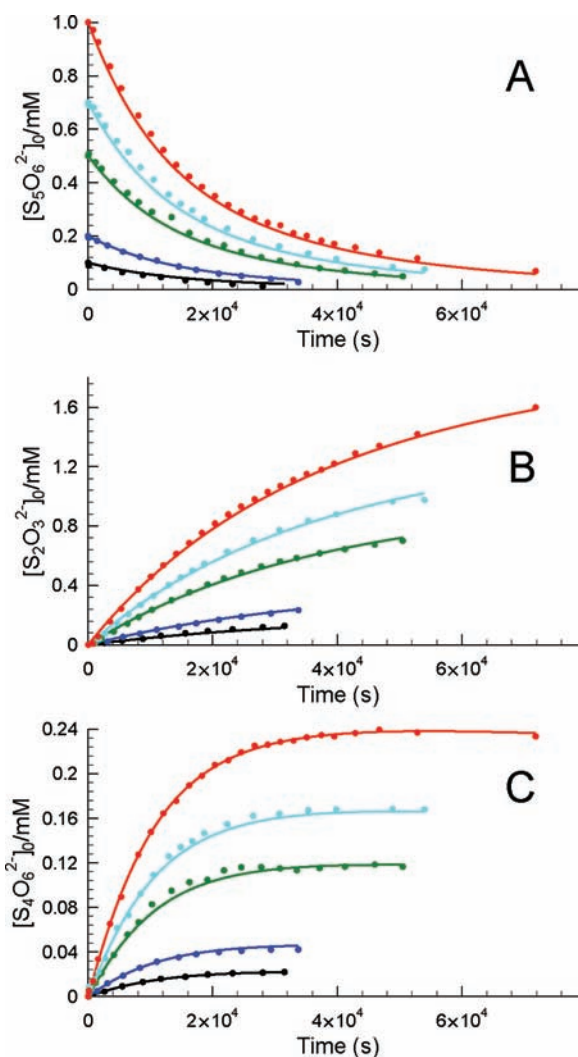
Figure 3. Measured (dotted lines) and calculated (solid lines) concentrations of pentathionate (A), thiosulfate (B), and tetrathionate (C) as a function of the time at pH = 10.77. $[S_5O_6^{2-}]_0$/mM = 0.1 (black), 0.2 (blue), 0.5 (green), 0.7 (cyan), and 1.0 (red).

Figure 4. Measured (dotted lines) and calculated (solid lines) concentrations of pentathionate (A), thiosulfate (B), and tetrathionate (C) as a function of the time at pH = 9.61. $[S_5O_6^{2-}]_0$/mM = 0.1 (black), 0.2 (blue), 0.5 (green), 0.7 (cyan), and 1.0 (red).

determined. Relatively high values of k_2 and k_3 also provide that $S_3O_3OH^-$ can be treated as a short-lived intermediate of the reaction. One may easily argue that hexathionate may as well be produced via thiosulfatolysis of pentathionate:

$$S_5O_6^{2-} + S_2O_3^{2-} \xrightarrow{k_N} S_6O_6^{2-} + SO_3^{2-} \qquad (6)$$

To check whether eq 6 has any contribution to the kinetics under our experimental circumstances, additional experiments were carried out in which the initial concentration of thiosulfate was varied. As seen from Figure 7, thiosulfate has no detectable effect on the decay of pentathionate; therefore, we concluded that eq 6 could not play a significant role in the formation of hexathionate under our experimental conditions. It does not necessarily mean that the role of eq 6 can be ruled out as a convenient source of hexathionate: there may be different conditions, probably at lower pHs, where thiosulfatolysis becomes the only source of hexathionate. For the sake of completeness as well as to be more convincing, we have also carried out an additional fitting with the replacement of step (R2) with eq 6. The average deviation increased a bit to 4.6%, which is still in the acceptable range,

and the values of some parameters changed as $k_1 = 0.748 \pm 0.064$ $M^{-1} s^{-1}$ and $k_4/k_9 = 1.47 \pm 0.13$ and that of the others remained basically the same within their standard deviations. This calculation has provided the value of 0.010 ± 0.001 $M^{-1} s^{-1}$ for k_N, but this value would, however, mean that the already 0.001 M initial amount of thiosulfate should have affected the decay of pentathionate. Because this effect was not realized experimentally (see previously), we concluded that value for k_N is overestimated. If, however, the real value for k_N is significantly lower, then the concentration of hexathionate formed during the reaction would be so low that its detection would have been impossible. On the basis of the experiments and the arguments presented here, we, therefore, concluded that hexathionate is most probably formed via step (R2) under our experimental conditions. Furthermore, it makes it also unlikely that the well-known rearrangement reaction of pentathionate

$$2S_5O_6^{2-} \rightarrow S_4O_6^{2-} + S_6O_6^{2-} \qquad (7)$$
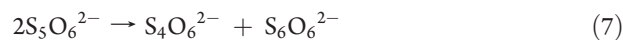
is the main source of hexathionate for two reasons under our experimental conditions: (i) thiosulfate does not influence the

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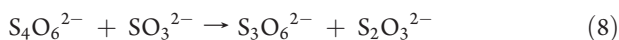dx.doi.org/10.1021/ic201424m |*Inorg. Chem.* 2011, 50, 9670–9677
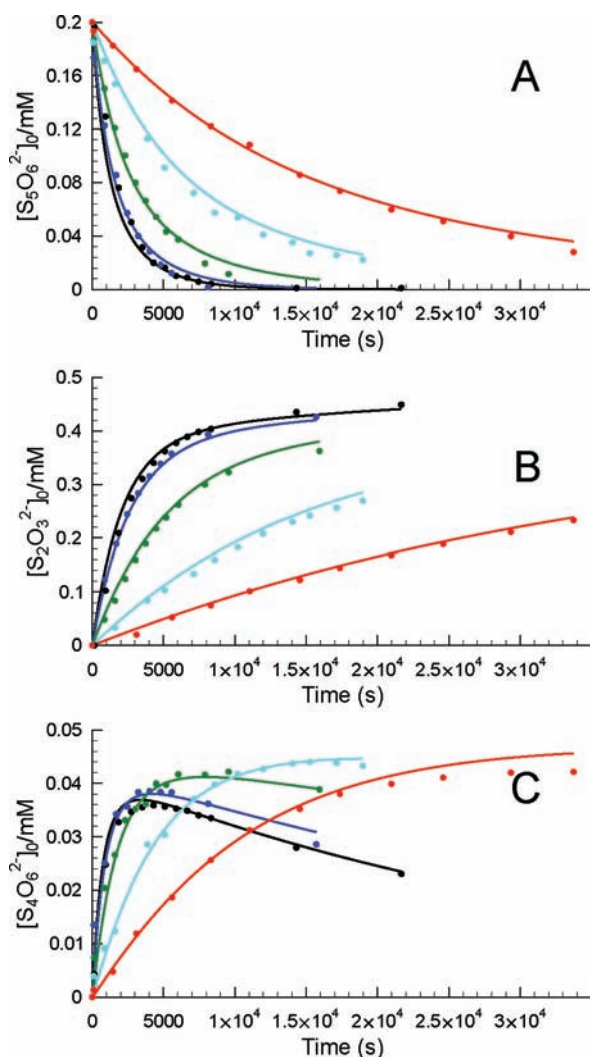
Figure 5. Measured (dotted lines) and calculated (solid lines) concentrations of pentathionate (A), thiosulfate (B), and tetrathionate (C) as a function of the time at different pHs and at $[S_5O_6^{2-}]_0 = 0.2$ mM. pH = 10.88 (black), 10.77 (blue), 10.45 (green), 10.01 (cyan), and 9.61 (red).

Figure 6. Measured (dotted lines) and calculated (solid lines) concentrations of pentathionate (A), thiosulfate (B), and tetrathionate (C) as a function of the time at different pHs and at $[S_5O_6^{2-}]_0 = 1.0$ mM. pH = 10.88 (black), 10.77 (blue), 10.45 (green), 10.01 (cyan), 9.61 (red), and 9.30 (magenta).
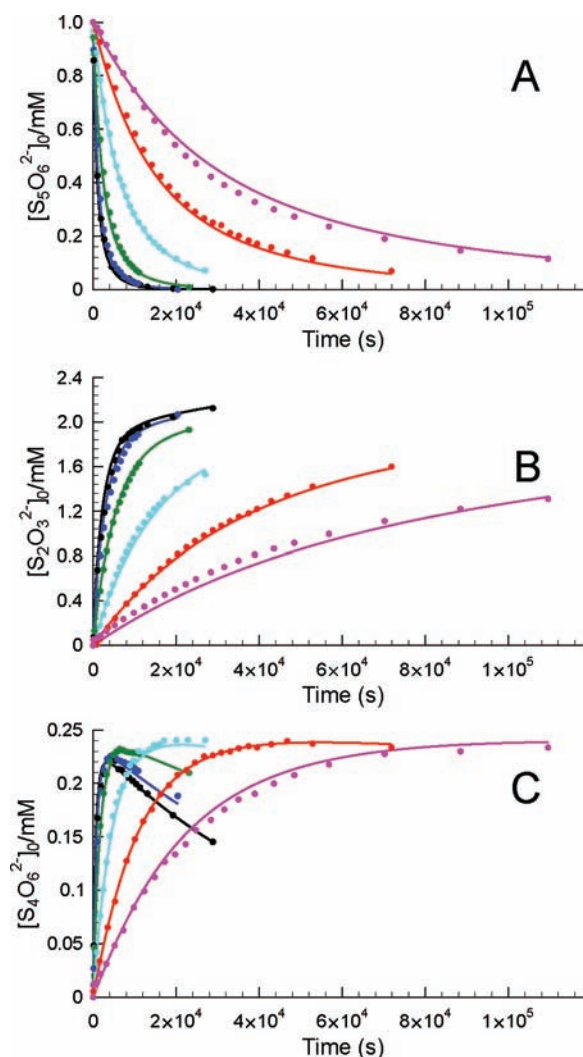
decay of pentathionate (see Figure 7), but it is generally accepted that the rearrangement starts with eq 6; (ii) if the rearrangement occurs, then the formal kinetic order of pentathionate should be significantly higher than 1, which is an explicit contradiction not only to our but also other's experimental results.[23]

Step (R3) converts $S_3O_3OH^-$ to thiosulfate and sulfoxylic acid via a rapid reaction. This reaction was already previously suggested.[23,25] As mentioned previously, k_3 cannot be calculated unambiguously; we could only set a lower limit for $k_3 \geq 10^3$ M^{-1} s^{-1}.

Step (R4) is a possible first step of the well-known sulfitolysis of pentathionate studied by Wagner and Schreier.[26] They studied this reaction in a high excess of sulfite that eventually led to the formation of trithionate. Application of a high excess of sulfite means that the sulfur-chain-shortening process does not terminate at tetrathionate because tetrationate may further react with sulfite as follows:

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \qquad (8)$$

In our experimental conditions, however, the sulfite concentration is relatively low, meaning that eq 8 is not able to produce

trithionate in detectable amounts. Of course, at the later phase of the reaction, where the sulfite concentration increases because of the well-known alkaline decomposition of tetrathionate, trithionate may as well appear as a final product. The individual rate coefficient of this step cannot be determined from our experiments because we found that the values of k_4 and k_9 are in total correlation with each other, meaning that we were able to calculate only the ratio of k_4/k_9. Our calculation yielded a lower limit for k_4 as $k_4 \geq 10^3$ M^{-1} s^{-1} to provide the sulfite concentration in a sufficiently low level during decomposition.

Step (R5) was already proposed in our previous work,[22] where we had also found that this reaction has to be rapid in agreement with the results presented here. Because this species cannot be accumulated during the course of the reaction and this was found to be the only step to consume $S_2O_3OH^-$, we could only set a lower limit for k_5 as 10^5 M^{-1} s^{-1}.

Step (R6) is the initiating step of the alkaline decomposition of hexathionate to produce thiosulfate and $S_4O_3OH^-$. It is well-known that the stability of polythionates in alkaline conditions

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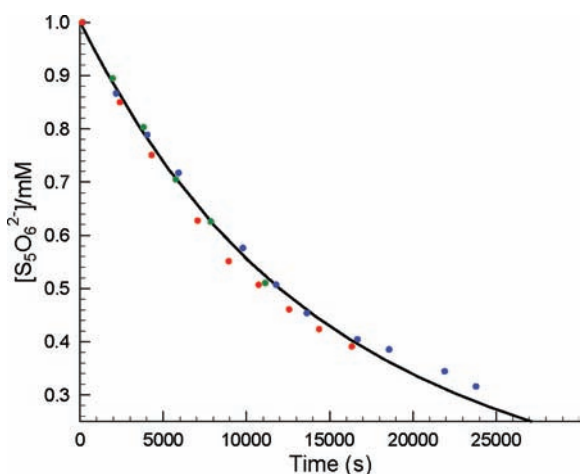
Figure 7. Measured (dotted line) pentathionate concentration as a function of the time with variation of the initial thiosulfate concentration. Conditions: pH = 9.61, $[S_5O_6^{2-}]_0 = 1.0$ mM, $[S_2O_3^{2-}]_0$/mM = 0 (blue), 0.5 (green), and 1.0 (red). The solid line represents the prediction for $[S_5O_6^{2-}]$ obtained by the proposed model.
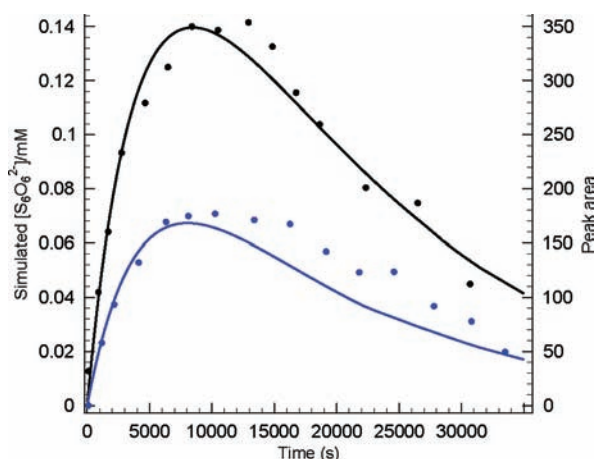
Figure 8. Measured (dotted lines) peak area of hexathionate and simulated (solid lines) hexathionate concentration by the proposed model as a function of the time. Conditions: pH = 9.61; $[S_5O_6^{2-}]_0 = $ 0.5 mM (blue) and 1.0 mM (black).

decreases with increasing sulfur chain. As expected, we found that the rate coefficient of the initiating step of the alkaline decomposition of hexathionate ($k_6 = 1.08 \pm 0.06$ M^{-1} s^{-1}) is somewhat higher than that of pentathionate ($k_1 = 0.513 \pm 0.037$ M^{-1} s^{-1}). This clearly means that hexathionate is a relatively long-lived intermediate; its formation and disappearance can conveniently be followed during the course of the reaction. The peak area of hexathionate could also be followed by HPLC, but as was mentioned previously, the lack of pure hexathionate prevented conversion of the peak area —times series to concentration—time ones. To further support directly our kinetic model, the peak area of hexathionate and the simulated concentration of hexathionate are compared in Figure 8. This clearly indicates a reasonable agreement that supports the validity of our model.

Step (R7) is also a fast reaction, and its individual rate coefficient cannot be determined independently from our

experiments. This process removes immediately $S_4O_3OH^-$ upon its formation from step (R6) and produces the thiosulfate ion, sulfoxylic acid, and HS(OH). Our calculation showed that the value of this rate coefficient has to be higher than 10^4 M^{-1} s^{-1}.

Step (R8) is the second-order decomposition of sulfoxylic acid to produce sulfite and HS(OH). It is well-known that under alkaline conditions this disproportionation is rapid.[34] We could, therefore, set only a lower limit to k_8 as 10^5 M^{-1} s^{-1} to treat sulfoxylic acid as a short-lived intermediate.

Step (R9) was already proposed by Wagner and Schreier,[25] in which soluble sulfur in the form of HS(OH) reacts with sulfite to produce thiosulfate. With the lack of sulfite, however, HS(OH) may be decomposed to form sulfur precipitation according to the following reaction:

$$HS(OH) \rightarrow S_{coll} + H_2O \qquad (9)$$

On the basis of these processes, now, it seems to be clear that the alkaline decomposition of higher polythionates such as pentathionate, hexathionate, etc., leads to the formation of sulfur precipitation in certain experimental conditions just because the relatively fast sulfitolysis of polythionates prevents the buildup of sulfite, which may react with HS(OH) to form thiosulfate, opening up the way for eq 9.

Step (R10) is the well-known initiating step of the alkaline decomposition of tetrathionate. Its rate coefficient was determined by several authors and found to be between 0.0051 and 0.38 M^{-1} s^{-1} depending on the ionic strength of the medium. A value of $k_{10} = 0.040 \pm 0.002$ M^{-1} s^{-1} obtained by this work fits in this range and can be treated as an acceptable value if someone takes into account that the ionic strength was set to 0.05 M in our experimental circumstances.

■ CONCLUSION

The work presented here is intended to elucidate the kinetics and mechanism of the alkaline decomposition of pentathionate to take advantage of the recently available experimental and computational methods. We have clearly demonstrated that hexathionate is a detectable intermediate during the course of the reaction, but our data support that the main source of hexathionate is step (R2) rather than the well-known thiosulfate-assisted rearrangement of pentathionate. As expected, it is also shown that HPLC is a very powerful tool for following independently the concentration of several sulfur-containing species as a function of the time. The independently measured concentration—time series along with the simultaneous evaluation of the kinetic curves made it possible to propose a comprehensive kinetic model that is able to take into account all of the most important characteristics of the measured quantities. The main advantage of this method is that the kinetic model can be obtained without any simplification or unnecessary assumptions, and the simultaneous fitting of the concentration—time series of several species measured by HPLC makes the proposed kinetic model more reliable. As seen, the sound quantitative agreement between the measured and calculated pentathionate, thiosulfate, and tetrathionate concentration—time curves along with a qualitative agreement between the peak area of hexathionate as a function of the time and the simulated $[S_6O_6^{2-}]$—time curves strongly supports the validity of the proposed kinetic model.

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■ 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) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 101–106.

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

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

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

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

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

(10) Xu, L.; Horváth, A. K.; Hu, Y.; Ji, C.; Zhao, Y. M.; Gao, Q. Y. *J. Phys. Chem. A* **2011**, *115*, 1853–1860.

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

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

(13) Kurin-Csörgei, K.; Orbán, M.; Rábai, G.; Epstein, I. R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2851–2855.

(14) Yuan, L.; Gao, Q. Y.; Zhao, Y. M.; Tang, X. D.; Epstein, I. R. *J. Phys. Chem. A* **2010**, *114*, 7014–7020.

(15) Rábai, G.; Hanazaki, I. *J. Phys. Chem. A* **1999**, *103*, 7268–7273.

(16) Druschel, G. K.; Hamers, R. T.; Banfild, J. F. *Geochim. Cosmochim. Acta* **2003**, *67*, 4457–4469.

(17) Bhattacharya, R. N.; Wiesner, H.; Berens, T. A.; Matson, R. J.; Keane, J.; Ramanathan, K.; Swartlander, A.; Mason, A.; Noufi, R. N. *J. Electrochem. Soc.* **1997**, *144*, 1376–1379.

(18) Janickis, V.; Maciuleviciuse, R.; Ivanauskas, R.; Ancutiene, I. *Colloid Polym. Sci.* **2003**, *281*, 84–89.

(19) (a) Naito, K.; Yoshida, M.; Shieh, M.; Okabe, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1365–1372. (b) Byerley, J. J.; Fouda, S. A.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 889–893. (c) Zhang, H.; Dreisinger, D. B. *Hydrometallurgy* **2002**, *66*, 59–65.

(20) (a) Naito, K.; Hayata, H.; Mochizuki, M. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1453–1457. (b) Rolia, E.; Chakrabarti, C. L. *Environ. Sci. Technol.* **1982**, *16*, 852–857.

(21) (a) Gutman, A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 509. (b) Riesenfeld, E. H. *Z. Anorg. Allg. Chem.* **1924**, *141*, 109. (c) Kurtenacker, A.; Kaufmann, M. *Z. Anorg. Allg. Chem.* **1925**, *148*, 43. (d) Goehring, M. *Fortschr. Chem. Forsch.* **1952**, *2*, 444. (e) Breuer, P. L.; Jeffrey, M. I. *Hydrometallurgy* **2004**, *72*, 335–338. (f) Zhang, H.; Jeffrey, M. I. *Inorg. Chem.* **2010**, *49*, 10273–10282.

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

(23) Christiansen, J. A.; Drost-Hansen, W.; Nielsen, A. *Acta Chem. Scand.* **1952**, *6*, 333–340.

(24) Goehring, M.; Heibing, W.; Appel, I. *Z. Anorg. Chem.* **1947**, *254*, 185–200.

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

(26) Wagner, H.; Schreier, H. *Phosphorus Sulfur Relat. Elem.* **1978**, *4*, 285–286.

(27) (a) Christy, A. A.; Egeberg, P. K. *Talanta* **2000**, *51*, 1049–1058. (b) Gao, Q. Y.; Liu, B.; Li, L.; Wang, J. *J. Phys. Chem. A* **2007**, *111*, 872–877. (c) Gao, Q. Y.; Wang, G.; Sun, Y.; Epstein, I. R. *J. Phys. Chem. A* **2008**, *112*, 5771–5773.

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

(29) Csekö, G.; Horváth, A. K. *J. Phys. Chem. A* **2010**, *114*, 6521–6526.

(30) *IUPAC Stability Constant Database*; Royal Society of Chemistry: London, 1992−1997.

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

(32) (a) Miura, Y.; Satoh, A.; Koh, T. *J. Chromatogr., A* **1997**, *770*, 157–164. (b) Miura, Y.; Satoh, A.; Kawaoi, A. *J. Chromatogr., A* **2000**, *884*, 81–87.

(33) Rauscher, E.; Csekö, G.; Horváth, A. K. *Inorg. Chem.* **2011**, *50*, 5793–5802.

(34) Makarov, S. *Russ. Chem. Rev.* **2001**, *70*, 885–895.