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Article

Kinetics and Mechanism of the Decomposition of Tetrathionate Ion in Alkaline Medium

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The kinetics of the alkaline decomposition of tetrathionate has been studied spectrophotometrically in the pH range of 9.2–12.2 using both phosphate/hydrogen phosphate and carbonate/hydrogen carbonate as buffer systems and by adjusting the ionic strength to $I = 0.5$ M with sodium perchlorate at $T = 25.0 \pm 0.1$ °C. Matrix rank analysis of the spectra recorded between 265 and 330 nm shows the presence of three independent absorbing species. Besides tetrathionate, thiosulfate and trithionate are identified as absorbing products of the decomposition, but sulfite and a trace amount of sulfate are also formed during the alkaline degradation process. With pentathionate, sulfoxylic acid ($S(OH)_2$), $S_2O_3OH^-$, and $S_3O_3OH^-$ as key intermediates, a 10-step kinetic model is proposed with six fitted kinetic parameters to take all the important characteristics of the experimental curves into account. On the basis of the stoichiometric measurements and the model proposed, it is also enlightened that the product distribution of the reaction continuously varies with pH; thus the kinetic traces cannot be evaluated by assuming a single stoichiometry in contrast to recent studies. Buffer dependence of the decomposition is also discussed.

Introduction

The leaching of copper, silver, and gold from their ores with thiosulfate seems to be a less harmful alternative method than the traditional cyanidation process. As a result, this promising method has been extensively studied by several research groups.[1-3] It is already known that metal ions can be readily brought into solution from their ores as metal–thiosulfate complexes, but recovery of the metal from the complexes continues to be a problem. As a possible solution, usage of strong base ion exchange resins has been suggested very recently.[4] It has been found, however, that polythionates (mainly tri- and tetrathionate) formed in the oxidation of thiosulfate by metal ions[5,6] may easily cause[4] the exchange resin to foul. It is therefore crucial to remove the polythionates from the leach prior to the ion exchange process.

Degradation of polythionates in alkaline medium seems to be a promising solution to this problem.

The alkaline decomposition of tetrathionate has been studied since the beginning of the last century. Gutman[7,8] and Riesenfeld[9] have independently reported that if tetrathionate was left for a long time in a strong alkaline medium, sulfite and thiosulfate were finally formed through the following equation.

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (1)$$
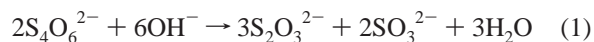
Kuertenacker et al.[10-12] and Goehring[13] have later shown that the decomposition strongly depends on the alkalinity of the solution. Initially, tetrathionate decomposes into trithionate and pentathionate according to the following equation.

$$2S_4O_6^{2-} \rightarrow S_3O_6^{2-} + S_5O_6^{2-} \quad (2)$$
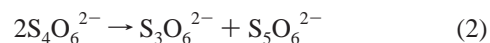
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 (2) Tao, J.; Jin, C.; Shi, X. XVIII International Mineral Processing Congress, Sydney, May 23–28, 1993; p 1141,
 (3) Abbruzzese, C.; Fornari, P.; Massidda, R.; Veglio, F.; Ubaldini, S. *Hydrometallurgy* **1995**, *39*, 265.
 (4) Zhang, H.; Dreisinger, D. B. *Hydrometallurgy* **2002**, *66*, 59.
 (5) Naito, K.; Yoshida, M.; Shieh, M.; Okabe, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1365.
 (6) Byerley, J. J.; Fouda, S. A.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1972**, 889.

 (7) Gutman, A. *Ber.* **1906**, *39*, 509.
 (8) Gutman, A. *Ber.* **1907**, *40*, 3614.
 (9) Riesenfeld, E. H. *Z. Anorg. Allg. Chem.* **1924**, *141*, 109.
(10) Kurtenacker, A.; Kaufmann, M. *Z. Anorg. Allg. Chem.* **1925**, *148*, 43.
(11) Kurtenacker, A.; Kaufmann, M. *Z. Anorg. Allg. Chem.* **1925**, *148*, 369.
(12) Kurtenacker, A.; Mutschin, A.; Stastny, F. *Z. Anorg. Allg. Chem.* **1935**, *224*, 339.
(13) Goehring, M. *Fortschr. Chem. Forsch.* **1952**, *2*, 444.

Table 1. Initial Composition of the Kinetic Runs[a]

no.	$[PO_4^{3-}]_0$	$[HPO_4^{2-}]_0$	$[S_4O_6^{2-}]_0$	$[S_2O_3^{2-}]_0$
1−7	52.5	10.5	0.3, 0.5, 0.7, 1.0, 1.4, 2.0, 3.0	0
8−13	52.5	10.5	1.0	0.3, 0.5, 0.7, 1.0, 2.0, 3.0
14−20	50.6	16.5	0.3, 0.5, 0.7, 1.0, 1.4, 2.0, 3.0	0
21−27	38.5	38.5	0.3, 0.5, 0.7, 1.0, 1.4, 2.0, 3.0	0
31−34	23.1	69.3	0.3, 0.5, 0.7, 1.0, 1.4, 2.0, 3.0	0
35−41	16.5	82.5	0.3, 0.5, 0.7, 1.0, 1.4, 2.0, 3.0	0
42−47	16.5	82.5	1.0	0.3, 0.5, 0.7, 1.0, 2.0, 3.0

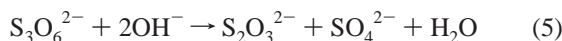| No.	$[CO_3^{2-}]_0$	$[HCO_3^-]_0$	$[S_4O_6^{2-}]_0$	$[S_2O_3^{2-}]_0$
48	67.5	7.5	0.6	0
49	63.0	21.0	0.6	0
50−52	50.25	50.25	0.3, 0.6, 1.0	0
53−55	50.25	50.25	0.6	0.3, 0.6, 1.0
56	35.0	105	0.6	0

[a] All concentrations are given in mM.

In very weak alkaline solutions (pH < 9.0), both trithionate and pentathionate are fairly stable toward further degradation. If, however, the pH slightly increases, pentathionate is no longer stable and decomposes according to the following equation[14]
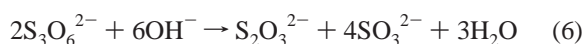
$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \qquad (3)$$

resulting in an overall process shown below.

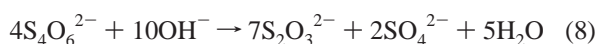$$4S_4O_6^{2-} + 6OH^- \rightarrow 2S_3O_6^{2-} + 5S_2O_3^{2-} + 3H_2O \quad (4)$$
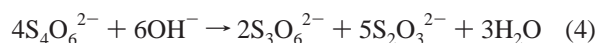
If the pH increases further (>12.0), disproportionation of trithionate starts to rise[5] according to equation

$$S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + H_2O \qquad (5)$$

or at pH=13 per equation.

$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \qquad (6)$$

It means that the overall degradation can be described by either of the following processes

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (7)$$

$$4S_4O_6^{2-} + 10OH^- \rightarrow 7S_2O_3^{2-} + 2SO_4^{2-} + 5H_2O \quad (8)$$
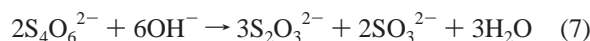
It has also been found that thiosulfate ion catalyzes the decomposition of tetrathionate in neutral solution[15−17] through the following steps.

$$S_4O_6^{2-} + S_2O_3^{2-} \rightleftharpoons S_5O_6^{2-} + SO_3^{2-} \qquad (9)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \qquad (10)$$
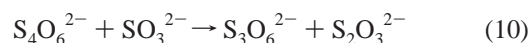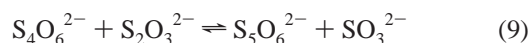
Later Rolia and Chakrabarti[18] have shown that thiosulfate catalysis also occurs at higher pH (10−12), where eq 4 is the dominating stoichiometry. The rate equation for the consumption of tetrathionate at $T = 35\ °C$ was found to be

$$-\frac{d[S_4O_6^{2-}]}{dt} = (0.1 + 12.6[S_2O_3^{2-}])[S_4O_6^{2-}][OH^-] \quad (11)$$

One of the latest studies on the alkaline decomposition of tetrathionate has shown[4] that the stoichiometry of the reaction is even more complicated than was thought because sulfide ion is also formed during the degradation, but this result is argued by a recent study of Breuer and Jeffrey.[19]

The aim of our paper is to set up a consistent kinetic model for the alkaline decomposition of tetrathionate that is able to take the changes of the stoichiometry into account properly and to provide a reliable starting point for the design of maximizing the recovery of thiosulfate from the leach after the alkaline treatment of the polythionates. To date no comprehensive kinetic and mechanistic studies are yet available in the literature.

Experimental Section

Materials and Buffers. Potassium trithionate was prepared by the reaction of potassium thiosulfate (Riedel-de Haën) with sulfur dioxide.[20] Its purity was checked[21] and found to be better than 98.5%. All other chemicals were of the highest purity, commercially available (potassium tetrathionate (Fluka), sodium thiosulfate, sodium phosphate, sodium hydrogen phosphate, sodium hydrogen carbonate, and sodium carbonate (Reanal), sodium perchlorate (Sigma-Aldrich)), and used without further purification. Four times distilled water was used to prepare all the stock solutions.

Two series of experiments were conducted in different buffer compositions. In the first series of experiments the pH was kept constant by using phosphate/hydrogen phosphate buffer ($pK_a = 11.75$), while in the other series carbonate/hydrogen carbonate buffer ($pK_a = 9.7$) was used.[35] The ionic strength was also kept constant ($I = 0.5$ M) by adding the necessary amount of sodium perchlorate to the buffer components. Table 1 contains the composition of the 56 kinetic runs.

Methods and Instrumentation. The kinetic measurements were carried out in a standard 1 cm quartz cuvette equipped with a Teflon cap and a magnetic stirrer. First, the buffer solution ($I = 0.5$ M)

(14) Wagner, H.; Schreier, H. *Phosphorus Sulf. Relat. Elem.* **1978**, *4*, 281.
(15) Goehring, M.; Helbing, W.; Appel, I. *Z. Anorg. Chem.* **1947**, *254*, 185.
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(17) Fava, A.; Bresadola, S. *J. Am. Chem. Soc.* **1955**, *77*, 5792.
(18) Rolia, E.; Chakrabarti, C. L. *Environ. Sci. Technol.* **1982**, *16*, 852.
(19) Breuer, P. L.; Jeffrey, M. I. *Hydrometallurgy* **2004**, *72*, 335.
(20) Brauer, G. *Handbook of Preparative Inorganic Chemistry,* 2nd ed.; Academic Press: New York, 1963; Vol. 1, p 398.
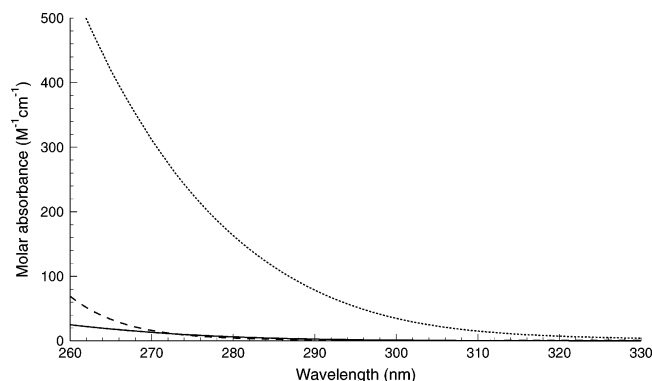(21) Koh, T. *Anal. Sci.* **1990**, *6*, 3.

Figure 1. Molar absorbances of tetrathionate (dotted line), trithionate (solid line), and thiosulfate (dashed line) used in the calculation procedure.

Table 2. Determination of the Formed Thiosulfate and Trithionate Concentration Versus the Initial Tetrathionate Concentration after the Reaction Is Completed in Phosphate Buffer[a]

pH	$[S_4O_6^{2-}]_0$	SR_2	SR_3	SI	SA
10.8	0.003	1.285	0.460	0.020	0.030
10.8	0.002	1.285	0.455	0.040	0.025
10.8	0.0014	1.286	0.450	0.056	0.022
10.8	0.001	1.290	0.440	0.080	0.020
10.8	0.0007	1.297	0.425	0.112	0.019
10.8	0.0005	1.305	0.405	0.160	0.015
10.8	0.0003	1.325	0.360	0.260	0.010
12.2	0.003	1.365	0.280	0.420	0.010
12.2	0.002	1.390	0.230	0.520	0.010
12.2	0.0014	1.410	0.190	0.600	0.010
12.2	0.001	1.425	0.157	0.672	0.007
12.2	0.0007	1.440	0.126	0.736	0.006
12.2	0.0005	1.454	0.097	0.796	0.005
12.2	0.0003	1.470	0.065	0.860	0.005
11.0	0.002	1.285	0.450	0.060	0.020
11.5	0.002	1.310	0.390	0.200	0.010
12.0	0.002	1.360	0.285	0.420	0.005

[a] SR_2 and SR_3 are defined as $[S_2O_3^{2-}]_\infty/[S_4O_6^{2-}]_0$ and $[S_3O_6^{2-}]_\infty/[S_4O_6^{2-}]_0$, respectively. SI and SA, defined as $[SO_3^{2-}]_\infty/[S_4O_6^{2-}]_0$ and $[SO_4^{2-}]_\infty/[S_4O_6^{2-}]_0$, respectively, are Calculated with the help of eqs 12 and 13.

was delivered into the cuvette followed by the thiosulfate solution ($I = 0.5$ M adjusted by sodium perchlorate if necessary). Finally, the tetrathionate solution ($I = 0.5$ M adjusted by sodium perchlorate) was added from a fast delivery pipet to start the reaction. The reaction was followed with a Zeiss Specord S10 diode array spectrophotometer within the 240–500 nm wavelength range. Each solution was illuminated only 300 times so as to minimize the photochemical decomposition of tetrathionate.[23] A separate experiment showed that the final spectra of the illuminated solution agreed well, within the experimental error, with the final spectra of the unilluminated solution of the same composition. Since the spectra of tetrathionate, thiosulfate, and trithionate are overlapping, it is crucial to determine the molar absorptivity of these species precisely for the simultaneous curve-fitting method. Thus, the molar absorbance of tetrathionate as well as that of trithionate and thiosulfate was calculated for each wavelength from three to eight different reagent concentrations. The calculated spectra of tetrathionate, thiosulfate, and trithionate depicted in Figure 1 agree satisfactorily with the data obtained by Lorenz and Samuel.[24] Sulfite and sulfate do not absorb the light over 265 nm at all.

For qualitative determination of the end products, a Bio-Rad Digilab Division dedicated FT-Raman spectrometer was used with laser-type Nd:YVO$_4$ at 1064 nm. After the decomposition had been completed, the solvent was evaporated under vacuum at 35 °C. The Raman spectrum of the solid material was registered for identification of the end products.

Data Treatment. For the Zeiss Specord S10 diode-array spectrophotometer, the constant uncertainty in the absorbance measurement is ±0.003 AU. As the absorbance increases beyond unity, the transmitted light intensity decreases and circuit noise begins to limit the precision with which the absorbance can be measured. For this reason we set an upper limit of 1.0 AU beyond which no kinetic data was used for further data analysis.

Matrix rank analysis studies[25] have been executed on those parts of the wavelength range of 240–500 nm where the absorbance did not exceed 1.0 AU. The experimental curves were analyzed with the program package ZiTa.[26] Seven different wavelengths have been chosen for simultaneous fitting of the kinetic data and they

(22) *IUPAC Stability Constant Database*; Royal Society of Chemistry: London, 1992–1997.
(23) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *J. Am. Chem. Soc.* **2002**, *124*, 10956.
(24) Lorenz, L.; Samuel, R. *Z. Phys. Chem.* **1932**, *B14*, 218.
(25) Peintler, G.; Nagypál, I.; Jancsó, A.; Epstein, I. R.; Kustin, K. *J. Phys. Chem. A* **1997**, *103*, 8013.
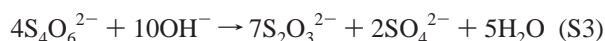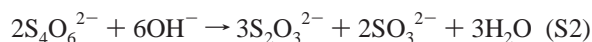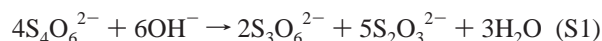(26) Peintler, G. *ZiTa*, version 5.0; a comprehensive program package for fitting parameters of chemical reaction mechanism; Attila József University: Szeged, Hungary, 1989–1998.

are 265, 270, 275, 280, 285, 290, and 295 nm. The reason for selecting these wavelengths was to gain as much information as possible about tetrathionate and the products since no wavelength could be found where any of the absorbing species had exclusive contribution. Since each kinetic curve contained 300 data pairs, the number of points in each run was reduced to 50 to avoid unnecessary and time-consuming calculations. The essence of the reduction method has already been described elsewhere.[27] Altogether, almost 19600 experimental points from 56 absorbance–time series (each containing 50 points) were used for simultaneous fitting. The sum of squares of the deviations between the measured and calculated absorbances was selected as the parameter to be minimized. Our quantitative criterion for an acceptable fit was that the average deviation for the absolute fit approach 0.003 AU, which is close to the uncertainty of the spectrophotometer.

Results

Stoichiometry. Identification of the end products, including classical analytical procedures (gravimetry, iodometry) and Raman spectroscopy, has clearly shown that thiosulfate, trithionate, and sulfite were the main products of the decomposition but trace amount of sulfate could also be detected in a relatively wide pH range of 9.2–12.2. Since trithionate and thiosulfate absorb light in the wavelength range of 265–330 nm, the ratio of the formed trithionate over consumed tetrathionate concentration (SR_3) as well as that of the formed thiosulfate over consumed tetrathionate concentration ratio (SR_2) could be determined from the final spectra of the solutions. After the reaction had been completed, the thiosulfate and the trithionate concentrations were determined from the final spectrum of the solution at the wavelength range of 265–295 nm. With the final concentration values of thiosulfate and trithionate, one can easily calculate the final concentrations of sulfite and sulfate taking the mass and oxidation number balance into consideration according to the following equations.

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

$$[SO_4^{2-}]_\infty = 2[S_2O_3^{2-}]_\infty + [S_3O_6^{2-}]_\infty - 3[S_4O_6^{2-}]_0 \quad (12)$$

$$[SO_3^{2-}]_\infty = 7[S_4O_6^{2-}]_0 - 4[S_2O_3^{2-}]_\infty - 4[S_3O_6^{2-}]_\infty \quad (13)$$

The corresponding results can be seen in Table 2 together with the ratio of each of final concentration of the sulfate and sulfite over the initial tetrathionate concentration determined by eqs 12 and 13, respectively. It is clearly indicated that SR_2 slightly increases with decreasing initial tetrathionate concentration and with increasing pH. The opposite effect is observed in the dependence of SR_3 against the initial tetrathionate concentration and the pH. It is also important to note that the relative amount of sulfite formed during the decomposition increases with increasing pH and with decreasing initial tetrathionate concentration. The amount of sulfate formed seems to be subtle, but later we shall see that the route, which produces sulfate, plays an important role in determining the kinetic behavior of the system. From Table 2, it is clear that the stoichiometry of the reaction is very complex and must be augmented with the following equations.

$$4S_4O_6^{2-} + 6OH^- \rightarrow 2S_3O_6^{2-} + 5S_2O_3^{2-} + 3H_2O \quad (S1)$$

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (S2)$$

$$4S_4O_6^{2-} + 10OH^- \rightarrow 7S_2O_3^{2-} + 2SO_4^{2-} + 5H_2O \quad (S3)$$

As we shall see later, stoichiometry S1, with slight contribution of S3, governs the reaction at slightly alkaline pHs where pentathionate is not a stable end product due to its fast alkaline degradation.[14] The importance of eq S3 increases with increasing tetrathionate concentration. As the pH increases, however, the contribution of eq S2 quickly rises and starts to dominate the stoichiometry in a strong alkaline solution. These stoichiometries can be easily understood by the proposed kinetic model of the degradation process (explained later). We also would like to stress that trithionate can be treated as an end product only in our kinetic time-scale. It is well-known[18,28] that trithionate hydrolyzes at a much longer time-scale meaning that this process cannot have a significant effect in our experimental circumstances.

MRA Studies. Figure 2 shows a typical absorbance change during the course of the reaction within the 260–330 nm wavelength range. Since there is no explicit sign in the absorbance–time sections for formation of a long-lived intermediate, detailed matrix rank analysis[25] has been executed in the wavelength range of 265–330 nm on all the measured series simultaneously where the measured values did not exceed 1.0 AU. This study has clearly revealed three absorbing species (tetrathionate, thiosulfate, and trithionate) in the wavelength range in question meaning that there is no absorbing intermediate formed in significant concentration.

Proposed Kinetic Model. The method, with which the best fitting model was found, has already been successfully
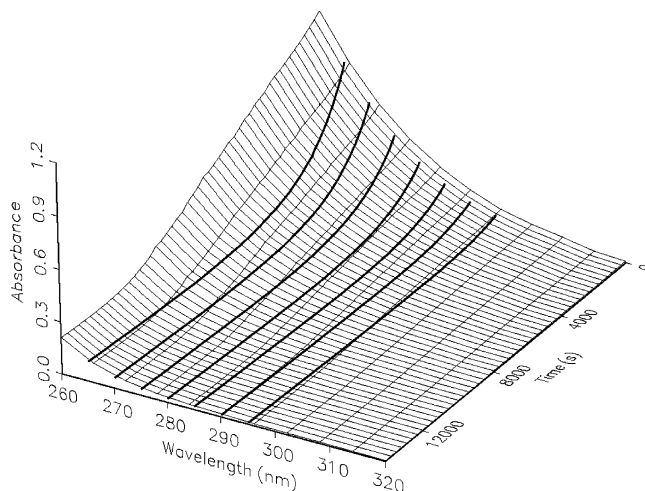

Figure 2. Typical absorbance change during the alkaline decomposition of tetrathionate in the UV range. $[S_4O_6^{2-}]_0 = 0.002$ M, pH = 11.5 (adjusted by phosphateEnDash/hydrogen phosphate buffer), $[S_2O_3^{2-}]_0 = 0$ M. Lines with boldface type represent the seven selected wavelengths, where the fitting procedure was executed.

applied in several kinetic systems studied previously.[27,29−32] The essence of the procedure is to take all of the chemically plausible mono- and bimolecular reactions and start the fitting with rate coefficients assigned to the reactions in such a way that the initial mean square deviation between the measured and calculated absorbances is sensitive to each of them. Parameters that become insensitive, meaning that the corresponding process does not affect the fitted curves, are omitted at each step. Finally, only the most sensitive parameters remain in the model. The most critical part of this procedure is to choose the set of species involved in the mono- and bimolecular reactions. In fact the reactants, the end products, and the solvent must be included. This group consists of $S_4O_6^{2-}$, $S_2O_3^{2-}$, $S_3O_6^{2-}$, SO_3^{2-}, SO_4^{2-}, OH^-, and H_2O. Additional intermediates $S_5O_6^{2-}$, $S_2O_3OH^-$, $S_3O_3OH^-$, $HS(OH)$, and $S(OH)_2$ were chosen for the following reasons:
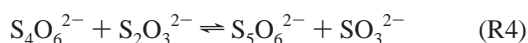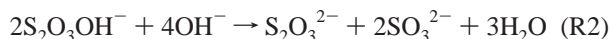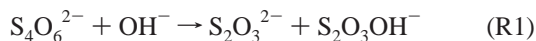
(i) The role of $S_2O_3OH^-$ has already been well-established[27,33,34] in the redox reactions of tetrathionate. Since $S_2O_3OH^-$ plays a central role in the tetrathionate−hydrogen peroxide and the tetrathionate−chlorite reactions, it looks reasonable to postulate it as an intermediate.

(ii) Pentathionate is known to participate in catalytic rearrangement of tetrathionate;[15−17] therefore this species must also be included as an intermediate.

(iii) $S_3O_3OH^-$, $HS(OH)$, and $S(OH)_2$ have already been considered in the degradation process of pentathionate;[14] therefore these species may also play important roles in the alkaline decomposition of tetrathionate.

This set of reactants, intermediates, and end products leads to 25 plausible mono- or bimolecular steps. Because the

(28) Naito, K.; Hayata, H.; Mochizuki, M. *J. Inorg. Nucl. Chem.* **1975**, *37*, 889.

(29) Horváth, A. K.; Nagypál, I. *J. Phys. Chem. A* **1998**, *102*, 7267.
(30) Horváth, A. K.; Nagypál, I.; Peintler, G.; Epstein, I. R.; Kustin, K. *J. Phys. Chem. A* **2003**, *107*, 6966.
(31) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *J. Phys. Chem. A* **2003**, *107*, 10063.
(32) Horváth, A. K.; Nagypál, I. *J. Phys. Chem. A* **2006**, *110*, 4753.
(33) Kurin-Csörgei, K.; Orbán, M.; Rábai, G.; Epstein, I. R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2851.
(34) Voslar, M.; Matejka, P.; Schreiber, I. *Inorg. Chem.* **2006**, *45*, 2624.

decomposition is strongly affected by the pH, hydroxide-catalyzed pathways of all the 25 reactions were also considered initially. After a long but straightforward reduction procedure, the following kinetic model emerged.

$$PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-} \qquad (E1)$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \qquad (E2)$$

$$S_4O_6^{2-} + OH^- \rightarrow S_2O_3^{2-} + S_2O_3OH^- \qquad (R1)$$

$$2S_2O_3OH^- + 4OH^- \rightarrow S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (R2)$$

$$S_4O_6^{2-} + S_2O_3OH^- \rightarrow S_5O_6^{2-} + SO_4^{2-} + H^+ \quad (R3)$$

$$S_4O_6^{2-} + S_2O_3^{2-} \rightleftharpoons S_5O_6^{2-} + SO_3^{2-} \qquad (R4)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \qquad (R5)$$

$$S_5O_6^{2-} + OH^- \rightarrow + S_2O_3^{2-} + S_3O_3OH^- \quad (R6)$$

$$S_3O_3OH^- + OH^- \rightarrow S_2O_3^{2-} + S(OH)_2 \qquad (R7)$$

$$S_4O_6^{2-} + S_3O_3OH^- \rightarrow S_5O_6^{2-} + S_2O_3OH^- \qquad (R8)$$

$$2S(OH)_2 + 2OH^- \rightarrow SO_3^{2-} + HS(OH) + 2H_2O \quad (R9)$$

$$S_2O_3^{2-} + HS(OH) \rightarrow S_2O_3^{2-} + H_2O \qquad (R10)$$
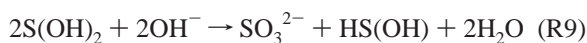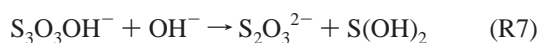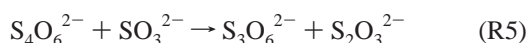
The rapid de- and reprotonation processes (E1 and E2) were taken into account with known equilibrium constants[35] to follow the small change in pH during the decomposition ($pK_{E1} = 11.5$, $pK_{E2} = 9.7$). These acid dissociation reactions may be regarded as auxiliary processes, necessary only for detailed calculations, but they are not the central part of the proposed model.

Discussion

Step R1 is the initiating rate-determining step of the alkaline decomposition of tetrathionate that proceeds via scission of the inner S−S bond yielding thiosulfate and $S_2O_3OH^-$. The formation of the adduct $S_4O_6OH^{3-}$ is probably followed by the heterolytic inner S−S bond cleavage resulting in the nucleophilic displacement of thiosulfate by hydroxide ion. Our fitting procedure has yielded a value of 0.044 ± 0.004 M^{-1} s^{-1} for k_{R1} that is approximately an order of magnitude higher than that could be calculated from Rolia and Chakrabarti's study[18] but an order of magnitude lower than that determined by Zhang and Dreisinger.[4] They have obtained respective values of 0.0051 and 0.38 M^{-1} s^{-1} for the rate-determining step of the alkaline decomposition. This difference is, however, due to the effect of ionic strength as noted by Breuer and Jeffrey.[19] Rolia and Chakrabarti have conducted their experiments without buffer and supporting electrolyte resulting in an ionic strength (approximately 0.02 M) as determined by tetrathionate and the products. In contrast, Zhang and Dreisinger have used high buffer concentration yielding higher ionic strength (approximately

1.5 M) where the rate coefficient of the decomposition was obtained. Thus, taking the positive kinetic salt effect into consideration, the difference between the value determined in the present and the previous studies can easily be explained.

Step R2 is the second-order decomposition of $S_2O_3OH^-$ producing thiosulfate and sulfite. Evidently, this reaction is not elementary, and it probably proceeds via the following consecutive processes.

$$2S_2O_3OH^- \rightarrow S_2O_3^{2-} + S_2O_5^{2-} + 2H^+ \qquad (14)$$

$$S_2O_5^{2-} + H_2O \rightarrow 2SO_3^{2-} + 2H^+ \qquad (15)$$
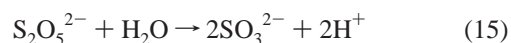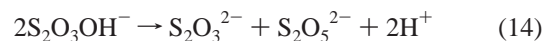
The calculations have revealed that the rate coefficient k_{R2} is in total correlation with k_{R3}; thus we have fixed $k_{R2} = 10^7$ M^{-1} s^{-1} that is fast enough to treat $S_2O_3OH^-$ as a steady-state intermediate in accordance with MRA studies. This pathway directly leads to stoichiometry S2. The role of this step was confirmed by further calculation in which this step was omitted from the proposed model. The result showed on the one hand an unacceptably high average deviation and on the other hand a significant loss of source of sulfite. We, therefore, concluded that this step is strongly supported by the experiments.

Step R3 is the other route for conversion of the intermediate $S_2O_3OH^-$. Evidently, its role increases with increasing initial tetrathionate concentration. As one may notice, this step converts the reactants into sulfate and pentathionate. This pathway is responsible for the increasing amount of sulfate with increasing initial tetrathionate formation (see Table 2). Since the proposed kinetic model does not contain any other process than step R3 yielding sulfate, its role is essential. One might argue that the easily conceivable alkaline decomposition of trithionate

$$S_3O_6^{2-} + H_2O \rightarrow SO_4^{2-} + S_2O_3^{2-} + 2H^+ \qquad (16)$$
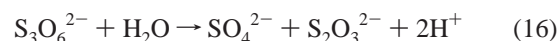
might also be a possible alternative for producing sulfate as an end product. If, however, step R3 was substituted with eq 16, then not only would the average deviation increase to an unacceptably high 0.0141 AU but also k_{16} would be 0.018 ± 0.003 M^{-1} s^{-1}. It is, however, orders of magnitude higher than that obtained from independent measurements by Rolia and Chakrabarti.[18] Therefore, we have concluded that step R3 cannot be replaced by eq 16. Further support of step R3 is in our latest results on thiosulfate−hypochlorous acid system[36] that explains simultaneous formation of higher polythionates and sulfate. It should also be noted that stoichiometry S3 can be generated from 2*(R1) + 2*(R3) + 2*(R6) + 2*(R7) + (R9) + (R10).

Step R4 is the well-known thiosulfate-assisted rearrangement of tetrathionate studied by several research groups.[15−17] Recent result on the dynamic instability of the electrochemical oxidation of thiosulfate is also explained by the help of

(35) *IUPAC Stability Constant Database*; Royal Society of Chemistry: London, 1992−1997.
(36) Varga, D.; Horváth, A. K.; Nagypál, I. *J. Phys. Chem. B* **2006**, *110*, 2467.

this step.[37] Fava and Bresadola have determined[17] a value of 3.9×10^{-3} M^{-1} s^{-1} for the forward reaction at 50 °C and at an $I = 0.94$ M ionic strength in neutral solution, but they were not able to determine the individual rate coefficient of the reverse reaction. Foss and Kringlebotn have obtained[38] 1.3×10^{-3} M^{-1} s^{-1} for the rate coefficient of the forward reaction at 25 °C and at an $I = 1.15$ M ionic strength. Our calculation has yielded $k_{R4} = (1.94 \pm 0.08) \times 10^{-4}$ M^{-1} s^{-1}, which is approximately an order of magnitude lower than the value determined by Foss and Kringlebotn. This difference, however, can easily be explained by the kinetic salt effect of reaction between two like-charged ions. Nevertheless, the exact value of k_{-R4} cannot be determined from our measurements. The back reaction must be rapid enough to provide sufficiently low level of pentathionate, since it does not accumulate in detectable amount. Further details about the reactions of pentathionate will be discussed later (see paragraphs below), but we were able to calculate only the ratio of k_{R6}/k_{-R4} that was found to be 0.82 ± 0.01 with $k_{-R4} = 200$ M^{-1} s^{-1}. As one may notice thiosulfate acts as an autocatalyst of the decomposition of the tetrathionate, but the characteristic sigmoidal-shaped curve is not observed under our experimental circumstances. It is, however, due to the fact that k_{R4} is low compared to the value of k_{R1}, which means that the S-shaped kinetic curve cannot be manifested. The low value of k_{R4} also indicates that the forward reaction may be neglected from the proposed model. By use of $k_{R4} = 0$, we arrive to a somewhat higher, but acceptable, 0.0036 average deviation with slight changes ($<20\%$) of the remaining fitted parameters. Although the effect of this process is not striking under our experimental conditions, we have kept it in the final model for two reasons: first, it decreases the average deviation by 15% approximately; second, more importantly, the value for k_{R4} obtained by the present work is in complete coincidence with that of determined previously by independent works.[17,38]

Step R5 is the well-known sulfitolysis of tetrathionate. The reaction was first studied by Kurtenacker and Goldbach[39] and was reported to be applied for successful determination of polythionates.[40] The procedure was later modified by Iwasaki and Suzuki[41] to make it suitable for analyzing microamounts of polythionates. We have determined k_{R5} to be 0.547 ± 0.005 M^{-1} s^{-1} that agrees well with the value that could be estimated from the latter 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.[42] As one may notice stoichiometry S1 may be generated from 2*-(R1) + (R2) + 2*(R5).

Step R6 is the attack of hydroxide ion at the γ-sulfur atom of pentathionate yielding thiosulfate and $S_3O_3OH^-$. As it was already discussed, only the ratio of k_{R6}/k_{-R4} could be calculated from our measurements. Since pentathionate was not accumulated in detectable amount in our experimental circumstances, k_{-R4} must be higher than 200 M^{-1} s^{-1} that results in $k_{R6} \geq 164$ M^{-1} s^{-1}. The latter value is, however, 2 orders of magnitude higher than that obtained by Christiansen et al.[43] for the alkaline degradation of pentathionate but is in complete coincidence with the qualitative observation published by Wagner and Schreier,[14] who have stated that "The alkaline degradation of the $S_5O_6^{2-}$ proceeds very quickly". If we had decreased k_{R6} to 2 M^{-1} s^{-1} resulting in k_{-R4} to be 2.44 M^{-1} s^{-1}, then pentathionate would have been built up to such an extent ($>10^{-5}$ M) that the absorbance–time curves would have shown a maximum since pentathionate absorbs the UV light much stronger[24] than tetrathionate does. Nevertheless, MRA studies should have also indicated the presence of an absorbing intermediate. Thus, we have concluded that k_{-R4} must be higher than 200 M^{-1} s^{-1} to keep the pentathionate concentration under 10^{-7} M. Further consequence of the high rate coefficient of the alkaline decomposition of pentathionate is that nucleophilic displacement of the thiosulfate with sulfite group on pentathionate is more than 2 orders of magnitude higher compared to that of tetrathionate ion in our experimental circumstances. Our calculation has yielded $k_{-R4}/k_{R5} \geq 400$ that is at least 1 order of magnitude higher than obtained by Fava and Bresadola[17] or Foerster and Centner.[42] In both cases, however, the experiments were conducted at around neutral pHs, where significant amount of HSO_3^- was present beside SO_3^{2-} that may have influence on the apparent rate coefficient k_{R5} to be decreased by the different reactivities of SO_3^{2-} and HSO_3^- toward tetrathionate.

Step R7 is one of the possible routes for disappearance of $S_3O_3OH^-$ formed in step R6 and was already suggested by Wagner and Schreier.[14] Our calculation has revealed total correlation between parameters k_{R7} and k_{R8}; therefore we were able to determine only $k_{R8}/k_{R7} = 374 \pm 12$ with $k_{R7} \geq 10^3$ M^{-1} s^{-1}.

Step R8, the other pathway responsible for keeping the concentration of $S_3O_3OH^-$ low, has not been proposed so far. The role of this step was also confirmed by further calculations by omission this step from the proposed model. The results indicated an increase of the average deviation to 0.0139 from 0.003, meaning that the role of this step is strongly supported.

Steps R9 and R10 are fast processes and were already proposed by Wagner and Schreier.[14] Their individual rate coefficients could not be determined from our measurements, and only lower limits could be assigned to these processes. Although recent studies[44–46] consider sulfoxylate ion to have longer lifetime in 0.5 M NaOH solution, the protonated

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Table 3. Fitted and Fixed Rate Coefficients Used in the Fitting Procedure[a]

step	rate equation	parameter (M^{-1} s^{-1})
(R1)	$k_{R1}[S_4O_6^{2-}][OH^-]$	0.044 ± 0.004
(R2)	$k_{R2}[S_2O_3OH^-]^2$	10^7
(R3)	$k_{R3}[S_4O_6^{2-}][S_2O_3OH^-]$	57.3 ± 1.6
(R4)	$k_{R4}[S_4O_6^{2-}][S_2O_3^{2-}]$	$(1.94 \pm 0.08) \times 10^{-4}$
(−R4)	$k_{-R4}[S_5O_6^{2-}][SO_3^{2-}]$	1220 ± 40
(R5)	$k_{R5}[S_4O_6^{2-}][SO_3^{2-}]$	0.547 ± 0.005
(R6)	$k_{R6}[S_5O_6^{2-}][OH^-]$	1000
(R7)	$k_{R7}[S_3O_3OH^-][OH^-]$	1000
(R8)	$k_{R8}[S_4O_6^{2-}][S_3O_3OH^-]$	$(3.74 \pm 0.12) \times 10^5$
(R9)	$k_{R9}[S(OH)_2]^2$	$\geq 10^3$
(R10)	$k_{R10}[SO_3^{2-}][HS(OH)]$	$\geq 10^6$

[a] Note: the actual calculation has yielded the ratios of $k_{R3}/k_{R2} = (5.73 \pm 0.16) \times 10^{-6}$, $k_{R6}/k_{-R4} = 0.82 \pm 0.1$, and $k_{R8}/k_{R7} = 374 \pm 12$.
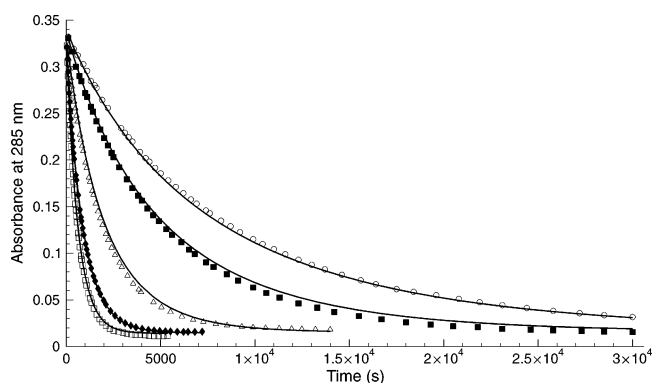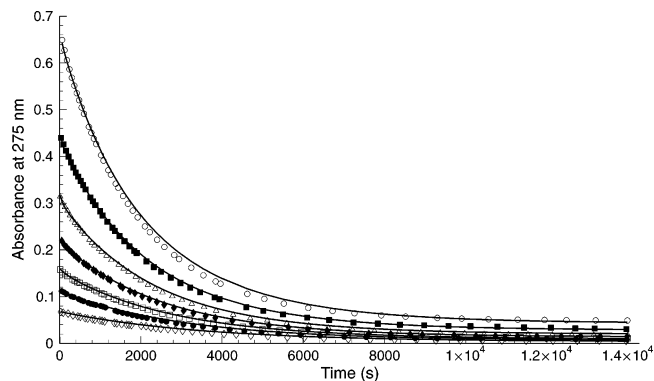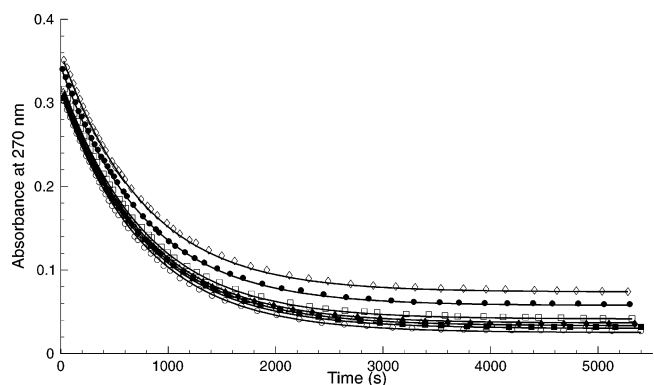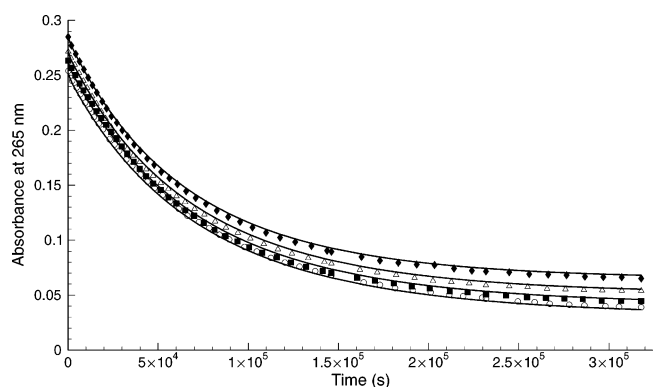

Figure 3. Measured (symbols) and calculated kinetic (solid lines) curves in the absence of thiosulfate at $[S_4O_6^{2-}]_0 = 3.0$ mM using phosphate buffer. pH = 10.80 (○), 11.02 (■), 11.50 (△), 11.99 (◆), 12.20 (□).
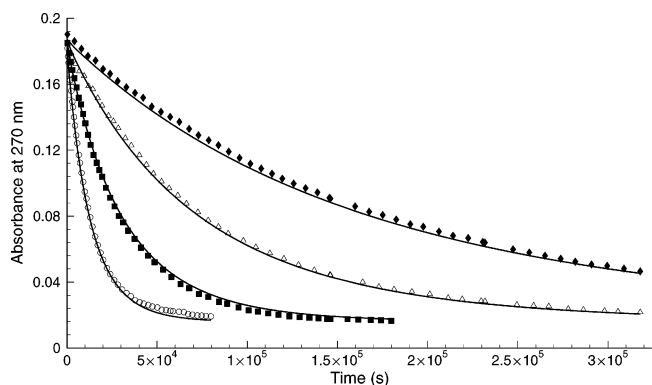
Figure 4. Measured (symbols) and calculated kinetic (solid lines) curves in the absence of thiosulfate at $[S_4O_6^{2-}]_0 = 0.6$ mM using carbonate buffer. pH = 10.65 (○), 10.18 (■), 9.70 (△), 9.22 (◆).

Figure 5. Measured (symbols) and calculated kinetic (solid lines) curves in the absence of thiosulfate at pH = 11.50 using phosphate buffer. $[S_4O_6^{2-}]_0 = 3.0$ (○), 2.0 (■), 1.4 (△), 1.0 (◆), 0.7 (3), 0.5 (●), 0.3 (◇) mM.

Figure 6. Measured (symbols) and calculated kinetic (solid lines) curves in the presence of thiosulfate at $[S_4O_6^{2-}]_0 = 1.0$ mM, pH = 12.2 using phosphate buffer. $[S_2O_3^{2-}]_0 = 0.0$ (○), 0.3 (■), 0.5 (△), 0.7 (◆), 1.0 (□), 2.0 (●), 3.0 (◇) mM.

Figure 7. Measured (symbols) and calculated kinetic (solid lines) curves in the presence of thiosulfate at $[S_4O_6^{2-}]_0 = 0.6$ mM using carbonate buffer. $[S_2O_3^{2-}]_0 = 0.0$ (○), 0.3 (■), 0.6 (△), 1.0 (◆) mM.

sulfoxylate ion (HSO_2^-) and especially sulfoxylic acid can disproportionate rapidly in weakly alkaline solution.[47] Therefore, we have set lower limits for the values of k_{R9} and k_{R10} as 10^3 and 10^6 M^{-1} s^{-1}, respectively, which keep the concentration levels of $S(OH)_2$ and $HS(OH)$ at sufficiently low values. One might argue that step R9 can also be written with elimination of $HS(OH)$ into the following form.

$$2S(OH)_2 + 2OH^- \rightarrow S_2O_3^{2-} + 3H_2O \qquad (17)$$

(46) Kudrik, E. V.; Makarov, S. V.; Zahl, A.; van Eldik, R. *Inorg. Chem.* **2005**, *44*, 6470.
(47) Makarov, S. V. *Russ. Chem. Rev.* **2001**, *70*, 885.

Since the alkaline decomposition of tetrathionate yields enough sulfite in our experimental conditions, it could be done without any change in the final results. If, however, the sulfite concentration decreases to a sufficiently low level, then spontaneous decomposition of $HS(OH)$ gives colloidal sulfur precipitation,

$$HS(OH) \rightarrow S + H_2O \qquad (18)$$
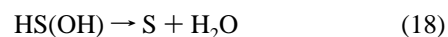
which is known to frequently accompany the later stages of the alkaline degradation of polythionates.[12,14,43] We have also tried to insert other reactions of $HS(OH)$; for instance
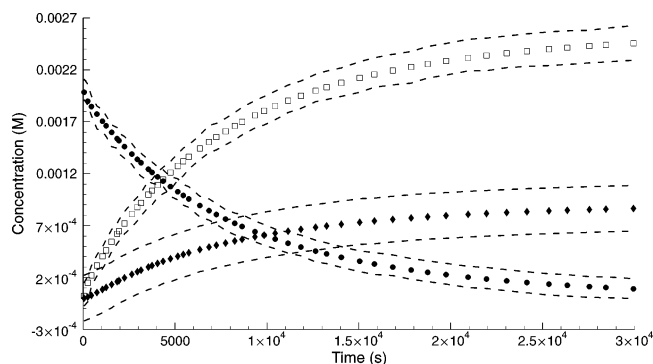
Figure 8. Calculated concentration−time series of tetrathionate (●), thiosulfate (□), and trithionate (◆) compared to the concentration ranges (dashed lines) obtained from the decomposition of the absorbance−time series of 265−295 nm wavelength range supposing that all the absorbances have ±0.003 AU uncertainty. $[S_4O_6^{2-}]_0 = 0.002$ M, pH = 10.80.

reactions with tetrathionate, pentathionate, thiosulfate, and the intermediates, but none of them proved to be necessary for quantitative description of the kinetic curves.

Table 3 contains the final parameter set obtained from our experiments. The average deviation was found to be 0.003 AU, which we believe to be close to the experimentally achievable limit of error. The final results can be illustrated in Figures 3−7. They clearly show that the model works nicely in wide concentration ranges of the reactants and pHs as well as using different buffer components.

It should also be mentioned that the absence of accumulating intermediates allows us to decompose the absorbance−time series into concentration−time series of tetrathionate, thiosulfate, and trithionate. As one may notice, this algebraic decomposition might be seriously affected by the error of the absorbance measurement especially in case of trithionate, since its molar absorbance is much lower than that of the tetrathionate. Therefore, we have also checked if the proposed model is able to predict properly the concentration−time series of tetrathionate, thiosulfate, and trithionate simultaneously that are obtained from the decomposition of the absorbance−time series. Figure 8 also provides further support for the proposed model, since the concentration−time series are well within the concentration range determined from the absorbance−time series supposing that all the measured absorbance have ±0.003 uncertainty.

Conclusion

Although the alkaline decomposition of the tetrathionate is thought to be a complex process for a long time, no comprehensive mechanism has yet been proposed to incorporate this feature. Our suggested model clearly shows that the product distribution of the reaction is strongly affected by pH, the initial concentration of tetrathionate, and the fact

that thiosulfate catalyzes the degradation process in agreement with Rolia and Chakrabarti.[18] Furthermore, it is also shown that the rate of decomposition does not depend on the buffer applied in the case of phosphate and carbonate buffer components. It follows from the indirect fact that the kinetic curves measured in the presence of different buffer components (phosphate and carbonate) can readily be treated together in the simultaneous curve-fitting procedure. It, however, does not mean that no specific buffer dependence of the alkaline decomposition of tetrathionate could be observed at all. Although it was not investigated in the present work, it seems firmly established that the decomposition is accelerated by ammonia[6] most probably through the formation[5] of $SO_3NH_2^-$. Certainly it is not a unique explanation, and therefore further investigations are needed to clarify the effect of ammonia on the decomposition.

The present study may also be helpful in explaining the experimentally observed multicomponent convection, in non-buffered medium, in the chlorite−tetrathionate reaction at high initial hydroxide concentration[48] where significant amounts of thiosulfate, trithionate, and sulfite may also be present in a short period of time as a result of the alkaline decomposition of tetrathionate. In fact, at a usual composition,[48] our proposed model in unbuffered medium predicts that the concentration of thiosulfate becomes commensurable with that of tetrathionate within 15 min. Since formation of the thiosulfate is accompanied by consumption of hydroxide ions, the pH of the solution reaches neutrality opening up the possibility of igniting the chlorite−thiosulfate reaction.[49] The contributory effect of thiosulfate, trithionate, or sulfite by their reactions with chlorite[49,50] to the mother reaction may, therefore, not be negligible.

We strongly believe that the model may also serve as a starting point to design lowering of polythionate concentration in the leaching processes of silver or gold ores as well as the maximum thiosulfate recovery for the recycling process.

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