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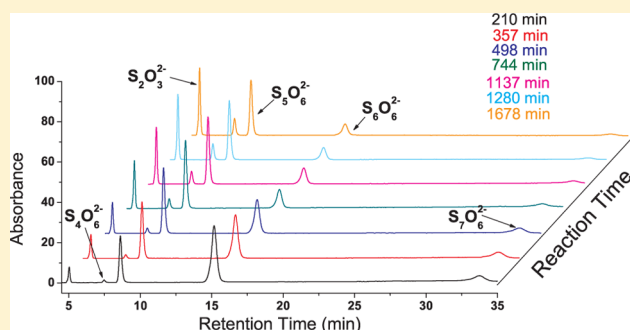
# Kinetics and Mechanism of the Alkaline Decomposition of Hexathionate Ion

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**ABSTRACT:** The alkaline decomposition of hexathionate has been investigated by high-performance liquid chromatography monitoring the concentration of polythionates (such as hexathionate, pentathionate, and tetrathionate) and that of thiosulfate simultaneously in buffered medium at a constant ionic strength. As a major final product, unlike in the case of the alkaline decomposition of tetrathionate and pentathionate, a significant amount of sulfur deposition was also observed. Nevertheless, the chromatograms clearly suggested that heptathionate also appears as a key intermediate in a detectable amount during the course of the reaction. On the basis of these observations an 11-step kinetic model with 9 fitted and 4 fixed rate coefficients is suggested to take all of the most important characteristics of the decomposition into account. The proposed model includes the well-known thiosulfate-assisted sulfur chain, increasing pathways for tetrathionate and pentathionate along with their rate coefficients, but among them that of the thiosulfate-assisted rearrangement of pentathionate has not been reported yet. Having these kinetic parameters in hand reveals a reasonable trend of these rate coefficients against the length of the sulfur chain, suggesting that the attack of the nucleophilic agents like hydroxide, thiosulfate, and sulfite ions is determined by the electron density in the vicinity of the given sulfur atom.



## INTRODUCTION

During the oxidation process of thiosulfate by different oxidants, leading eventually to sulfate, a rich variety of sulfur-containing intermediates is expected to be involved.<sup>1–3</sup> These transient species may react further not only with the reactants but also with each other making the reaction mechanisms particularly complicated.<sup>4</sup> Hexathionate, as one of the important intermediates in the redox transformations or metabolism of sulfur compounds in many environmental, industrial, and biological systems,<sup>5,6</sup> is formed in detectable amounts in recent kinetics studies of thiosulfate oxidation reactions<sup>1,2</sup> and may therefore contribute to the appearance of rich variety of nonlinear phenomena.<sup>7–12</sup>

The “thiosulfatolysis” has been widely accepted by researchers around the world as a potential alternative leaching approach for extracting gold from its ores due to the environmental harmfulness and unresolved practical difficulties in using the conventional cyanidation process.<sup>13</sup> However, the chemistry of the thiosulfate process for gold leaching and recovery is complex, because thiosulfate is often converted into various polythionates in aqueous solution.<sup>14</sup> Inevitably, the formation of polythionates followed by their strong absorption on the ion-exchange site of the resin reduces the efficiency of this method.<sup>15,16</sup> 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 polythionates in an alkaline medium increases with decreasing length of the sulfur chain; the most stable polythionate is, therefore, trithionate.<sup>17,18</sup> The alkaline degradation of tetrathionate and pentathionate has been studied by several research groups over decades;<sup>19–24</sup> therefore, comprehensive data are readily available under different experimental conditions.<sup>25</sup> Compared with tetrathionate and pentathionate, notably less is known about the alkaline degradation of hexathionate, although by now the involvement of this species in the oxidation reactions of thiosulfate has already been established.<sup>1,2</sup> Reactions of hexathionate with nucleophilic reagents on the basis of existing possibilities of heterolytic cleavage of S–S bonds have been widely discussed by Foss.<sup>26,27</sup> In his early articles, four possible schemes were proposed during the nucleophilic attack on the divalent sulfur atoms of hexathionate, followed by the elimination of thiosulfate rather than sulfite in the reaction of hexathionate with hydroxide, cyanide, sulfide ions, and so on; however, no detailed kinetic data were published to obtain the rate coefficients of these reactions directly. Our aim is therefore not only to simply determine the

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rate coefficient of the individual steps of the decomposition but also to judge between the possible pathways.

The classical methodologies for 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) offers a convenient tool to monitor simultaneously the concentration of some sulfur-containing species during the course of reaction.<sup>1,2,28</sup>

We present our investigations on the degradation of hexathionate at a weakly alkaline solution (at the pH range of 8.94 to 9.90) by HPLC.

## 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, sodium hydrogen carbonate, borax, and boric acid. Potassium trithionate was prepared as previously described<sup>29</sup> with slight modifications detailed elsewhere.<sup>30</sup> Its purity was found to be 98.5%. Potassium pentathionate was prepared following the description reported by Kelly and Wood<sup>29</sup> in which thiosulfate reacts with concentrated hydrochloric acid in the presence of arsenic trioxide as catalyst. Its purity was checked by HPLC (or CE) and by titration<sup>31</sup> with  $\text{HgCl}_2$  and found to be 98.37%. Potassium hexathionate was prepared following the description reported by Goehring and Feldmann.<sup>32</sup> Its purity was checked by HPLC (or CE) and by titration with  $\text{HgCl}_2$  and found to be 83.1%. The main impurity was found to be sodium chloride (16.0%). Separate experiments showed that this impurity does not influence the kinetics of decomposition of hexathionate ion. All solutions were prepared by Milli-Q distilled water with having specific conductivity of  $18.2 \text{ M}\Omega^{-1} \text{ cm}^{-1}$ . Stock solutions were prepared from deoxygenated distilled water bubbling through  $\text{N}_2$  for several minutes. In separate experiments we have also checked the effect of extra nitrogen protection through the whole course of the reaction, and no obvious effect has been found with or without further nitrogen protection. Borax/boric acid and carbonate/hydrogencarbonate buffers were used to maintain the pH between 8.94–9.25 and 9.6–9.90, taking the  $\text{pK}_a$  of boric and hydrogen carbonate as 9.23 and 10.3,<sup>33</sup> respectively. The ionic strength was regulated at 0.05 M with the use of appropriate concentration of the buffer components. The initial concentration of hexathionate was varied between 0.1 and 1.0 mM.

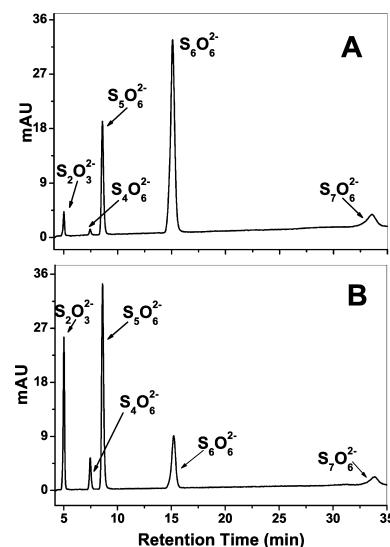
**Methods and Instrumentation.** The HPLC separation experiments were conducted on a Dionex-3 instrument equipped with a variable wavelength detector (VWD). We selected 230 nm for acquiring the chromatograms to detect various polythionates and thiosulfate simultaneously. A C18 silicon column was used; the mobile phase consisted of 7 mM tetra(*n*-butyl)ammonium hydroxide (TPAOH) as ion-pair agent and acetonitrile. The pH of the mobile phase was adjusted by the necessary amount of phosphoric acid. The separation performance was optimized to the ratio of 85:15 ( $\nu_{\text{water}}/\nu_{\text{acetonitrile}}$ ). Reactions were initiated by introducing an appropriate quantity of reactants into the buffer solutions. A portion of the solution from the reactor was withdrawn at regular intervals with a syringe and injected into the HPLC

system for analysis. All experiments, including the reaction and separation processes, were conducted at  $25.0 \pm 0.1^\circ\text{C}$ . Samples were filtered through a  $0.45 \mu\text{m}$  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 peaks representing thiosulfate, tetrathionate, pentathionate, and hexathionate are found to possess excellent linear correlation with their concentrations, where the correlation coefficient was always above 0.99. The experimental curves (concentration–time series of hexathionate, pentathionate, thiosulfate, and tetrathionate) were then analyzed simultaneously with the program package Zita.<sup>34</sup> Altogether, more than 1100 experimental points from 64 kinetic series were used for simultaneous data evaluation. Our quantitative criterion for an acceptable fit was that the average deviation for relative fit approached 5%, which is close to the experimentally achievable limit of error of concentration determination under present experimental circumstances.

## RESULT

**Identification of Sulfur-Containing Species.** Five sulfur-containing species exist in a detectable amount during the course of reaction in our experiments, including hexathionate, pentathionate, tetrathionate, thiosulfate, and heptathionate. Some species, such as thiosulfate and tetrathionate, were identified by comparing their retention times with those of standard solutions. Others, like pentathionate, hexathionate, and heptathionate were identified by comparing their HPLC retention factors with those found in literature.<sup>35</sup> Figure 1

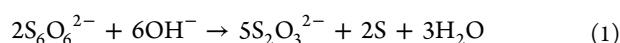


**Figure 1.** Detection of sulfur-containing species in the decomposition of hexathionate by HPLC:  $[\text{S}_6\text{O}_6^{2-}]_0 = 0.5 \text{ mM}$ , pH 9.29,  $\lambda = 230 \text{ nm}$  at (a):  $t = 273 \text{ min}$  and (b):  $t = 993 \text{ min}$ .

illustrates typical chromatograms measured during the decomposition. It obviously shows that hexathionate and its decomposition products were baseline-separated in a relatively short period of time. Therefore, the method was found to be suitable for kinetic studies and species analysis. Heptathionate peak area as a function was not converted into concentrations because no information is yet available in the literature to

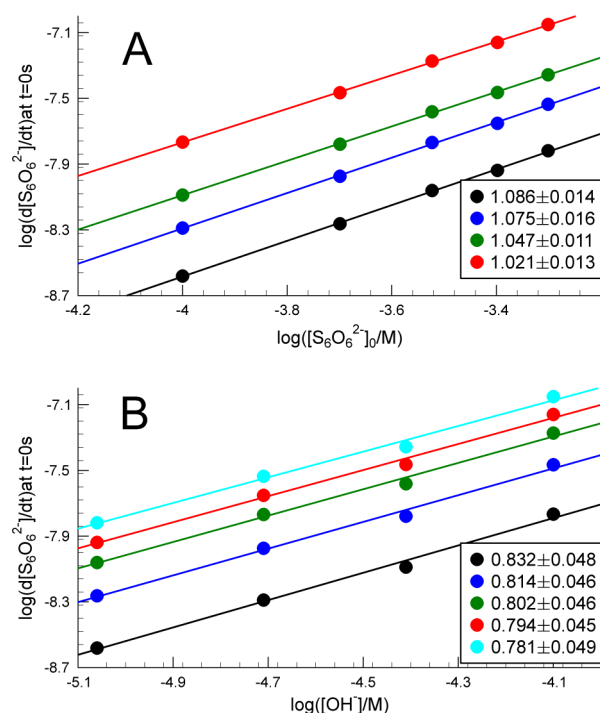
prepare heptathionate salt in sufficient purity to be used for calibration. Pentathionate was relatively stable at lower pH values, although on a longer time scale under our experimental conditions it is definitely an intermediate due to its well-known alkaline decomposition.<sup>21,22</sup> In very weak alkaline solutions (pH < 10), tetrathionate is fairly stable toward degradation, so it is also a sulfur-containing end product of the reaction under our experimental conditions. Nevertheless, the amount of tetrathionate is relatively small compared with that of pentathionate. Unlike during the decomposition of pentathionate, the amount of elementary sulfur formed during the alkaline decomposition of hexathionate becomes observable even by naked eye and continuously deposits in the bottom of the reactor. It should also be mentioned that trithionate was not detected under our experimental circumstances, although its role in the alkaline decomposition of tetrathionate is confirmed by several independent research groups.<sup>23,25</sup> This feature, however, can be readily explained by the fact that reaction of tetrathionate with sulfite (the main source of trithionate) cannot compete with other reactions of sulfite due to the low level of tetrathionate to be formed. Moreover, we shall also see later that although the sulfite concentration is controlled at a very low level it plays a key role in describing the decomposition process quantitatively.

**Stoichiometry.** On the basis of our experiments, it is difficult to establish the exact stoichiometry of the reaction. The end products of the decomposition of hexathionate may include thiosulfate, pentathionate, tetrathionate, and elementary sulfur under our experimental circumstances; however, under strongly alkaline conditions polythionates are no longer stable species and therefore thiosulfate and elementary sulfur eventually appear as final products according to the following reaction



However we would like to emphasize that this limiting stoichiometry was never reached under our experimental conditions. At moderately alkaline pH values, pentathionate and especially tetrathionate may disappear from the solution after only a fairly long period of time, and their concentrations could easily be recorded even after 2 days of decomposition. The complete disappearance would require more than 1 week or such a high pH where hexathionate decomposes within a short period of time, not allowing us to study the kinetics of its decomposition in detail. Because our present study focuses mainly on the alkaline decomposition of hexathionate, we monitored the reaction up to 90–95% conversion of initial reactant; therefore, it is easily understood why establishing the actual stoichiometry meets some difficulties.

**Initial Rate Studies.** Figure 2 shows the logarithm of the initial rate of the decomposition defined as  $v_0 = d[\text{S}_6\text{O}_6^{2-}]/dt$  at  $t = 0$  s. The initial rates for these experiments are summarized in Table 1. As seen, linear correlation is obtained, but the formal kinetic order of hexathionate is marginally more than unity in all cases and increases with decreasing pH. In contrast with this, the formal kinetic order of hydroxide ion is significantly less than one, suggesting that there should be a competing pH-dependent and pH-independent rate-limiting pathway. Moreover, the formal kinetic order of hydroxide ion seems to increase with decreasing  $[\text{S}_6\text{O}_6^{2-}]_0$ . As a consequence, two rate-determining processes have to be considered to describe the kinetics of the decomposition: the first one, which is first-order with respect to both reactants, and the second one,



**Figure 2.** Plots of the logarithm of the initial rate of decomposition of hexathionate (symbols) against (A)  $\lg([\text{S}_6\text{O}_6^{2-}]_0/\text{M})$  at pH 8.94 (black), 9.29 (blue), 9.59 (green), and 9.90 (red) and against (B)  $\lg([\text{OH}^-]_0/\text{M})$  at  $[\text{S}_6\text{O}_6^{2-}]_0/\text{mM} = 0.1$  (black), 0.2 (blue), 0.3 (green), 0.4 (red), and 0.5 (cyan). Solid lines were obtained by least-squares linear fit. The legend contains the slopes (and its standard deviations) of the corresponding fitted straight lines.

**Table 1. Experimentally Determined Initial Rates under Different Initial Conditions**

$[\text{S}_6\text{O}_6^{2-}]_0/\text{mM}$	pH	$10^8 \cdot v_0/(\text{M} \cdot \text{s}^{-1})$
0.1	8.94–9.90	0.262, 0.514, 0.816, 1.71
0.2	8.94–9.90	0.546, 1.06, 1.66, 3.42
0.3	8.94–9.90	0.869, 1.70, 2.62, 5.33
0.4	8.94–9.90	1.15, 2.23, 3.43, 6.92
0.5	8.94–9.90	1.52, 2.91, 4.41, 8.89

which is second-order with respect to the concentration of hexathionate and independent of pH.

**Proposed Kinetic Model.** The approach we have chosen to analyze our data set has already been successfully applied in several cases of previous works, and the essence of this method has already been published elsewhere.<sup>4,22,36</sup> The most critical part of this method is to postulate the set of species (reactants, intermediates, and products) involved in the reaction. Besides the reactants (hexathionate, hydroxide ions), the products (thiosulfate, sulfur, tetrathionate), and the intermediates identified by HPLC or CE methods (pentathionate, heptathionate) and by isotope trace labeling method<sup>37</sup> (sulfite), several other intermediates likely to participate in the reaction are postulated such as heptathionate,  $\text{S}_2\text{O}_3\text{OH}^-$ ,  $\text{S}_3\text{O}_3\text{OH}^-$ , and  $\text{S}_4\text{O}_3\text{OH}^-$ . We then considered all of the possible mono- and bimolecular reactions between these species having a rate equation consisting of two terms: the first one is independent of pH, and the second one is proportional to  $[\text{OH}^-]$ . 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 hexathionate:

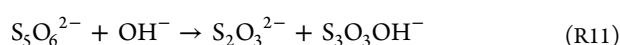
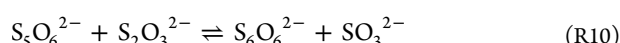
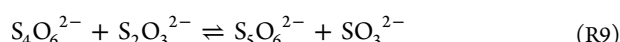
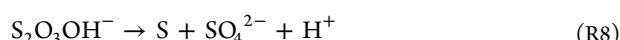
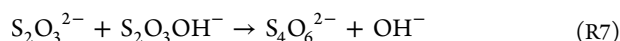
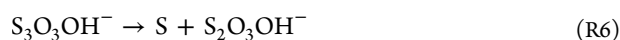
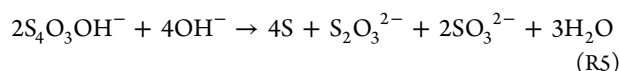
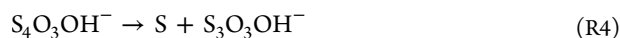
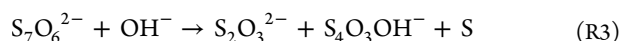
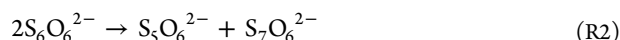
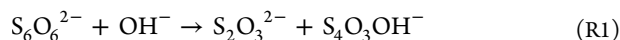


Table 2 contains the parameter set determined by simultaneous evaluation of the kinetic curves, and the results

**Table 2. Fitted and Fixed Rate Coefficients of the Proposed Kinetic Model<sup>a</sup>**

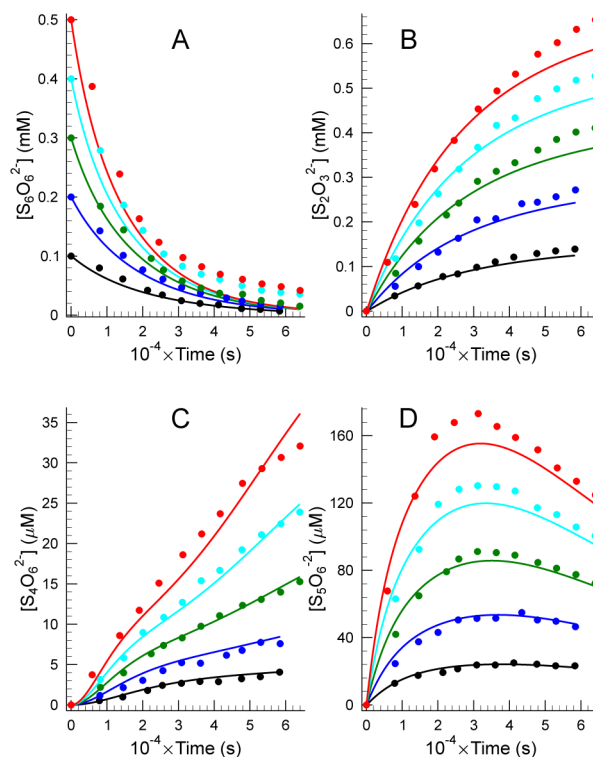
no.	rate equation	parameter
R1	$k_{\text{R1}}[\text{S}_6\text{O}_6^{2-}][\text{OH}^-]$	$1.28 \pm 0.09 \text{ M}^{-1} \text{ s}^{-1}$
R2	$k_{\text{R2}}[\text{S}_6\text{O}_6^{2-}]^2$	$(4.70 \pm 0.86) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
R3	$k_{\text{R3}}[\text{S}_7\text{O}_6^{2-}][\text{OH}^-]$	$1.64 \pm 0.29 \text{ M}^{-1} \text{ s}^{-1}$
R4	$k_{\text{R4}}[\text{S}_4\text{O}_3\text{OH}^-][\text{OH}^-]$	$\geq 10^2 \text{ M}^{-1} \text{ s}^{-1}$
R5	$k_{\text{R5}}[\text{S}_3\text{O}_3\text{OH}^-]$	$k_{\text{R5}}/k_{\text{R4}} = (3.47 \pm 0.64) \times 10^{-5} \text{ M}$
R6	$k_{\text{R6}}[\text{S}_3\text{O}_3\text{OH}^-]$	$\geq 1 \text{ s}^{-1}$
R7	$k_{\text{R7}}[\text{S}_2\text{O}_3^{2-}][\text{S}_2\text{O}_3\text{OH}^-]$	$\geq 100 \text{ M}^{-1} \text{ s}^{-1}$
R8	$k_{\text{R8}}[\text{S}_2\text{O}_3\text{OH}^-]$	$k_{\text{R7}}/k_{\text{R8}} = 694 \pm 95 \text{ M}^{-1}$
R9	$k_{\text{R9}}[\text{S}_4\text{O}_6^{2-}][\text{S}_2\text{O}_3^{2-}]$	$0.733 \pm 0.095 \text{ M}^{-1} \text{ s}^{-1}$
	$k_{-\text{R9}}[\text{S}_5\text{O}_6^{2-}][\text{SO}_3^{2-}]$	$k_{-\text{R9}}/k_{-\text{R10}} = 0.526 \pm 0.060$
R10	$k_{\text{R10}}[\text{S}_5\text{O}_6^{2-}][\text{S}_2\text{O}_3^{2-}]$	$0.0361 \pm 0.0041 \text{ M}^{-1} \text{ s}^{-1}$
	$k_{-\text{R10}}[\text{S}_6\text{O}_6^{2-}][\text{SO}_3^{2-}]$	$\geq 1900 \text{ M}^{-1} \text{ s}^{-1}$
R11	$k_{\text{R11}}[\text{S}_5\text{O}_6^{2-}][\text{OH}^-]$	$0.744 \pm 0.018 \text{ M}^{-1} \text{ s}^{-1}$

<sup>a</sup>No error indicates that the value in question was fixed during the fitting procedure.

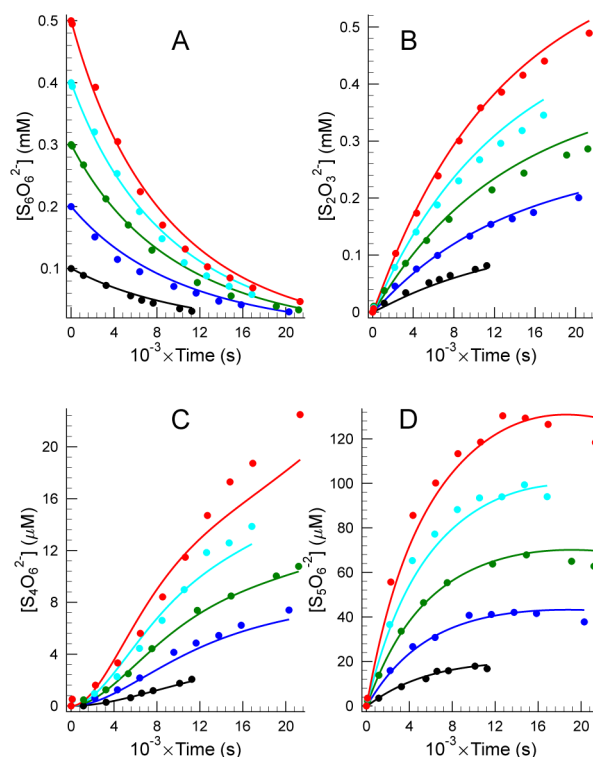
are illustrated in Figures 3–6. The 5.4% relative average deviation indicates that the proposed model is working properly within the concentration range used in the experiments.

## DISCUSSION

Step R1 is the initiating rate-determining step of the alkaline decomposition of hexathionate that proceeds via scission of the inner S–S bond between the  $\gamma$ - and  $\beta$ -S heterolytically yielding  $\text{S}_4\text{O}_3\text{OH}^-$  and thiosulfate. This step is similar to the

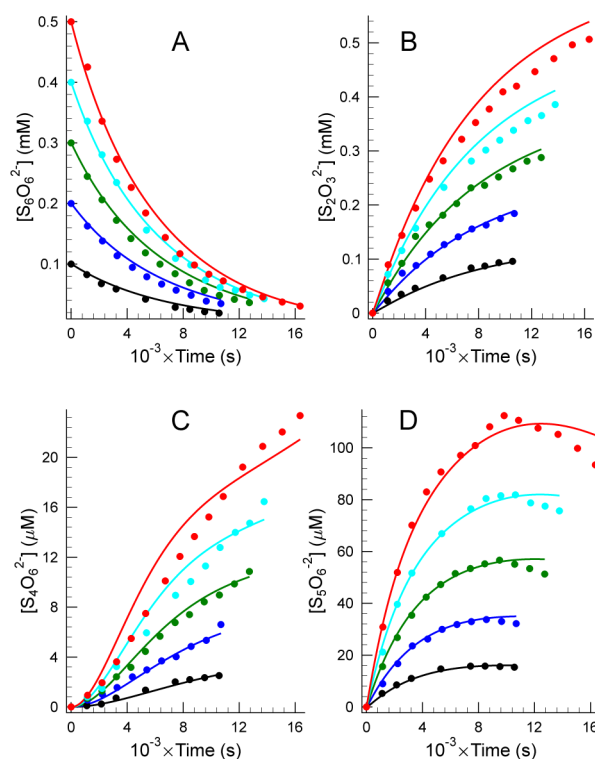


**Figure 3.** Measured (dots) and calculated (solid lines) concentration of hexathionate (A), thiosulfate (B), tetrathionate (C), and pentathionate (D) as a function of time at pH 9.29.  $[\text{S}_6\text{O}_6^{2-}]_0/\text{mM} = 0.1$  (black), 0.2 (blue), 0.3 (green), 0.4 (cyan), and 0.5 (red).

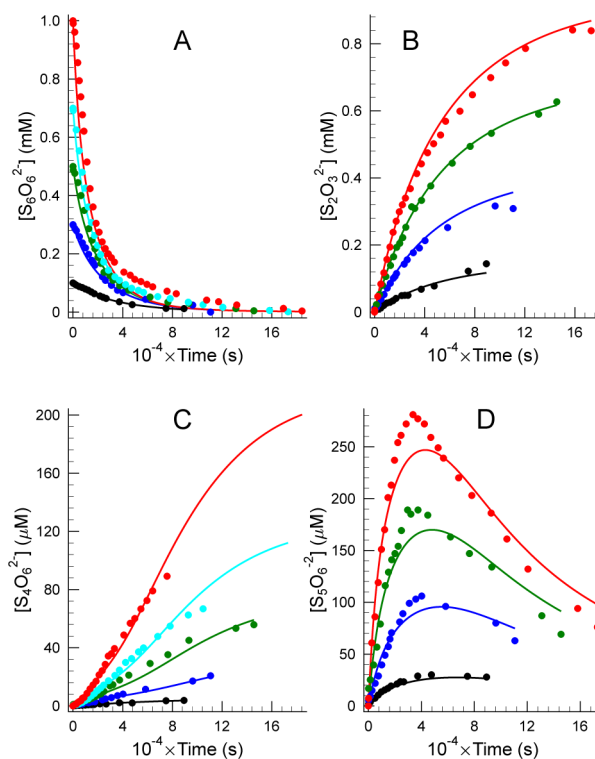


**Figure 4.** Measured (dots) and calculated (solid lines) concentration of hexathionate (A), thiosulfate (B), tetrathionate (C), and pentathionate (D) as a function of time at pH 9.59.  $[\text{S}_6\text{O}_6^{2-}]_0/\text{mM} = 0.1$  (black), 0.2 (blue), 0.3 (green), 0.4 (cyan), and 0.5 (red).



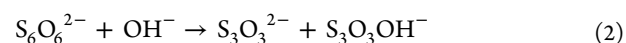


**Figure 5.** Measured (dots) and calculated (solid lines) concentration of hexathionate (A), thiosulfate (B), tetrathionate (C), and pentathionate (D) as a function of time at pH 9.90.  $[S_6O_6^{2-}]_0/\text{mM}$  = 0.1 (black), 0.2 (blue), 0.3 (green), 0.4 (cyan), and 0.5 (red).



**Figure 6.** Measured (dots) and calculated (solid lines) concentration of hexathionate (A), thiosulfate (B), tetrathionate (C), and pentathionate (D) as a function of time at pH 8.94.  $[S_6O_6^{2-}]_0/\text{mM}$  = 0.1 (black), 0.3 (blue), 0.5 (green), 0.7 (cyan), and 1.0 (red).

situation of pentathionate decomposition<sup>22</sup> in which  $S_3O_3OH^-$  and thiosulfate were produced from the attack of the  $\gamma$ -S of the sulfur chain in pentathionate by hydroxide ion. This step was previously suggested by several research groups<sup>20,26,37</sup> and it was reasonably supported that the hydroxide ion attacks the  $\gamma$ -S of the sulfur chain of hexathionate on the molecular level. It should be emphasized, however, that there is a big difference between pentathionate and hexathionate. After nucleophilic attack of hydroxide on the  $\gamma$ -S of both polythionates in the case of pentathionate there is no other choice to break up the sulfur chain than heterolytic cleavage of the  $\beta$ - $\gamma$  sulfur bond. In the case of hexathionate, however, both the  $\beta$ - $\gamma$  and  $\gamma$ - $\gamma'$  bonds are ready to be split after the attack, so alternatively the following sequence of reaction is also a conceivable pathway for the decomposition:

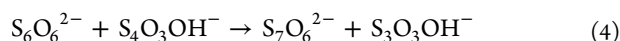


This sequence was also tried to replace step R1 entirely or partially in our fitting procedure with no success. Therefore, we concluded that bond breakage of the sulfur chain most probably takes place between  $\beta$ - and  $\gamma$ -S atoms.

It is well known that stability of polythionates under alkaline conditions decreases with the increase in sulfur chain. As expected, we found that the rate coefficient of the initiating step of the alkaline decomposition of hexathionate ( $k_{R1} = 1.28 \pm 0.09 \text{ M}^{-1} \text{ s}^{-1}$ ) is somewhat higher than that of pentathionate.<sup>22</sup> This is in accordance with the fact that in the sulfur chain of hexathionate,  $\gamma$ - and  $\gamma'$ -S are equally favorable places to be attacked by hydroxide ion due to their identical electron density. Because the electron density around the  $\gamma$ -S atom of pentathionate is expected to be a bit higher than that of hexathionate and there are twice as many sites to be attacked in the case of hexathionate, it plausibly suggests that the nucleophilic attack of hydroxide should at least be two times as probable in the latter case. This expectation is reflected in the corresponding rate coefficients of polythionates determined by our present and previous works. For the sake of completeness, it should be emphasized that this value is in a very reasonable agreement with the previous one determined indirectly through the alkaline decomposition of pentathionate.<sup>22</sup>

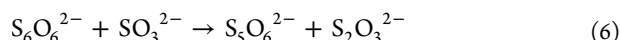
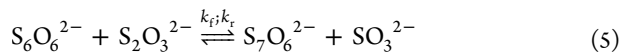
Step R2 is the second-order decomposition of hexathionate into pentathionate and heptathionate. Direct attack of a polythionate to another polythionate has not yet been observed in the case of lower polythionates. Our initial rate study and simultaneous evaluation of the kinetic curves clearly suggested that without this step systematic deviations occur between the measured and calculated kinetic curves. The reason may be understood as follows. Nucleophilic attack of the  $\beta$ -S atom of hexathionate to the  $\gamma$ -S atom of another hexathionate is easily conceivable, resulting in a breakage of the original sulfur chain, followed by the formation of a shorter and longer sulfur chains. The probability of this nucleophilic arrangement expectably increases with increasing sulfur chain, and this may be the reason why it is so difficult to prepare pure hexathionate or higher polythionates. The rate coefficient of this step was found to be  $0.0470 \pm 0.0086 \text{ M}^{-1} \text{ s}^{-1}$ , and its necessity was supported by further calculation indicating that elimination of this step from the kinetic model would result in an unacceptably high 11.5% average deviation.

To produce heptathionate, one might also consider the following reaction as a possible source



but it turned out to be completely unnecessary for the description of the kinetic curves. We therefore concluded that eq 4 cannot be responsible for the appearance of heptathionate.

Alternatively, the following sequence of reaction might also explain the fact that the formation of heptathionate as well as the formal kinetic order of hexathionate are higher than one



Therefore, we tried to replace step R2 by eq 5. In that case, the average deviation was found to be 7.0%, so one might argue that this agreement is also satisfactory. However, here we address a couple of issues why it is not likely that eq 5 can unambiguously substitute step R2. First, the majority of parameters remained basically unchanged except  $k_{R9}$ ,  $k_{R10}$ , and  $k_{-R9}/k_{-R10}$  (those are found to be  $2.37 \text{ M}^{-1} \text{ s}^{-1}$ ,  $0.15 \text{ M}^{-1} \text{ s}^{-1}$ , and 0.513, respectively); meanwhile,  $k_f = 0.14 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_t/k_{-R9} = 0.026$  were calculated. In general, the trend of the rate coefficients of the forward reactions remained the same; however,  $k_{-R10}$  was indicated to be the largest rate coefficient among the backward reactions. These findings would be difficult to account for simply by the change of the electron density around the inner sulfur of sulfur chain of the corresponding polythionate. Second, it means that the equilibrium indicated by eq 5 is not established instantaneously, so eq 6 cannot be the rate-determining step of this sequence. As a result, the formal kinetic order of hexathionate should be strictly one in this case, which contradicts our initial rate studies. Taking into account these arguments along with the fact that the average deviation, appearing systematically between the measured and calculated kinetic curves, increased non-negligibly, we rather tend to include step R2 in the final model; however, these arguments also suggest that eq 5 may have a significant role under different experimental conditions, especially at lower pH values, where the alkaline decomposition of polythionates is prevented. Under these conditions eq 5 is a favorable source of the formation of heptathionate in the presence of initially added thiosulfate. These investigations are being carried out in our laboratory and will be published later.

Step R3 is the alkaline decomposition of heptathionate formed in the previous step. This reaction probably also starts with a nucleophilic attack of hydroxide ion on the  $\gamma$ ,  $\gamma'$ , or  $\delta$ -S atom. Basically there is not much difference between the electron densities of these atoms; therefore, it is more probable that the attack occurs on the  $\gamma$  (or  $\gamma'$ ) sulfur atom of the chain, although the opposite case cannot be ruled out entirely. Attack of hydroxide similar to the case of other polythionates results in the scission of the sulfur chain that produces thiosulfate, elementary sulfur, and  $\text{S}_4\text{O}_3\text{OH}^-$ . We found this rate coefficient to be  $1.64 \pm 0.29 \text{ M}^{-1} \text{ s}^{-1}$ , which is slightly higher than the corresponding rate coefficient of hexathionate. This trend can easily be explained by the fact that there are three sulfur atoms in a single heptathionate molecule, around where the electron density should approximately be close to zero, but only two of those exist in case of hexathionate. Furthermore this rate coefficient also suggests that heptathionate may be detected at a relatively low concentration during our experiment. Indeed, as

seen in Figure 1, at a quite long retention time a small peak appears, indicating heptathionate in the reacting solution. As previously mentioned, preparation of pure heptathionate is not yet available; therefore, we were not able to convert its peak area into concentrations.

Steps R4 and R5 are the possible decomposition of the short-lived intermediate  $\text{S}_4\text{O}_3\text{OH}^-$ . One of the important differences is that step R5 directly yields sulfite ion, whereas the other route starting with step R4 does not produce sulfite. The second difference is that rate of step R4 is proportional to  $[\text{OH}^-]$ . As we shall see later, despite the fact that concentration of sulfite is relatively low under our experimental conditions ( $<10^{-6} \text{ M}$ ) it plays a crucial role in shortening the sulfur chain of polythionates via steps R9 and R10 (see later). The individual rate coefficients of  $k_{R4}$  and  $k_{R5}$  were found to be in total correlation with each other, meaning that both processes have to be fast and their balance depending on  $[\text{OH}^-]$  controls the sulfite concentration. The ratio of  $k_{R5}/k_{R4}$  was found to be  $(3.47 \pm 0.64) \times 10^{-5} \text{ M}$ ; therefore, supposing a relatively high value for  $k_{R4} = 10^8 \text{ M}^{-1} \text{ s}^{-1}$  leads to  $k_{R5} = 3470 \pm 640 \text{ s}^{-1}$ .

Step R6 yields elementary sulfur and another short-lived intermediate  $\text{S}_2\text{O}_3\text{OH}^-$ . The individual rate coefficient of this reaction cannot be determined from our experiments; any value higher than  $1 \text{ s}^{-1}$  leads to the same final result. Therefore, we fixed  $k_{R4}$  to be  $10^3 \text{ s}^{-1}$  throughout the whole fitting procedure. Any other reactions with this intermediate were found to be unnecessary to improve the quality of the fit.

Steps R7 and R8 are two competing reactions of the short-lived intermediate  $\text{S}_2\text{O}_3\text{OH}^-$ ; the first one produces only tetrathionate, whereas the other one yields sulfate and elementary sulfur as well. Both reactions have to be fast, and we found  $k_{R7}$  and  $k_{R8}$  to be in total correlation with each other. It means that we could only calculate  $k_{R7}/k_{R8} = 694 \pm 95 \text{ M}^{-1}$ .

Step R9 is the well-known thiosulfate-assisted rearrangement of tetrathionate that was first studied thoroughly by Fava and Bresadola,<sup>38</sup> although the reverse reaction (sulfitolysis of pentathionate) had been previously discovered by several research groups independently.<sup>19,27</sup> Despite the early knowledge of this reaction, we are unaware of a single study that was able to determine both the forward and reverse rate coefficient of this equilibrium. Our present study, however, indicated that both rate coefficients of the equilibrium can be calculated with great precision if  $k_{-R10}$  is fixed due to a total correlation between  $k_{-R9}$  and  $k_{-R10}$ . The chemistry behind the correlation is easily understood because the concentration of sulfite is very low ( $<10^{-6} \text{ M}$ ), meaning that only the relative rates of the sulfitolysis of both polythionates could be calculated from our experiments.  $k_{R9}$  was found to be  $0.733 \pm 0.095 \text{ M}^{-1} \text{ s}^{-1}$ , whereas  $k_{-R9}/k_{-R10} = 0.526 \pm 0.060$  at the concentration range of our study.

Step R10 is the thiosulfate-assisted rearrangement of pentathionate, and its reverse reaction was suggested to determine quantitatively hexathionate.<sup>37,39</sup> Evidently, the importance of this reaction increases with conversion, and once enough pentathionate is present in the solution the forward reaction regenerates the reactant in some extent to prevent its complete disappearance. As previously mentioned, the reverse rate coefficient is in total correlation with  $k_{-R9}$ ; therefore, only the forward rate coefficient ( $k_{R10} = 0.0361 \pm 0.0041 \text{ M}^{-1} \text{ s}^{-1}$ ) could be calculated from our experiments. To be consistent with our previous paper<sup>22</sup> indicating that  $k_{-R9}$  should be at least  $1000 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{-R10} \geq 1.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  inequality has to be fulfilled; therefore, we fixed  $k_{-R10}$  to its lower

limit during the whole calculation process. For the sake of completeness, it should be mentioned that the present findings are in apparent contradiction with our previous result about the investigation of the decomposition of pentathionate.<sup>22</sup> In that paper we suggested that hexathionate is more probably formed via the direct reaction of pentathionate with  $\text{S}_3\text{O}_3\text{OH}^-$  by a simple sulfur insertion in the sulfur chain. Thiosulfate-assisted rearrangement of pentathionate as a possible source was examined and was not ruled out entirely; we stated that “there may be different conditions, probably at lower pHs, where thiosulfatolysis becomes the only source of hexathionate.” The present study was conducted at lower pH values than the previous one on the pentathionate decomposition, so it partially solves the problem. Moreover, it was also demonstrated that alkaline decomposition of pentathionate can almost equivalently be described if the direct pentathionate– $\text{S}_3\text{O}_3\text{OH}^-$  reaction is replaced by the thiosulfate-assisted rearrangement of pentathionate with a slight change of some kinetic parameters in the model. Among them, the most surprising change was the rate coefficient of the initiating reaction between pentathionate and hydroxide ion.<sup>22</sup> We have explicitly pointed out that replacement of the reaction between pentathionate and  $\text{S}_3\text{O}_3\text{OH}^-$  with the present step R10 increases the rate coefficient of initiating pentathionate–hydroxide reaction from 0.513 to 0.748  $\text{M}^{-1} \text{s}^{-1}$  and basically the quality of the fit remains the same. In the next paragraph about the discussion on step R11 we shall see that the present study supports 0.744  $\pm$  0.018  $\text{M}^{-1} \text{s}^{-1}$  for the rate coefficient of this reaction, which is in an unbelievable agreement between the results of these independent studies. It clearly makes us reconsider that even at higher pH values the formation of hexathionate occurs via the thiosulfate-assisted rearrangement rather than via the direct pentathionate– $\text{S}_3\text{O}_3\text{OH}^-$  reaction.

Step R11 is the well-known initiating step of the alkaline decomposition of pentathionate.<sup>20–22</sup> The rate coefficient ( $k_{\text{R11}} = 0.744 \pm 0.018 \text{ M}^{-1} \text{s}^{-1}$ ) obtained here was very consistent with the one reported in our previous work.<sup>22</sup> In accordance with previous findings,<sup>3,22</sup> pentathionate is attacked by hydroxide ion at the  $\gamma$ -sulfur atom, yielding thiosulfate and  $\text{S}_3\text{O}_3\text{OH}^-$  as an initiating step.

This study also enables us to compare the rate-determining step of the alkaline decomposition of polythionates. In general, it is well known that the longer sulfur chain is the less the stability of the polythionate is under alkaline conditions; therefore, the most stable polythionate toward alkaline degradation is trithionate. The corresponding rate coefficient of the trithionate–hydroxide ion reaction was basically found to be on the order of  $10^{-5}$  to  $10^{-6} \text{ M}^{-1} \text{s}^{-1}$  at  $>40^\circ\text{C}$ .<sup>17,40</sup> It means that at room temperature trithionate is very stable even under moderately alkaline conditions. Rolia et al.,<sup>18</sup> Varga et al.,<sup>23</sup> and Zhang et al.<sup>16</sup> have independently estimated the rate coefficient of the initiating step of the alkaline decomposition of tetrathionate. Depending on the experimental conditions, 0.0051 to 0.38  $\text{M}^{-1} \text{s}^{-1}$  value was obtained. The corresponding rate coefficient of the alkaline decomposition of pentathionate was found to be 0.51 to 1  $\text{M}^{-1} \text{s}^{-1}$  in previous works.<sup>21,22</sup> The present work suggests that for hexathionate this rate coefficient is 1.28  $\text{M}^{-1} \text{s}^{-1}$ , whereas for heptathionate it is 1.64  $\text{M}^{-1} \text{s}^{-1}$ . As common sense suggests (apart from the terminal sulfurs, but those are sterically hidden), less negatively charged sulfur atoms are found in the middle of the sulfur chain. We already pointed out in a recent work<sup>41</sup> that in the case of pentathionate the electron density is only  $-0.029$  around the  $\gamma$ -sulfur and further

significant change in the electron density cannot be anticipated with the insertion of an additional inner sulfur atom to the chain. In the case of trithionate and tetrathionate, only  $\beta$ -S exists and its electron density is  $-0.411$  and  $-0.203$ , respectively. What it means is that no significant increase in the reactivity is expected when at least  $\gamma$ -S exists in the sulfur chain. This reflects the point that the corresponding rate coefficients in the pentathionate, hexathionate, and heptathionate order increase by only a factor of 2, whereas increase in the electron density of  $\beta$ -sulfur significantly decreases the possibility of the nucleophilic attack of hydroxide ion, resulting in greater stability toward alkaline degradation.

## CONCLUSIONS

The kinetics of alkaline decomposition of hexathionate was studied for the first time in this article, exploiting the advantage of the recently available experimental and computer methods. By means of HPLC, several sulfur-containing species such as hexathionate, pentathionate, tetrathionate, and thiosulfate could be simultaneously monitored during the course of reaction, and simultaneous evaluation of all of these concentration–time curves can strongly support the validity of the proposed kinetic model. Our present work also provides a reasonable explanation about the trends observed in the alkaline decomposition of polythionates. It was also discussed that the rate coefficients of the reactions between several nucleophilic agents and polythionates suggest a reasonable correlation against the electron density in the vicinity of the sulfur atom of the sulfur chain to be attacked. These observations allow us to support strongly whether the  $\beta$ - or  $\gamma$ -sulfur of the polythionate chain is a favorable place to initiate the given nucleophilic reaction. Moreover, the studies on stability and reactivity of polythionates in aqueous solution would provide new information for application fields such as clean energy, mining, leaching, and environmental protection.

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### Notes

The authors declare no competing financial interest.

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