Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 10273–10282 **10273**
DOI: 10.1021/ic9023025

A Kinetic Study of Rearrangement and Degradation Reactions of Tetrathionate and Trithionate in Near-Neutral Solutions

Hongguang Zhang* **and Matthew I. Jeffrey**

Parker Centre (CSIRO Process Science and Engineering) P.O. Box 7229, Karawara, WA 6152, Australia

Received November 20, 2009

The kinetics of reactions of trithionate and tetrathionate via different reaction pathways were studied in near-neutral solutions. In the case of trithionate, the predominant degradation reaction is hydrolysis to thiosulfate and sulfate. The pseudofirst-order rate constant is independent of pH and measured to be $(6.2 \pm 0.2) \times 10^{-7}$ s^{-1} for the pH range of 5.5−10.5. With tetrathionate, the reaction in both neutral and alkaline solutions occurs via a thiosulfate catalyzed rearrangement reaction to trithionate and pentathionate followed by their further reactions. The data suggest that when thiosulfate is completely absent, this first step will not occur, and in the presence of thiosulfate, the rate of the first step is independent of pH in the pH range 6−8. The secondary reactions include the hydrolysis of trithionate and the further rearrangement and degradation of pentathionate. This mechanism explains the dominant reaction products for both neutral and alkaline solutions. In the presence of thiosulfate and at near-neutral pH, the rearrangement reactions dominate over the degradation reactions and exhibit second-order kinetics, with the rate constants in the pH range of 6−8 determined to be (4.24 ± 0.26) and $(1.89 \pm 0.18) \times 10^{-4}$ M^{-1} s^{-1} for tetra- and pentathionates, respectively. At extremely low thiosulfate concentrations, the main secondary reaction is the hydrolysis of trithionate at pH < 7, and at pH > 7, the degradation of pentathionate.

1. Introduction

The leaching of gold using a thiosulfate solution as an alternative to the well-known cyanidation process has been an active area of research in the last 30 years following the work by Berezowsky and Sefton.[1] The conventional thiosulfate process, carried out under alkaline conditions, employs a copper salt (usually cupric sulfate) as the oxidant and ammonia (usually as ammonium thiosulfate) to stabilize the copper. Numerous studies have been conducted on the thiosulfate−copper−ammonia process, and a number of reviews are available.[2,3] One of the major problems of the process is the rapid oxidation of thiosulfate by the copper(II). This not only causes serious losses of thiosulfate but also generates polythionates which are detrimental to the subsequent gold recovery process with ion exchange resins.[4,5] In addition, there has been increasing concerns about the use of ammonia for environmental reasons.

More recently an alternative thiosulfate leaching process under neutral or slightly acidic conditions has been reported.[6,7] A small amount of thiourea is used as a catalyst for the oxidation of gold in thiosulfate solutions in the absence of ammonia and copper. A ferric complex with EDTA (FeEDTA) or oxalate (Fe-Ox) can be used as the oxidant.[8] Both FeEDTA and Fe-Ox have been shown to have a low reactivity with thiosulfate in homogeneous solutions, and promising leach performances have been obtained with oxide gold ores.[6,8] However, sulfide minerals, such as pyrite, have been found to catalyze the oxidation of thiosulfate under the leaching conditions.[9,10] Thiosulfate is oxidized rapidly to tetrathionate, which then rearranges to generate tri-, penta-, and hexathionates. The rearrangement reactions are known to be catalyzed by thiosulfate.[11] Unlike the alkaline conditions for the thiosulfate−copper−ammonia process where the higher polythionates are not stable, all the polythionates can accumulate to reasonably high concentrations under the neutral conditions used for the thiosulfate−thiourea process.[9] Since the adsorption of polythionates on the resins becomes stronger as the sulfur chain increases,[12] a good understanding of the chemistry and reaction kinetics of the

---

*Corresponding author. E-mail: hongguang.zhang@csiro.au. Telephone: 61 8 93348937.

(1) Berezowsky, R.M.G.S; Sefton, V. B. 108th AIME Annual Meeting, New Orleans, LA, February 18−22, 1979.

(2) Aylmore, M. G.; Muir, D. M. *Miner. Eng.* **2001**, *14*, 135–174.

(3) Molleman, E.; Dreisinger, D. *Hydrometallurgy* **2002**, *66*, 1–21.

(4) Zhang, H.; Dreisinger, D. B. *Hydrometallurgy* **2002**, *66*, 67–76.

(5) Nicol, M. J.; O'Malley, G. P. *Cyanide: Social, Industrial and Economic Aspects*; Young, C. A., Tidwell, L. G., Anderson, C. G., Eds.; TMS: Warrendale, PA, 2001; pp 469−483.

(6) Zhang, H. Improved thiosulphate leach process. International Patent Publication: WO 2005/017215 A1, 2005.

(7) Zhang, H.; Nicol, M. J.; Staunton, W. P. *Treatment of gold ores*; Deschenes, G., Hodouin, D., Lorenzen, L., Eds.; Canadian Institute of Mining, Metallurgy and Petroleum: Montreal, 2005, pp 243−257.

(8) Chandra, I.; Jeffrey, M. I. *Hydrometallurgy* **2005**, *77*, 191–201.

(9) Zhang, H.; Jeffrey, M. *Hydrometallurgy 2008*; Courtney, A. Y., Patrick, R. T., Corby, G. A., Yeonuk, C., Eds.; Society for Mining, Metallurgy and Exploration, Inc.:Littleton, CO, 2008; pp 769−778.

(10) Heath, J. A.; Jeffrey, M. I.; Zhang, H.; Rumball, J. A. *Miner. Eng.* **2007**, *21*, 424–433.

(11) Lyons, D.; Nickless, G. In *Inorganic Sulfur Chemistry*; Nickless, G., Ed.; Elsevier Publishing Company: Amsterdam, 1968; p 509.

(12) Jeffrey, M. I.; Brunt, S. D. *Hydrometallurgy* **2007**, *89*, 52–60.

thiosulfate/polythionates system is critical for the control of the leaching and the recovery of gold.

The chemistry of sulfoxy anions, including the reactions of thiosulfate and polythionates, has been extensively studied, and the early works are well documented in some comprehensive reviews.[11,13] A very important mechanism in the sulfur chemistry is the bimolecular nucleophilic displacement reaction (S_N2), which is also involved in the rearrangement of various polythionates.[11,14] However, kinetic data of these reactions are incomplete for near-neutral conditions. This is probably because of the complexity of the reaction systems. First, there exists multiple reaction pathways, and therefore, the exact mechanisms are ambiguous. Second, the mechanisms may change during the reactions, as a result of changes in reaction conditions (e.g., changes in pH). Third, the reactions often generate complex mixtures of metastable sulfur species which are difficult to separate and analyze. In more recent years, nevertheless, effective methods and procedures for prompt analysis of complex sulfur compounds have been developed using high-performance liquid chromatography (HPLC).[12,15] This has made kinetic measurements much more convenient. In this work, an attempt was made to study the kinetics of the rearrangement and degradation reactions of tri- and tetrathionates over a range of pH values with the focus on near-neutral solutions.

2. Experimental Section

The analysis for thiosulfate ($S_2O_3^{2-}$) and polythionates ($S_xO_6^{2-}$, $x = 3-6$) with HPLC was based on the method of Jeffrey and Brunt.[12] A Waters 2695 HPLC separation module was used in conjunction with a Dionex IonPac AS16 ion exchange column equipped with an IonPac AG16 guard column. The mobile phase was a solution of sodium perchlorate (0.075–0.2 M). In most cases a concentration of 0.125 M was initially used, with which species up to $S_5O_6^{2-}$ could be well resolved and eluted within 12 min. Then the eluant concentration was increased to 0.2 M to reduce the retention time of $S_6O_6^{2-}$. The separated anions were detected using UV with a Waters 2996 Photodiode Array detector. All the species were quantified at a wavelength of 214 nm except $S_3O_6^{2-}$, which was quantified at 192 nm. Higher polythionates with $x \geq 7$ were not detected in this study. A sample chromatogram is shown in Figure 1a.

Sulfate (SO_4^{2-}) and sulfite (SO_3^{2-}) were analyzed through an IonPac AS17-C column and AG17-C guard column using a Waters 432 conductivity detector. The eluant was NaOH solution containing acetonitrile; initially the eluent contained a low concentration of NaOH to effect the separation of sulfite and sulfate, which was followed by a step in the NaOH concentration to enable the rapid elution of thiosulfate. This method has been described in detail by Breuer et al.[16] and was found to be effective in the elution and separation of SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$ but not $S_xO_6^{2-}$. Therefore all $S_xO_6^{2-}$ species were adsorbed onto the guard column at the commencement of the injection, which was then taken offline automatically using a switching valve. During the analysis stage, the guard column was back-flushed using 0.1 M NaOH to remove the adsorbed polythionates prior to the next injection. A sample chromatogram is shown in Figure 1b. The accuracy in the sulfate analysis using this technique was within ca. ± 0.01 mM.

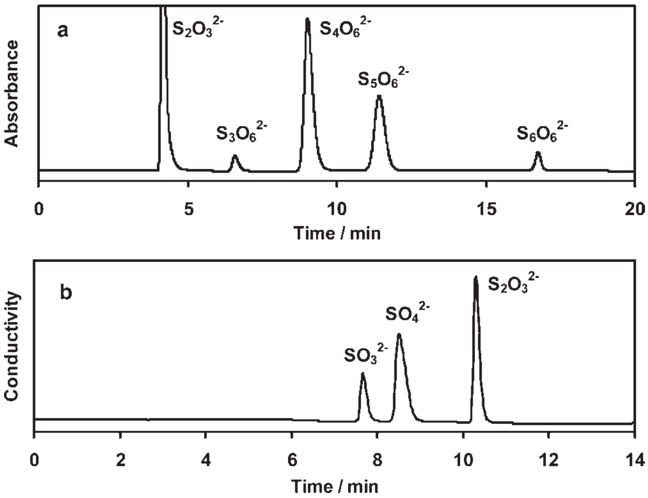

Figure 1. HPLC chromatograms for the analysis of (a) mixture of thiosulfate and polythionates using a UV detector and (b) mixture of sulfate, sulfite, and thiosulfate using a conductivity detector.

The experiments were conducted in the sample vials of HPLC, where injections for analysis were made automatically at the set times. Whenever necessary, two sets of HPLC systems were used to run both columns at the same time for the same reaction solution. The eluant flow rate was 1 mL min^{-1}. The ambient temperature was 22–23 °C. The reaction solutions were buffered with CH_3COOH/CH_3COO^- (pH 4–5), $H_2PO_4^-/HPO_4^{2-}$ (pH 5–8), $B_4O_7^{2-}$ (pH 9), and HCO_3^-/CO_3^{2-} (pH 10–10.5). These chemicals were found not to interfere with the analysis.

All solutions were prepared with either analytical grade or synthesized chemicals and Millipore water. Tri-, penta-, and hexathionate were prepared using the method of Kelly and Wood.[17] The purity of the synthesized tri-, penta-, and hexathionate was checked using two methods: (a) For pentathionate and hexathionate, the reaction with excess sulfite to generate trithionate and thiosulfate, with quantification of the generated thiosulfate; and (b) the reaction of trithionate with sulfide to generate thiosulfate. The purity was also checked by determining the concentration of the main impurity species.

3. Results and Discussion

3.1. Reaction Pathways and Kinetic Considerations.

The rearrangement of polythionates refers to the following general disproportionation reaction:[18,19]

$$2S_xO_6^{2-} \rightarrow S_{x-1}O_6^{2-} + S_{x+1}O_6^{2-} \qquad (x > 3) \quad (1)$$

Trithionate does not rearrange according to this reaction since dithionate ($S_2O_6^{2-}$) cannot be formed from the interactions of polythionates.[11] Reaction 1 is strongly catalyzed by thiosulfate, and an established mechanism is one involving S_N2 reactions:[11]

$$S_xO_6^{2-} + S_2O_3^{2-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} S_{x+1}O_6^{2-} + SO_3^{2-} \qquad (x \geq 3) \quad (2)$$

The direction at which reaction 2 occurs depends on the pH and the relative nucleophilicity of the sulfoxy intermediates ($HSO_3^{2-} < S_2O_3^{2-} < SO_3^{2-}$). Given p$K_{a2}$ = 6.91 for

---

(13) Szekeres, L. *Talanta* **1974**, *21*, 1–44.

(14) Moses, C. O.; Nordstrom, D. K.; Herman, J. S.; Mills, A. L. *Geochim. Cosmochim. Acta* **1987**, *51*, 1561–1571.

(15) O'Reilly, J. W.; Dicinosky, G. W.; Shaw, M. J.; Haddad, P. R. *Anal. Chim. Acta* **2001**, *432*, 165–192.

(16) Breuer, P. L., Hewitt, D. M., Sutcliffe, C. A., Jeffrey, M. I. *World Gold 2009 Conference*, Proceedings of The South African Institute of Mining and Metallurgy, Johannesburg, South Africa, October 26–30, 2009; Johannesburg, 2009, pp 287–294.

(17) Kelly, D. P.; Wood, A. P. *Methods Enzymol.* **1994**, *243*, 475–501.

(18) Steudel, R.; Holdt, G. *J. Chromatogr.* **1986**, *361*, 379–384.

(19) Takano, B; Watanuki, K. *Talanta* **1988**, *35*, 847–854.

HSO_3^-,[20] it is generally understood that at pH < 7 the reaction is driven to the right by $S_2O_3^{2-}$ (S-chain lengthening), and at pH > 7 the reaction is driven to the left (S-chain shortening) by SO_3^{2-}.[14]

Reaction 2 explains the rearrangement reactions of polythionates shown in reaction 1. For example, the mechanism shown in reactions 3 and 4 below explains the overall reaction of tetrathionate, reaction 5, in which thiosulfate serves as a catalyst:

$$S_4O_6^{2-} + S_2O_3^{2-} \rightarrow S_5O_6^{2-} + SO_3^{2-} \qquad (3)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \qquad (4)$$

$$2S_4O_6^{2-} \rightarrow S_3O_6^{2-} + S_5O_6^{2-} \qquad (5)$$

A similar reaction mechanism applies for the thiosulfate catalyzed rearrangement of pentathionate. However, reactions leading to the formation of higher polythionates ($S_xO_6^{2-}$, $x > 6$) are not considered because they were not detected under the conditions of this study, though polythionates with up to 20 sulfur atoms have been reported in strong acid solutions.[18,19]

Some early work has been done to measure the kinetics of the individual steps involved in the rearrangement reactions. For example, Foss and Kringlebotn[21] determined the second-order rate constant of reaction 3 in phosphate buffered solutions by using formaldehyde as a sulfite scavenger and by assuming further reactions between the higher polythionates generated and the thiosulfate having the same rate constant. Fava and Bresadola[22] attempted to study the kinetics of thiosulfate catalyzed rearrangement of tetrathionate in a neutral solution based on the following mechanism:

$$S_4O_6^{2-} + S_2O_3^{2-} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} S_5O_6^{2-} + SO_3^{2-} \qquad (6)$$

$$S_4O_6^{2-} + SO_3^{2-} \xrightarrow{k_c} S_3O_6^{2-} + S_2O_3^{2-} \qquad (7)$$

A rate equation was established for the disappearance of $S_4O_6^{2-}$ by applying steady-state approximation to SO_3^{2-}:

$$-\frac{dS_4}{dt} = \frac{2k_a k_c S_4^2 S_2}{k_c S_4 + k_b S_5} \qquad (8)$$

Here, k_a, k_b and k_c are the rate constants of the respective elementary steps, whereas S_x is the concentration of thiosulfate or polythionate with x indicating the number of sulfur atoms. At the beginning, when S_5 is exceedingly small, eq 8 becomes

$$-\left(\frac{dS_4}{dt}\right)_{t=0} = 2k_a S_4 S_2 \qquad (9)$$

Therefore k_a could be determined from the initial rate. While analytical solutions for k_b and k_c were not possible, the authors obtained the ratio of k_b/k_c by assuming that the further reaction of $S_5O_6^{2-}$ was negligible. However, this last assumption was found to be invalid. An experiment by Fava and Bresadola[22] was repeated in this work. As shown in Figure 2, under the strong conditions used (high $S_2O_3^{2-}$ and elevated temperature), $S_6O_6^{2-}$ was detected shortly after the reaction started and significant deviations between S_3 and S_5 were observed. This is believed to be mainly due to the rearrangement of $S_5O_6^{2-}$ to give $S_4O_6^{2-}$ and $S_6O_6^{2-}$. In addition, there was a steady increase in S_2, which was attributed by Fava and Bresadola[22] to the hydrolysis of $S_3O_6^{2-}$ via reaction 10. If these reactions had not occurred, then S_3 and S_5 would have stayed equal during the experiment according to the stoichiometry of reaction 5:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (10)$$

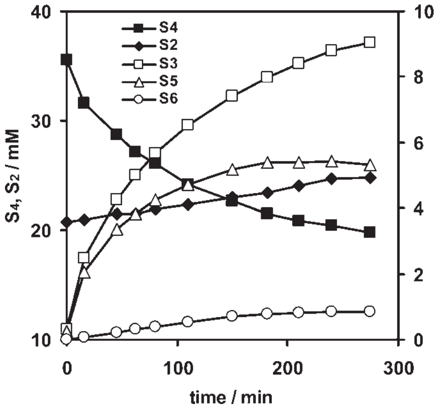

Figure 2. Rearrangement of tetrathionate under similar conditions of Fava and Bresadola:[22] 36 mM $S_4O_6^{2-}$, 21 mM $S_2O_3^{2-}$, 0.2 M SO_4^{2-}, 50 °C, pH 7.12 buffered with 0.1 M KH_2PO_4/K_2HPO_4.

More recently, Varga et al.[23] determined the values of k_a, k_b, and k_c in alkaline solutions (pH 9.2−12.2) along with the rate constants associated with the alkaline degradation of tetrathionate. However, the overall stoichiometry of the reaction is different in near-neutral solutions, and so the kinetics may change, particularly around pH 7 since the formation of HSO_3^- may affect the rate of the rearrangement.[14] The kinetic data obtained in alkaline solutions then cannot be used directly to neutral solutions without experimental proof. Therefore, one of the objectives of this work is to investigate the kinetics of the rearrangement reaction in near-neutral solutions. While it is possible to use numerical methods to calculate the k values for each of the elementary steps from the concentrations of various species measured, a different approach was adopted in the current study. Overall reactions, such as reaction 5, instead of individual steps were considered in the kinetic treatments. Such treatments lead to the rate constants for overall reactions which meet the needs of estimating and controlling polythionate concentrations during the leaching processes.

The difficulty in the kinetic measurements in near-neutral solutions is that the reaction pathways are not clear. Apart from the rearrangement, other reactions of the polythionates may also occur at the same time. The stability of polythionates has been studied by a number

---

[20] *CRC Handbook of Chemistry and Physics*, 67th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1987.

[21] Foss, O.; Kringlebotn, I. *Acta Chem. Scand.* **1961**, *15*, 1608–1609.

[22] Fava, A.; Bresadola, S. *J. Am. Chem. Soc.* **1955**, *77*, 5792–5794.

[23] Varga, D.; Hovath, A. K. *Inorg. Chem.* **2007**, *46*, 7654–7661.

of researchers.[19,24–26] One type of reaction is the oxidation to sulfate. It was found that all polythionates were quite resistant to oxidation in acidic solutions at room temperature in the presence of a moderately strong oxidant, Fe^{3+},[19,27] though the oxidation could occur at 70 °C.[28] Druschel et al.[28] claimed that the oxidation required both Fe^{3+} and oxygen to generate appreciable sulfate, and the rate was three orders of magnitude slower at 25 °C than at 70 °C. Since the current work was done at normal temperature and in the absence of Fe^{3+}, the oxidation of polythionates was therefore not considered.

It is known that trithionate degrades to thiosulfate and sulfite in strongly alkaline solutions:[13]

$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \quad (11)$$

In neutral to weakly alkaline solutions, however, it is generally accepted that the hydrolysis reaction 10 is the main pathway for the degradation of trithionate.[29] This is consistent with the observation in this work that equal molarities of $S_2O_3^{2-}$ and $S_3O_6^{2-}$ were detected along with a drop in pH, which will be discussed in Section 3.2.

For tetrathionate, the hydrolysis reaction is not well-defined. Although a similar pathway to reaction 10 is possible for tetrathionate and higher polythionates,[24,27] i.e.:

$$S_xO_6^{2-} + H_2O \rightarrow S_{x-1}O_3^{2-} + SO_4^{2-} + 2H^+ \quad (12)$$

it is unlikely since $S_{x-1}O_3^{2-}$ is not stable in aqueous solutions.[11] To explain the degradation of tetrathionate in acid solutions, Meyer and Ospina[24] proposed a mechanism which involved the rearrangement reaction 5 to form $S_3O_6^{2-}$ and $S_5O_6^{2-}$, followed by the hydrolysis of $S_3O_6^{2-}$ via reaction 10. In alkaline solutions, the following reactions are known for the degradation of polythionates,[11,13,30] and higher polythionates tend to degrade more rapidly than tetrathionate:[25]

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \quad (13)$$

$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \quad (14)$$

$$S_6O_6^{2-} \rightarrow S_5O_6^{2-} + S \quad (15)$$

The kinetics of tetrathionate degradation in alkaline solutions has been studied by a number of researchers,[23,31,32] all confirming that the predominant pathway is reaction 13.

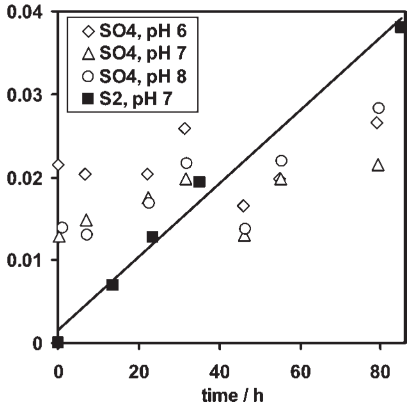

Figure 3. Formation of SO_4^{2-} and $S_2O_3^{2-}$ during the degradation of tetrathionate (5 mM) at a different pH buffered with $H_2PO_4^-/HPO_4^{2-}$ (total 35 mM) in the absence of initial thiosulfate.

The work by Varga et al.[23] shows slight contributions from the following stoichiometry:

$$4S_4O_6^{2-} + 10OH^- \rightarrow 7S_2O_3^{2-} + 2SO_4^{2-} + 5H_2O \quad (16)$$

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (17)$$

but these reactions can be obtained by combining reaction 13 with that of 10 or 11 and so do not represent different pathways parallel to 13. The lowest pH used to study reaction 13 was 9.2.[23] However, it is considered that the reaction is possible in near-neutral solutions but at much slower rates. The kinetics of reaction 14 have been studied by Chritiansen et al.,[33] indicating that the reaction can occur at pH 7.

Therefore, in near-neutral solutions, the degradation of tetrathionate is complex without an obvious predominant pathway. To examine the reaction pathways, experiments were conducted in buffered solutions in the pH range of 6–8, to follow the degradation products. Over 85 h only $S_3O_6^{2-}$, $S_5O_6^{2-}$, $S_2O_3^{2-}$, and SO_4^{2-} were detected as significant products (Figure 3). The formation of $S_3O_6^{2-}$ and $S_5O_6^{2-}$ is believed to be due to the rearrangement reaction 5. The slight increase in SO_4^{2-} from the initial level (as an impurity in tetrathionate) may be attributed to the hydrolysis of $S_3O_6^{2-}$ (reaction 10), as proposed by Meyer and Ospina.[24] However, reaction 10 alone cannot explain the apparently faster increase in $S_2O_3^{2-}$. The extra $S_2O_3^{2-}$ is presumably formed through the degradation of $S_5O_6^{2-}$ via reaction 14, which generates more thiosulfate by stoichiometry. Therefore, the overall pathways for the degradation of tetrathionate may well be described as a rearrangement reaction followed by the degradation of both primary products.

It should be noted that reactions 5 and 14 can be combined to give the overall reaction 13. As will be shown in Section 3.3, the hydrolysis of trithionate may be ignored under certain conditions. In this case, rearrangement reaction 5 and degradation reaction 13 may be used to best describe the reaction of tetrathionate. Obviously, reactions 5 and 13 are

---

(24) Meyer, B.; Ospina, M. *Phosphorus Sulfur Relat. Elem.* **1982**, *14*, 23–26.
(25) Zou, H.; Jia, Z.; Zhang, Y.; Lu, P. *Anal. Chim. Acta* **1993**, *284*, 59–65.
(26) Xu, Y.; Schoonen, M. A. A.; Norstrom, D. K.; Cunningham, K. M.; Ball, J. W. *J. Volcanol. Geotherm. Res.* **2000**, *97*, 407–423.
(27) Schippers, A.; Jozsa, P. G.; Sand, W. *Appl. Environ. Microbiol.* **1996**, *62*, 3424–3431.
(28) Druschel, K. D.; Hamers, R. J.; Banfield, J. F. *Geochim. Cosmochim. Acta* **2003**, *67*, 4457–4469.
(29) Naito, K.; Hayata, H.; Mochizuki, M. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1453–1457.
(30) Burns, D. T.; Townshend, A.; Carter, A. H. *Inorganic Reaction Chemistry, Reactions of the Elements and Their Compounds, Part B: Osmium to Zirconium*; Ellis Harwood Limited: New York, 1981; Vol. 2, p 429.
(31) Rolia, E.; Chakrabarti, C. L. *Environ. Sci. Technol.* **1982**, *16*, 852–857.
(32) Zhang, H.; Dreisinger, D. B. *Hydrometallurgy* **2002**, *66*, 59–65.
(33) Christiansen, J. A.; Drost-Hansen, W.; Nielsen, A. *Acta Chem. Scand.* **1952**, *6*, 333–340.

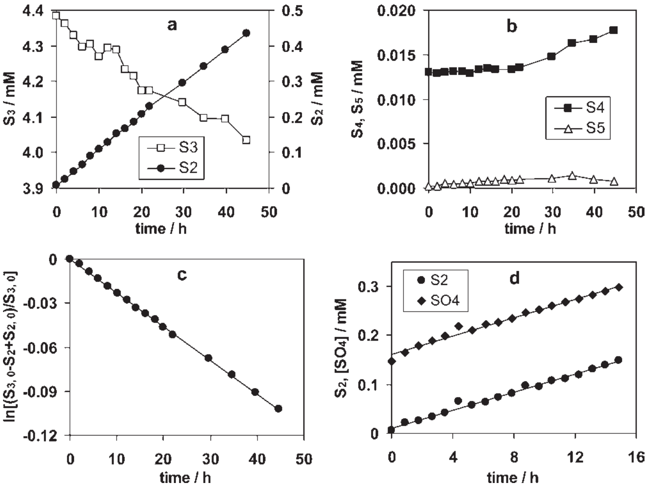

Figure 4. Hydrolysis of trithionate (4.4 mM) at pH 6.5 buffered with $H_2PO_4^-/HPO_4^{2-}$ (total 35 mM).

not parallel, but the former is included in the latter. Details of these reactions are discussed in Section 3.3.

Finally, degradation of polythionates involving the formation of elemental sulfur has been frequently observed.[19,24,27] However, this occurs almost always when the solution is made highly acidic, which involves complex changes in reaction pathways and is beyond the scope of this work. The formation of sulfur in neutral to alkaline solutions is possible through reaction 15 when $S_6O_6^{2-}$ reaches a high concentration, but this is not the case of the current study. In fact, no elemental sulfur was observed in the current study.

Based on these considerations, the current study only deals with the rearrangement and degradation of tri- and tetrathionates in buffered near-neutral solutions.

3.2. Trithionate Hydrolysis. As discussed in Section 3.1, trithionate degrades mainly through hydrolysis (see reaction 10). The kinetics of this reaction have been studied quite extensively.[29,31,34,35] However, the dependence of the kinetics on pH, which is of obvious interest as the reaction generates protons, has not been convincingly established. Much of the early work was conducted at elevated temperatures and either in a limited pH range or without proper pH control. Therefore, this work aims at investigating the kinetics at room temperature as a function of pH over a wider pH range. The possible changes in side reactions are also discussed.

Some typical results of trithionate hydrolysis are shown in Figure 4. It can be seen from Figure 4a that less than 10% of the $S_3O_6^{2-}$ is reacted in 45 h and that S_2 increases approximately linearly as S_3 remains relatively constant (zero order). This conforms to the conclusion that the reaction is first order with respect to both trithionate and water.[29] The precisions for the measurements of S_3 are not as good as for S_2 because the relative changes in S_3 are small compared to the errors of the measurements. A trace amount of $S_4O_6^{2-}$ is present initially as an impurity of the trithionate (Figure 4b). The concentration is little changed for about 20 h before it starts to increase slowly. This change is more pronounced at lower pH but diminishes at pH ≥ 9. It is believed that $S_4O_6^{2-}$ is formed by $S_3O_6^{2-}$ reacting with $S_2O_3^{2-}$ generated from the hydrolysis, the reaction being suppressed at increased pH because the product, $S_4O_6^{2-}$, becomes unstable. Similarly, the presence of $S_5O_6^{2-}$, presumably as a result of the rearrangement of $S_4O_6^{2-}$, is detectable only at the lower pH but not at pH ≥ 9. Nevertheless, these side reactions are negligible within the period of the experiments.

Table 1. Pseudofirst-Order Rate Constant for the Hydrolysis of Trithionate

pH	$S_{3,0}$ (mM)	$10^7\,k_1^{H3}$ (s^{-1}) from $S_2O_3^{2-}$	$10^7\,k_1^{H3}$ (s^{-1}) from SO_4^{2-}
5.5[a]	4.63	6.44 ± 0.19	
6.5[a]	4.36	6.39 ± 0.07	
7.5[a]	4.51	6.53 ± 0.05	
9.0[b]	4.94	6.06 ± 0.11	
10.5[c]	4.94	6.50 ± 0.15	
5.5[d]	8.42	5.81 ± 0.14	
5.5[d]	9.61	5.81 ± 0.13	
5.5[d]	3.42	5.94 ± 0.28	
5.5[a]	4.49	6.39 ± 0.45	6.44 ± 0.45
6.5[a]	4.46	5.83 ± 0.09	6.17 ± 0.56
7.5[a]	4.52	5.97 ± 0.30	6.00 ± 0.39

[a] 35 mM $H_2PO_4^-/HPO_4^{2-}$, run for 45 h. [b] 35 mM $B_4O_7^{2-}$, run for 24 h. [c] 35 mM HCO_3^-/CO_3^{2-}, run for 22 h. [d] 50 mM CH_3COOH/CH_3COO^-, run for 12 h.

The pseudofirst-order rate equation for reaction 10 is

$$-\frac{dS_3}{dt} = k_1^{H3} S_3 \tag{18}$$

where k_1^{H3} is the rate constant with the subscript 1 being for first order and superscript H3 for trithionate hydrolysis. To determine k_1^{H3}, the S_2 data are used instead of S_3 data which are more scattered. Given $S_2 = S_{2,0}$ at $t = 0$ and $S_2 - S_{2,0} = S_{3,0} - S_3$ at t, the integrated rate equation can be obtained as

$$\ln \frac{S_{3,0} - S_2 + S_{2,0}}{S_{3,0}} = -k_1^{H3} t \tag{19}$$

A linear plot of $\ln[(S_{3,0} - S_2 + S_{2,0})/S_{3,0}]$ vs t is shown in Figure 4c, and k_1^{H3} is determined from the slope.

Figure 4d shows the results of a separate experiment under the same conditions, where both concentrations of $S_2O_3^{2-}$ and SO_4^{2-} were measured. Despite the initial difference (as impurities of the trithionate), both concentrations increase at the same rate, confirming the stoichiometry shown in reaction 10. Using an equation similar to eq 19, the rate constant, k_1^{H3}, can also be determined from the measurements of SO_4^{2-} concentrations.

The values of the pseudofirst-order rate constant so obtained at various initial S_3 and pH values are presented in Table 1. As can be seen, k_1^{H3} is essentially independent of pH in a wide range 5.5−10.5 in spite of different buffers used. An average of the rate constant is obtained to be $(6.2 \pm 0.2) \times 10^{-7}$ s^{-1}, which corresponds to a half-life time ($t_{1/2}$) of 13 days at room temperature. This result compares well with those obtained by Naito et al.[29] (6.12×10^{-7} s^{-1}) and Hofman-Bang[34] (7.66×10^{-7} s^{-1}) from sodium acetate solutions after a suitable conversion from a biomolecular rate constant to a pseudofirst-order rate constant as well as a temperature correction to 25 °C using the reported activation energy. The slightly higher value of Hofman-Bang may be

---

(34) Hofman-Bang, N. *Acta Chem. Scand.* **1950**, *4*, 1005–1013.

(35) Kurtenacker, A.; Mutschin, A.; Stastny, F. Z. *Anorg. Allgem. Chem.* **1935**, *224*, 399–419.

attributed to the high ionic strength used (0.1 M potassium trithionate and 0.5 M sodium acetate). Similarly, a slightly smaller number (4.3×10^{-7} s^{-1}) calculated from the work by Rolia and Chakrabarti[31] may be explained by the low ionic strength used (mMs of trithionate only).

Naito et al.[29] reported that the degradation of trithionate was accelerated in the presence of thiosulfate in a sodium acetate solution, which was attributed to the $S_2O_3^{2-}-S_3O_6^{2-}$ reaction to form tetrathionate (the forward reaction of 2 for trithionate). According to Naito et al.,[29] the second-order rate constant for the hydrolysis, k_w, and that for the $S_2O_3^{2-}-S_3O_6^{2-}$ reaction, k_t, both increase as the temperature changes from 40 to 80 °C, but the latter increases less rapidly. From the data provided, it is estimated that the ratio $k_w \times [H_2O]/k_t$ is 7.5 at 80 °C, suggesting that the rates of the two reactions are comparable when the concentration ratio S_3/S_2 is about 7.5. At 25 °C, the ratio changes to 40 indicating the $S_2O_3^{2-}-S_3O_6^{2-}$ reaction is more competitive at lower temperatures. In the current work the effect of this side reaction can be seen from Figure 4 but not as significant as expected from the above calculation, indicating the kinetic measurements for the hydrolysis reaction are not interfered by the side reaction in the given time scale. In terms of the overall degradation of trithionate, however, the $S_2O_3^{2-}-S_3O_6^{2-}$ reaction may become predominant when high concentrations of thiosulfate are present, like in the case of thiosulfate leaching.

The effect of thiosulfate on the overall rate of trithionate degradation has also been studied by Rolia and Chakrabarti[31] at 70−85 °C. The authors confirmed the observation by Naito et al.[29] at pH 5.5−8, but at pH 11, the rate becomes independent of thiosulfate. This agrees with the current observation that the $S_2O_3^{2-}-S_3O_6^{2-}$ reaction is suppressed at pH $\geq$ 9. A more likely side reaction at high pH is the alkaline degradation of trithionate as shown in reaction 11,[23] as indicated by the slightly higher concentration of SO_4^{2-} than that of $S_2O_3^{2-}$ as the reaction products. The extra SO_4^{2-} is presumably from the oxidation of SO_3^{2-} generated from reaction 11. Accordingly, the activation energy of 91.7 kJ mol^{-1} obtained at the high pH is also slightly different from the value of 87.0 kJ mol^{-1} measured at lower pH by Naito et al.[29]

It is therefore reasonable to conclude from the above discussion that the hydrolysis remains the predominant pathway for the degradation of trithionate over a wide range of conditions (pH 5.5−11 and temperature 25−85 °C) until a high level of thiosulfate relative to trithionate is reached. The side reactions are not to significantly change the stoichiometry shown in reaction 10. This is consistent with the measurements by Kurtenacker et al.[35] that the rate of overall trithionate degradation is largely constant over pH 2.2 −12 at 50 °C.

3.3. Tetrathionate Degradation without Initial Thiosulfate. It was expected that the rearrangement of tetrathionate (reaction 5) would be slow in the absence of initial thiosulfate and that the degradation (reaction 13) would also be slow in neutral solutions. The objective of this section was to obtain an estimation of the relative rates of both reactions. Figure 5 shows typical concentration profiles of $S_2O_3^{2-}$, $S_3O_6^{2-}$, and $S_5O_6^{2-}$ measured as the major products during tetrathionate degradation. As can be seen, the reactions are indeed very slow with less than 1% of the initial $S_4O_6^{2-}$ reacted in 60 h (Figure 5a). As a result, approximately linear increases in S_2, S_3, and S_5 are observed at pH $\leq$ 9 (Figure 5b−d). The slopes of the straight lines obtained under different conditions are presented in Table 2. No $S_5O_6^{2-}$ was detected at pH > 9 due to its rapid degradation. Accordingly the increases in $S_2O_3^{2-}$ and $S_3O_6^{2-}$ are no longer linear but, instead, show first-order behavior. This is discussed later.

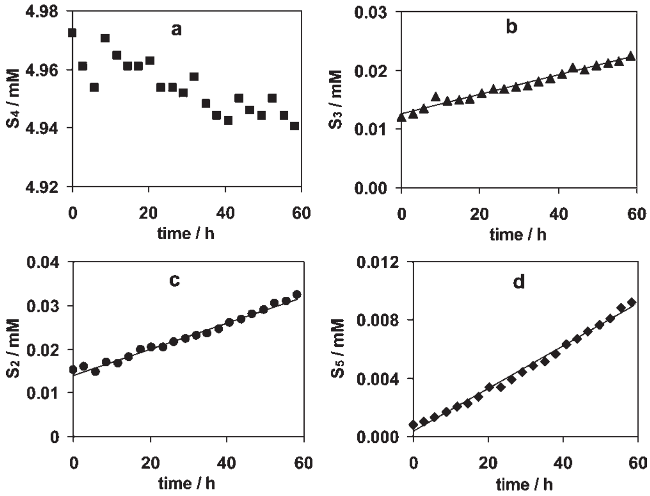

Figure 5. Concentration profiles for the degradation of tetrathionate (5 mM) in the absence of initial thiosulfate at pH 7.0 buffered with $H_2PO_4^-/HPO_4^{2-}$ (total 35 mM).

Table 2. Formation Rates of Various Products during Tetrathionate Degradation in the Absence of Initial Thiosulfate under Different Conditions

pH	$S_{4,0}$	10^8 dS_3/dt (mM s^{-1})	10^8 dS_2/dt (mM s^{-1})	10^8 dS_5/dt (mM s^{-1})	10^8 dS_5'/dt (mM s^{-1})
4[a]	4.93	0.90	0.73	1.4	1.6
6[a]	3.48	0.68	1.1	1.4	1.8
6[b]	5.02	1.8	5.1	2.6	4.6
6[a]	6.96	3.7	2.2	3.1	4.0
6[b]	9.86	7.4	8.9	8.2	12
6[b]	14.5	18	12	19	24
6[a]	17.7	26	6.3	29	31
7[a]	3.54	2.7	5.7	2.6	4.9
7[a]	4.97	4.5	8.2	4.0	7.3
7[b]	7.26	10	16	7.6	14
7[b]	9.71	15	21	13	21
7[b]	14.9	35	31	29	41
7[a]	17.9	48	32	46	59
8[b]	3.79	22	50	6.8	27
8[a]	4.96	33	65	13	39
8[a]	17.9	219	225	131	221
9[c]	5.04	275	638	27	283

[a] 35 mM $H_2PO_4^-/HPO_4^{2-}$, run for 60 h. [b] 35 mM $H_2PO_4^-/HPO_4^{2-}$, run for 46 h. [c] 35 mM $B_4O_7^{2-}$, run for 24 h.

Based on the discussions in Section 3.1, tetrathionate degrades through rearrangement to tri- and pentathionate followed by their degradations. It can be seen from Table 2 that S_3 and S_5 increase at about the same rate at pH 6−7 indicating that, following the rearrangement, the degradations of $S_3O_6^{2-}$ and $S_5O_6^{2-}$ occur at comparable rates. However, at pH $\leq$ 6, it seems that dS_3/dt is somewhat smaller than dS_5/dt, but the trend is reversed at pH $\geq$ 7. With increasing pH the degradation of $S_5O_6^{2-}$ is accelerated, as indicated by the increasing differences between dS_3/dt and dS_5/dt. This is in contrast to the hydrolysis of $S_3O_6^{2-}$ which is unaffected by pH in the investigated range. If the hydrolysis of $S_3O_6^{2-}$ is ignored, then all the thiosulfate is attributed to the degradation of $S_5O_6^{2-}$, and from the stoichiometry of reaction 14, $S_5' = S_5 + (2/5)S_2$, where S_5' is the total concentration of $S_5O_6^{2-}$ generated from tetrathionate rearrangement (reaction 5). Table 2 shows that dS_5'/dt matches well with dS_3/dt at the higher pH values 8–9, suggesting that the degradation of $S_5O_6^{2-}$ is dominant compared to $S_3O_6^{2-}$ hydrolysis at the higher pH.

Table 2 also shows the complications of thiosulfate which catalyzes the rearrangement reaction. As can be seen, dS_3/dt (or dS_5'/dt) increases at higher $S_{4,0}$ (due to increasing initial S_2 as an impurity) and higher pH (due to increasing dS_2/dt as a result of $S_5O_6^{2-}$ degradation). However, this does not change the general linear relationships, as shown in Figure 5, because of the generally low levels of S_2.

To simplify the kinetic treatment, the hydrolysis of $S_3O_6^{2-}$ is ignored, and so the degradation is described with reactions 5 and 13 in Section 3.1. As has been pointed out, reaction 5 is the first step in the overall reaction 13. Under conditions where the rearrangement is faster than the subsequent degradation, $S_5O_6^{2-}$ is accumulated, and the two reactions may be treated separately. Conversely, when the degradation of $S_5O_6^{2-}$ is faster (e.g., high pH), only one overall reaction, that is reaction 13, is evident stoichiometrically.

According to eq 9, rearrangement reaction 5 is possibly first order with respect to S_4. Since $S_3O_6^{2-}$ hydrolysis is ignored, the reaction rate can be expressed by the appearance of $S_3O_6^{2-}$. Similarly, the rate of tetrathionate degradation (reaction 13) can be expressed by the appearance of $S_2O_3^{2-}$ assuming pseudofirst-order kinetics at constant pH. Therefore:

$$-\frac{dS_4}{dt} = 2\frac{dS_3}{dt} = k_1^{R4}S_4 \approx k_1^{R4}S_{4,0} \qquad (20)$$

$$r_D = \frac{4}{5}\frac{dS_2}{dt} = k_1^{D4}S_4 \approx k_1^{D4}S_{4,0} \qquad (21)$$

where k_1^{R4} and k_1^{D4} denote first-order rate constants for the rearrangement and degradation of tetrathionate respectively, whereas r_D is the rate of degradation (reaction 13). As dS_x/dt is approximately constant at pH ≤ 9, k_1^{R4} and k_1^{D4} can be estimated as

$$k_1^{R4} \approx 2(dS_3/dt)/S_{4,0} \qquad (22)$$

$$k_1^{D4} \approx (4/5)(dS_2/dt)/S_{4,0} \qquad (23)$$

At pH > 9, all $S_5O_6^{2-}$ formed is rapidly degraded, and first-order changes in S_2–S_4 were observed (Figure 6). It is evident from Figure 6 that the formation of $S_2O_3^{2-}$ and $S_3O_6^{2-}$ conforms strictly to the stoichiometry of reaction 13 with the total sulfur balanced very well to the reacted $S_4O_6^{2-}$. Under these circumstances, therefore, $-dS_4/dt = r_D$, and $k_1^{R4} = k_1^{D4} = k_1$, i.e.:

$$-\frac{dS_4}{dt} = k_1S_4 \qquad (24)$$

Integrate this equation and given $S_4 = S_{4,0} - 2(S_3 - S_{3,0}) = S_{4,0} - 4/5(S_2 - S_{2,0})$ at any time t, then k_1 can be determined from the data of S_2 or S_3. The first-order rate constants so obtained along with those determined from eqs 22 and 23 for pH ≤ 9 are presented in Table 3.

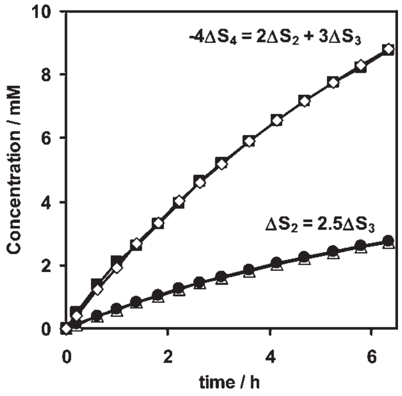

Figure 6. First-order behavior of the degradation of tetrathionate (5 mM) at pH 10.5 buffered with HCO_3^-/CO_3^{2-} (total 50 mM).

Table 3. First-Order Rate Constants for Tetrathionate Rearrangement and Degradation in the Absence of Initial Thiosulfate under Various Conditions

pH	$S_{4,0}$	S_2 (av) (mM)	$10^8\ k_1^{R4}$ (s^{-1})	$10^8\ k_1^{R4}$ (s^{-1})	$10^4\ k_1^{R4}/S_2$ ($M^{-1}\ s^{-1}$)
4	4.93	0.0036	0.37	0.12	10
6	3.48	0.0082	0.39	0.25	4.8
6	5.02	0.013	0.72	0.81	5.6
6	6.96	0.014	1.1	0.25	7.4
6	9.86	0.026	1.5	0.72	5.8
6	14.5	0.044	2.6	0.68	5.8
6	17.7	0.042	2.9	0.28	7.1
7	3.54	0.017	1.5	1.3	9.1
7	4.97	0.023	1.9	1.3	8.2
7	7.26	0.028	2.8	1.8	10
7	9.71	0.035	3.1	1.8	8.9
7	14.5	0.053	4.8	1.7	9.0
7	17.9	0.078	5.4	1.4	7.0
8	3.79	0.051	12	11	23
8	4.96	0.083	14	11	16
8	17.9	0.28	25	10	8.9
9	5.04	0.26	114	101	44
10	4.97	0.63	978	997	155
10.5	4.91	1.5	2622	2658	180

From Table 3 it seems that the rearrangement rate constant, k_1^{R4}, increases with both initial $S_{4,0}$ and pH. However, this may be attributed solely to the increase in thiosulfate. With increasing $S_{4,0}$, the initial thiosulfate concentration increases as an impurity; while with increasing pH, thiosulfate is generated more rapidly as a result of accelerated degradation of $S_5O_6^{2-}$. Figure 7 shows the dependence of k_1^{R4} on the average thiosulfate concentration over each experiment. It is demonstrated that k_1^{R4} increases linearly with the average S_2 regardless of pH, up to pH 7. The same can be seen from the rate constants normalized to unity thiosulfate concentration (k_1^{R4}/S_2, Table 3), which are reasonably constant up to pH 7. At higher pH, the S_2 changes too rapidly (initial and final values differ by at least more than an order of magnitude), and so the average value cannot be used as an estimation of thiosulfate concentration.

Figure 7 also shows that the straight line can be extrapolated to pass very close to the origin, indicating that the rearrangement reaction may not proceed in the absence of thiosulfate. This result suggests that the thiosulfate catalyzed S_N2 reactions 6 and 7 may be the only mechanism

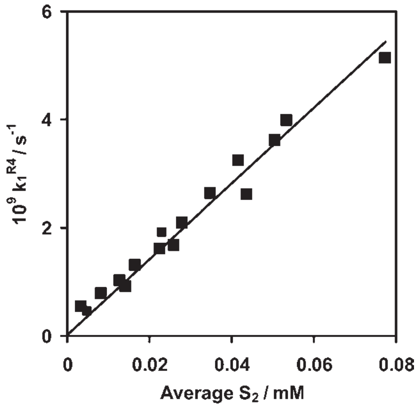

Figure 7. Dependence of the first-order rate constant of tetrathionate rearrangement on the average thiosulfate concentration.

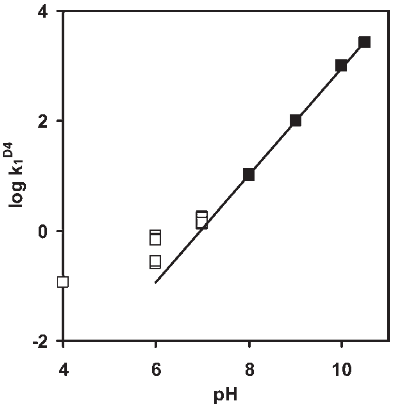

Figure 8. First-order dependence of tetrathionate hydrolysis on hydroxide ion.

for tetrathionate rearrangement. Nevertheless, thiosulfate is almost always present in the solutions containing polythionates, either as an impurity or as being generated from other reactions. Therefore the rearrangement reaction can be initiated, and then it may become autocatalytic as more thiosulfate is generated.

For reaction 13, it is evident from Table 3 that k_1^{D4} is independent of $S_{4,0}$, particularly at higher pH, confirming the hydrolysis is first order with respect to tetrathionate. The dependence of k_1^{D4} on pH is shown in Figure 8. At pH > 7 a linear relationship between $\log k_1^{D4}$ and pH is obtained with a slope of 0.97, suggesting that the degradation reaction is also first order with respect to the OH^- ion. Similar results have been reported in previous studies in strongly alkaline solutions.[23,31,32] At pH < 7, however, k_1^{D4} becomes less dependent on the pH indicating a change in the reaction mechanism. As k_1^{D4} is estimated from the formation of thiosulfate, this result suggests that, at the lower pH values, the formation of thiosulfate is increasingly dominated by trithionate hydrolysis (reaction 10), which is pH independent. Such a result seems to support the mechanism proposed by Meyer and Ospina[24] for the degradation of tetrathionate in acidic solutions, which involves the rearrangement followed by trithionate hydrolysis.

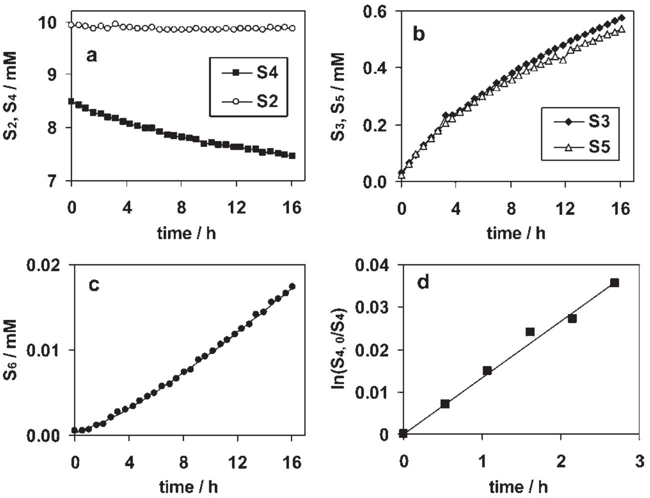

Figure 9. Rearrangement of tetrathionate (8.5 mM) in the presence of 10 mM initial thiosulfate at pH 6.0 buffered with $H_2PO_4^-/HPO_4^{2-}$ (total 20 mM).

Rolia and Chakrabarti[31] observed that reaction 13 is catalyzed by initial thiosulfate in alkaline solutions. This may be explained by the fact that, in alkaline solutions, the rate of reaction 13 is limited by the first step in the mechanism, namely the tetrathionate rearrangement, which is catalyzed by thiosulfate. At near-neutral pH (≤ 8), the data in Table 3 clearly demonstrate that k_1^{D4} is not affected by S_2 if the pH is fixed. This is because the degradation of $S_5O_6^{2-}$ following the rearrangement is rate limiting at near-neutral pH, which is not catalyzed by thiosulfate.

3.4. Tetrathionate Rearrangement in the Presence of Thiosulfate.

As has been shown, k_1^{R4} and k_1^{D4} have the same order of magnitude at near-neutral pH in the absence of initial thiosulfate. The former increases with S_2 but the latter does not. It is therefore expected that, when S_2 is sufficiently high, the catalyzed rearrangement will be dominant, and the hydrolysis reactions of tri- and tetrathionates may be ignored provided the pH is not too high, e.g., pH < 9. This is indeed the case from Figure 9. The concentration of $S_4O_6^{2-}$ decreases much more rapidly in the presence of 10 mM initial thiosulfate than without, with $S_3O_6^{2-}$ and $S_5O_6^{2-}$ as the main products. The thiosulfate concentration remains constant due to the fact that the thiosulfate generated from subsequent degradation reactions is very small compared to the initial concentration (Figure 9a and b). On the other hand, however, the further rearrangement of pentathionate becomes significant as $S_6O_6^{2-}$ is detected at reasonable concentrations (Figure 9c). For simplification, the reaction between $S_3O_6^{2-}$ and $S_2O_3^{2-}$, according to raction 2, is not considered, but this should not affect the determination of the rate constants using the method described below. The following reactions are considered as the main pathways in the kinetic measurements, reactions 5 and 25:

$$2S_5O_6^{2-} \rightarrow S_4O_6^{2-} + S_6O_6^{2-} \qquad (25)$$

Reaction 25 has a similar mechanism to reaction 5, and so it is reasonable to assume first-order kinetics with respect to S_5. Therefore the following rate equations can be written:

$$-\frac{\mathrm{d}S_4}{\mathrm{d}t} = k_1^{\mathrm{R4}} S_4 - \frac{1}{2} k_1^{\mathrm{R5}} S_5 \tag{26}$$

$$\frac{\mathrm{d}S_5}{\mathrm{d}t} = \frac{1}{2} k_1^{\mathrm{R4}} S_4 - k_1^{\mathrm{R5}} S_5 \tag{27}$$

$$\frac{\mathrm{d}S_6}{\mathrm{d}t} = \frac{1}{2} k_1^{\mathrm{R5}} S_5 \tag{28}$$

where the superscript R5 denotes rearrangement of $S_5O_6^{2-}$. A simplified approach is used to determine the rate constants k_1^{R4} and k_1^{R5}. First, at the initial stage of reaction where S_5 is very small, eq 26 approximates to

$$-\left(\frac{\mathrm{d}S_4}{\mathrm{d}t}\right)_{t \to 0} = k_1^{\mathrm{R4}} S_4 \tag{29}$$

This is evident from Figure 9b that the measured S_3 and S_5 are the same at this stage. Therefore k_1^{R4} can be determined by plotting ln($S_4/S_{4,0}$) vs t, using the $S_4 - t$ data of the first 3 h (Figure 9d). Second, k_1^{R5} can be calculated from eq 28:

$$k_1^{\mathrm{R5}} = 2(\mathrm{d}S_6/\mathrm{d}t)/S_5 \tag{30}$$

where dS_6/dt is calculated for any time t from a polynomial fit of the $S_6 - t$ data (Figure 9c). The values of k_1^{R5} so obtained at different times are approximately constant, except for the first few points where $S_5 \to 0$, and S_6 is so small that accurate measurements are often difficult (Figure 10). The slight decline in the later stage is probably due to the degradation of $S_6O_6^{2-}$ according to reaction 15, though the formation of elemental sulfur is not apparent. Such a reaction reduces the rate of the increase in S_6. In addition, Figure 10 shows that the results of k_1^{R5} are irrespective of the orders of the polynomial fit between 2 and 4.

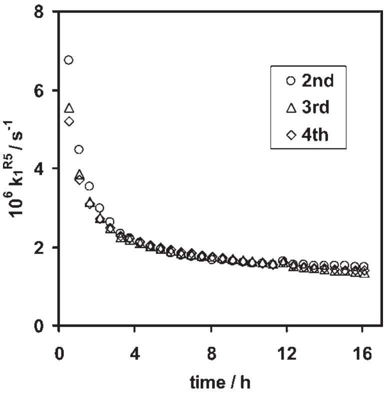

Figure 10. Calculated rate constant for pentathionate rearrangement at different times using different orders of polynomial fit to $S_6 - t$ data (from the same data as shown in Figure 9).

The values of k_1^{R4} and k_1^{R5} (average excluding the first few points) obtained at various conditions are presented in Table 4. As can be seen, k_1^{R4} and k_1^{R5} are quite similar under all conditions investigated. Such results are not unexpected because the mechanisms for both rearrangement reactions are the same. In fact, in the study of the kinetics of reaction 3, Foss and Kringlebotn[21] assumed the same rate constant for the reaction between thiosulfate and all polythionates (except $S_3O_6^{2-}$). At constant pH and thiosulfate concentration, Table 4 shows that k_1^{R4} is largely independent of the initial tetrathionate concentration, confirming first-order kinetics with respect to tetrathionate. The same reaction order is also expected for the pentathionate rearrangement.

It is evident from Table 4 that both k_1^{R4} and k_1^{R5} are largely independent of pH in the range 6−8. According to Moses et al.,[14] pH 7 is the turning point for S-chain lengthening or shortening (reaction 2), as the more nucleophilic intermediate SO_3^{2-} is converted to the less nucleophilic HSO_3^-. However, this change does not seem to affect the kinetics of the overall rearrangement reactions.

Table 4 also shows the rate constants normalized to unity thiosulfate concentration. As demonstrated, the normalized rate constants k_1^{R4}/S_2 and k_1^{R5}/S_2 are approximately constant irrespective of S_2, suggesting first-order kinetics with respect to thiosulfate. As can be seen, the data of k_1^{R4}/S_2 in Table 4 agree quite well with those shown in Table 3 for the same pH range despite the different methods used. Therefore, the rearrangement reactions 5 and 25 are of the second order with the complete rate equations as:

$$-(\mathrm{d}S_4/\mathrm{d}t) = k_2{}^{\mathrm{R4}} S_2 S_4 \tag{31}$$

$$-(\mathrm{d}S_5/\mathrm{d}t) = k_2{}^{\mathrm{R5}} S_2 S_5 \tag{32}$$

where $k_2^{\mathrm{R4}} = k_1^{\mathrm{R4}}/S_2$, and $k_2^{\mathrm{R5}} = k_1^{\mathrm{R5}}/S_2$ when S_2 is constant. Average values of k_2^{R4} and k_2^{R5} are obtained from Table 4

Table 4. Rate Constants for Thiosulfate Catalysed Rearrangement of Tetra- And Pentathionates under Various Conditions

pH[a]	S_2 (mM)	$S_{4,0}$ (mM)	$10^6\ k_1^{\mathrm{R4}}$ (s^{-1})	$10^6\ k_1^{\mathrm{R5}}$ (s^{-1})	$10^4\ k_1^{\mathrm{R4}}/S_2$($M^{-1}s^{-1}$)	$10^4\ k_1^{\mathrm{R5}}/S_2$($M^{-1}s^{-1}$)
6.0	2.04	5.07	0.811	0.511	3.98	2.50
6.0	5.03	5.14	2.06	1.08	4.10	2.15
6.0	9.95	2.03	4.64	2.10	4.66	2.11
6.0	9.97	3.46	3.44	1.98	3.46	1.99
6.0	10.1	5.02	4.28	1.94	4.22	1.92
6.0	10.1	7.22	4.83	1.76	4.80	1.74
6.0	9.87	8.48	3.69	1.85	3.74	1.87
6.0	9.99	9.91	3.69	1.84	3.70	1.84
6.0	14.9	4.91	6.11	2.28	4.09	1.53
6.0	15.0	5.04	7.17	2.22	4.79	1.48
6.0	19.9	5.05	8.94	2.66	4.50	1.34
7.0	10.1	4.98	4.17	2.04	4.13	2.02
8.0	10.1	4.95	4.97	2.09	4.92	2.07

[a] Buffered with 20 mM total $H_2PO_4^-/HPO_4^{2-}$, and all experiments run for 14−18 h.

to be (4.24 ± 0.26) × 10^{-4} M^{-1} s^{-1} and (1.89 ± 0.18) × 10^{-4} M^{-1} s^{-1}, respectively, for pH 6−8. To compare with the results from the literature, it is established from eqs 9 and 29 that $k_2^{R4} = 2k_a$. Based on this, the k_2^{R4} value is found to agree well with the k_a value obtained by Foss and Kringlebotn[21] (1.3×10^{-3} M^{-1} s^{-1}) at 25 °C in neutral solution and by Varga et al.[23] (1.94×10^{-3} M^{-1} s^{-1}) at 25 °C and pH 9.2−12.2. It therefore appears that the kinetics for tetrathionate rearrangement in near-neutral solutions may be the same as in alkaline solutions, despite possible formation of HSO_3^-.

4. Conclusions

The predominant reaction in the initial stage of the degradation of trithionate in the pH range 5.5−10.5 is the hydrolysis reaction 10. In this range the pseudofirst-order rate constant is determined to be (6.2 ± 0.2) × 10^{-7} s^{-1}, which is independent of pH.

The rearrangement of tetrathionate (and pentathionate) displays second-order kinetics with respect to the polythionate and thiosulfate. The data suggest that the reaction is only initiated by thiosulfate through a bimolecular S_N2 displacement reaction and may not proceed without thiosulfate. The second-order rate constants for the rearrangement of tetra-and pentathionates in the pH range 6−8 are (4.24 ± 0.26) × 10^{-4} and (1.89 ± 0.18) × 10^{-4} M^{-1} s^{-1}, respectively, and are independent of pH.

The reaction of tetrathionate in the initial stage takes place through the rearrangement to trithionate and pentathionate followed by their subsequent degradations, including hydrolysis of trithionate and further rearrangement and degradation of pentathionate. In the presence of thiosulfate and at near-neutral pH, the rearrangement of pentathionate dominates over the degradation reaction. At extremely low thiosulfate concentrations, the main secondary reaction is the hydrolysis of trithionate at pH < 7, but at pH > 7, it is the degradation of pentathionate. In alkaline solutions, the rearrangement and the degradation of pentathionate are combined, and hence it approximates a single reaction. This mechanism explains the observed dominant reaction products in both neutral and alkaline solutions.

The degradation reaction of tetrathionate, 13, is independent of thiosulfate in the neutral pH range. It has been previously suggested that reaction 13 is catalyzed by initial thiosulfate in alkaline solutions. However this is explained by the fact that, in alkaline solutions, the rate of reaction 13 is limited by the first step in the mechanism, namely the tetrathionate rearrangement, which is catalyzed by thiosulfate.

Acknowledgment. The support of the Parker CRC for Integrated Hydrometallurgy Solutions (established and supported under the Australian Government's Cooperative Research Centres Program) is gratefully acknowledged.