70 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(1), 70—75 (1976) [Vol. 49, No. 1

The Chemical Behavior of Low Valence Sulfur Compounds. X.[1] Disproportionation of Thiosulfate, Trithionate, Tetrathionate and Sulfite under Acidic Conditions

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(Received February 25, 1975)

The disproportionation of thiosulfate, trithionate, tetrathionate and sulfite in acidic solutions has been studied at relatively high temperatures. Thiosulfate hardly decomposes in the absence of sulfuric acid, even at 150 °C, but decomposes very easily in the presence of sulfuric acid at 70 °C, forming elemental sulfur, tetrathionate and sulfite. Trithionate decomposes to thiosulfate and sulfate at 70 °C, while tetrathionate decomposes only at temperatures above 130 °C after an induction period forming thiosulfate as an intermediate. Sulfite undergoes disproportionation, giving thiosulfate and sulfate at 150 °C, and then elemental sulfur and sulfate accompanied by intermediate formation of tetrathionate. A disproportionation pathway of low valence sulfur oxyacids including thiosulfate, trithionate, tetrathionate and sulfite has been proposed.

Investigations of disproportionation of low valence sulfur compounds such as thiosulfate,[2–4] polythionates[4–8] and sulfite[9–11] have been carried out by a number of workers. It has been shown that some kinds of polythionates play important roles as intermediates in these reactions, but no systematic study seems to have been made, partly because of the lack of a simple and accurate method of analysis. A photometric method for thiosulfate and polythionates[1] described in the previous paper, has been found to be useful.

The disproportionation of thiosulfate, trithionate, tetrathionate and sulfite has been investigated in acidic solutions at relatively high temperatures to obtain the basic data concerning the treatment of waste waters containing low valence sulfur compounds. Sulfuric acid was used as an acidic medium, as this acid is used most widely in industrial fields.

Experimental

Materials. All chemicals except polythionates were of analytical reagent grade. Potassium trithionate and potassium tetrathionate were prepared by Stamm's method[12] and Martin's method,[13] respectively. The concentrations of the stock solution of trithionate and tetrathionate were determined by Procedures C and B, respectively.[1]

Procedure. The reactions were carried out in 25 ml sealed glass tubes. Each tube was sealed soon after the transfer of 15 ml of sample solution together with 0.5 ml of sulfuric acid of different concentration, and placed in a glycerol bath regulated at the desired temperature. The sealed tubes were removed from the bath after a definite period of time, and quickly cooled to room temperature, when necessary, in an ice bath.

Analysis. The seals of the glass tubes were removed and a clear supernatant solution was withdrawn. The sample solution was diluted to a suitable concentration and analyzed for thiosulfate, trithionate, tetrathionate, sulfite and sulfate as follows:

Thiosulfate, Trithionate and Tetrathionate: Since the higher polythionates above tetrathionate were proved by paper chromatography to be absent in the reaction mixtures,[14] the photometric method[1] was used for the determination of the concentrations of thiosulfate, trithionate and tetrathionate. The calibration curves were prepared with a standard thiosulfate solution. The standard addition method was employed to eliminate interferences caused by various chemical compositions of the samples.

Sulfite: The total amount of thiosulfate and sulfite was determined by iodometry. The amount of sulfite was determined by substracting the amount of thiosulfate obtained by photometry from the total amount of thiosulfate and sulfite.

Sulfate: The total amount of sulfite and sulfate was determined gravimetrically as barium sulfate, after oxidizing thiosulfate and sulfite with iodine to tetrathionate and sulfate, respectively. The amount of sulfate formed in the disproportionation was determined by substracting the amount of sulfite and that of sulfuric acid added.

Elemental Sulfur: The elemental sulfur deposited in the glass tubes was dissolved in carbon disulfide. After being washed with water, the carbon disulfide layer was poured into a 200 ml beaker, and then warmed to about 35 °C to evaporate carbon disulfide. The residual elemental sulfur was determined gravimetrically as barium sulfate after oxidation to sulfate with a mixture of potassium chlorate and nitric acid.

Results and Discussion

Disproportionation of Thiosulfate Solution. The effect of reaction time on the decomposition degree of thio-

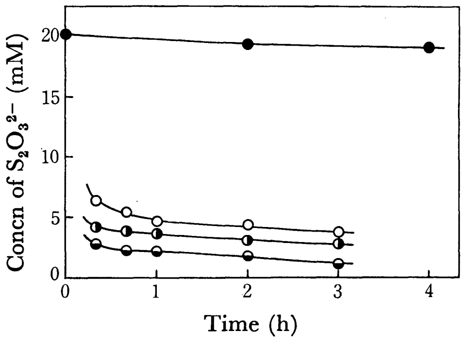

Fig. 1. Effect of reaction time on the decomposition degree of thiosulfate solution.
Initial concn of H_2SO_4: 20 mM, temp (°C): ○70, ◑110, ◒150. Without H_2SO_4, temp. (°C): ●150.

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TABLE 1. EFFECT OF REACTION TEMPERATURE ON THE DISPROPORTIONATION OF ACIDIC THIOSULFATE SOLUTION

Temp (°C)	Composition of the reaction mixtures (mg atom-S/1)								pH
	$S_2O_3^{2-}$	S	$S_3O_6^{2-}$	$S_4O_6^{2-}$	HSO_3^-	SO_4^{2-}	Total-S	S_{calcd}[a]	
70	8.9	13.5	1.0	4.8	11.3	1.2[b]	40.7	13.6	2.25
90	7.3	12.2	0.5	11.0	8.5	1.1[b]	40.6	12.3	2.00
110	5.9	11.5	0.5	13.6	6.9	1.4[b]	39.8	11.7	1.95
130	4.7	10.6	0	17.0	5.2	2.0[b]	39.4	11.4	2.17
150	3.6	14.6	0	11.0	4.6	6.1[b]	39.6	13.5	1.98

Initial concn of $Na_2S_2O_3$: 39.7 mg atom-S/1, initial concn of H_2SO_4: 20 mM, time: 2 h. a) Calculated values obtained by assuming that the first stage of thiosulfate decomposition is represented by the reactions shown by Eqs. (1) and (2), and also that the formation of sulfate is attributed to air oxidation of sulfite formed according to the reaction shown by Eq. (2). b) The amount of sulfuric acid added was substracted.

sulfate is shown in Fig. 1. We see that thiosulfate hardly decomposes in the absence of sulfuric acid even at 150 °C, while it decomposes very easily in the presence of sulfuric acid at 70 °C.

The effect of reaction temperature was determined in the range 70—150 °C. The material balance of sulfur atoms can be explained well, taking into consideration elemental sulfur, trithionate, tetrathionate, sulfite and sulfate as reaction products (Table 1). Trithionate can be regarded to be of minor importance as a decomposition product. Thiosulfate decomposes in acidic solution, forming elemental sulfur as a lower oxidation state species, and tetrathionate, sulfite and sulfate as higher oxidation state species. The reactions can be represented by the following equations:

$$5S_2O_3^{2-} + 6H^+ = 2S + 2S_4O_6^{2-} + 3H_2O \qquad (1)$$

$$S_2O_3^{2-} + H^+ = S + HSO_3^- \qquad (2)$$

$$3S_2O_3^{2-} + 2H^+ = 4S + 2SO_4^{2-} + H_2O \qquad (3)$$

When considered thermodynamically,[11,15] hydrogen sulfide besides elemental sulfur is considered to be formed as a lower oxidation state species. However, all the reaction mixtures in the present investigation gave no characteristic odor of hydrogen sulfide.

The amount of tetrathionate formed increases with an increase of reaction temperature in the range 70—130 °C, while that of sulfite decreases with an increase of reaction temperature (Table 1). On the other hand, the amount of sulfate formed is independent of reaction temperature and is as low as about 1 mg atom-S/1. The values of S_{calcd} (Table 1) were calculated by

$$S_{calcd}(\text{mg atom-S/1}) = 0.25(S_4O_6^{2-})\ (\text{mg atom-S/1}) + (HSO_3^-)\ (\text{mg atom-S/1}) + (SO_4^{2-})\ (\text{mg atom-S/1}).$$

The amount of elemental sulfur formed is in good agreement with the calculated values of S_{calcd} in the temperature range 70—130 °C. Therefore, it can be said that tetrathionate and sulfite are formed according to the reactions shown by Eqs. (1) and (2), respectively, and that the formation of sulfate is not attributed to disproportionation of tetrathionate or sulfite but rather to air oxidation of sulfite formed as shown by Eq. (2). On the other hand, it is noted that at the reaction temperature of 150 °C, yields of elemental sulfur and sulfate are higher than those at 130 °C, while the yield of tetrathionate is correspondingly lower. It seems that the reaction shown by Eq. (3) proceeds favorably at 150 °C. The successive occurrence of reactions shown by Eqs. (1) and (8) or Eqs. (2) and (11), however, lead to the overall reaction of Eq. (3), which therefore need not necessarily be considered as a separate reaction.

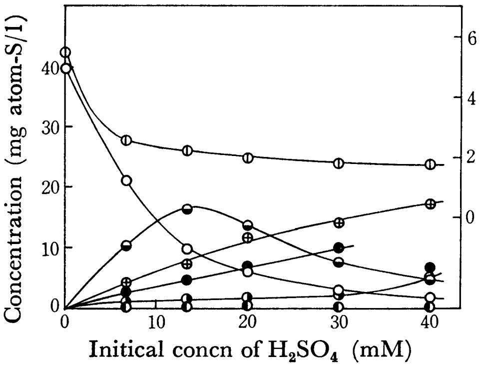


Fig. 2. Effect of sulfuric acid concentration on the disproportionation of thiosulfate solution.
Initial concn of $S_2O_3^{2-}$: 19.9 mM, temp: 110 °C, time: 2 hr.
⊕: S, ○: $S_2O_3^{2-}$, ◐: $S_3O_6^{2-}$, ◒: $S_4O_6^{2-}$, ●: HSO_3^-, ◑: SO_4^{2-},[a] ⦶: pH.
a) The amount of sulfuric acid added was substracted.

The decomposition of thiosulfate was carried out in sulfuric acid solutions of barious concentrations at 110 °C. From the results (Fig. 2), it is evident that the amount of tetrathionate increases gradually with an increase of sulfuric acid concentration, and after reaching a maximum, finally falls off. On the other hand, the amount of sulfite shows a steady increase with an increase of sulfuric acid concentration. The reason why the amount of sulfite is not so high as to compensate the decrease in the amount of tetrathionate at sulfuric acid concentrations of 30 and 40 mM is that the sulfite formed escapes to the gaseous phase.

Figure 3 shows the tetrathionate concentrations in the final reaction mixtures as functions of temperature and sulfuric acid concentration. At a definite acid concentration, the amount of tetrathionate formed increases with an increase of reaction temperature in the range 70—130 °C. Tetrathionate, however, decomposes above 130 °C, the final concentration decreasing with increasing temperature in the temperature range. The reason why the amount of tetrathionate shows a maximum at a certain concentration of sulfuric acid is not clear.

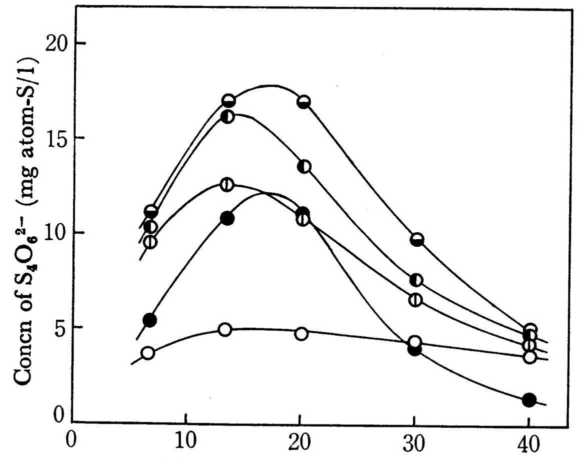


Fig. 3. Effect of reaction temperature and sulfuric acid concentration on the formation of tetrathionate from thiosulfate.
Initial concn of $S_2O_3^{2-}$: 19.9 mM, time: 2 h.
Temp (°C): ○70, ⦶90, ◐110, ◒130, ●150.

In the experiments shown in Figs. 2 and 3, a fixed reaction time of 2 h was used. However, the decomposition velocity of thiosulfate is very high at even 70 °C, while tetrathionate decomposes hardly below 130 °C. Thus, the amount of tetrathionate formed might not change much even if the reaction time is extended.

It is well known that some kinds of polythionates as well as elemental sulfur and sulfite are formed in the acid decomposition of thiosulfate.[2–4] Many investigators reported that the reaction

$$S_nO_6^{2-} + S_2O_3^{2-} + H^+ \rightleftharpoons S_{n+1}O_6^{2-} + HSO_3^- \quad (n \geq 3) \qquad (4)$$

played an important role not only in the formation of polythionates[6,7,16,17] but also in their decomposition.[2] The amount of trithionate in the final reaction mixtures was extremely small, compared with that of tetrathionate (Table 1 and Fig. 2). Blasius and Krämer[3] suggested that tetrathionate is formed exclusively in the reaction of thiosulfate with concentrated hydrochloric acid at room temperature. Thus, it may be said that tetrathionate does not always exist in equilibrium with trithionate as shown by Eq. (4), and that the formation reaction of trithionate is represented by

$$4HSO_3^- + S_2O_3^{2-} + 2H^+ = 2S_3O_6^{2-} + 3H_2O \qquad (5).^{18,19)}$$

Polythionates except tetrathionate are unstable and decompose readily at high temperature, so the formation reaction of tetrathionate shown by Eq. (1) is the most important in the acid decomposition of thiosulfate solution at relatively high temperature. Janickis[2] reported abnormally higher polythionates, but they might be formed only in highly concentrated acid solutions at a low temperature.

Disproportionation of Trithionate Solution. Trithionate solution undergoes a noticeable decomposition at relatively low temperature.[5,20] The decomposition reaction which takes place in weakly acidic to weakly alkaline solution is represented by

$$S_3O_6^{2-} + H_2O = S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (6)^{5-7)}$$

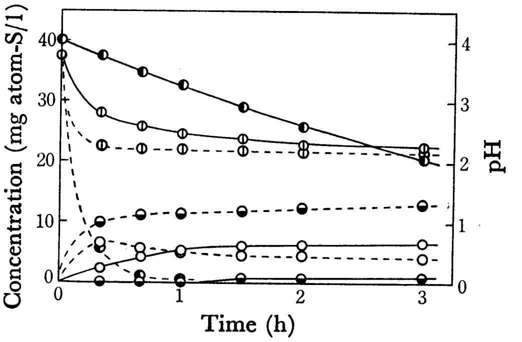


Fig. 4. Disproportionation of potassium trithionate solution.
—○—: $S_2O_3^{2-}$ (70 °C), —◐—: $S_3O_6^{2-}$ (70 °C), —◒—: $S_4O_6^{2-}$ (70 °C), —⦶—: pH (70 °C), ---○---: $S_2O_3^{2-}$ (110 °C), ---◐---: $S_3O_6^{2-}$ (110 °C), ---◒---: $S_4O_6^{2-}$ (110 °C), ---⦶---: pH (110 °C).
The numbers in parentheses represent reaction temperatures.
The amounts of elemental sulfur, sulfite and sulfate formed were not determined.

The results of the thermal decomposition of potassium trithionate solution at 70 and 110 °C are shown in Fig. 4. Trithionate solution is very unstable and tends to decompose readily without the addition of acid at as low as 70 °C, as compared with the case of thiosulfate and tetrathionate. The decomposition at 110 °C is characterized by the fact that the velocity is considerably high, and that the amount of tetrathionate formed is large. The phenomena that the amount of tetrathionate formed at 110 °C is larger than that formed at 70 °C is consistent with the results obtained in the present experiments on acid decomposition of thiosulfate solution.

The results of the disproportionation of trithionate solution in the presence of sulfuric acid are shown in Fig. 5. It is seen that elemental sulfur, thiosulfate, tetrathionate, sulfite and sulfate are formed in the decomposition of trithionate solution, and that the composition of reaction mixtures at sulfuric acid concentrations of 0, 10 and 20 mM are almost the same as that of decomposition products of thiosulfate at

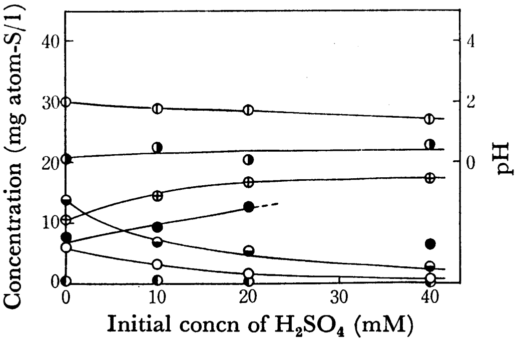


Fig. 5. Effect of sulfuric acid concentration on the disproportionation of trithionate solution.
Initial concn of $S_3O_6^{2-}$: 19.5 mM, temp: 110 °C, time: 2 h.
⊕: S, ○: $S_2O_3^{2-}$, ◐: $S_3O_6^{2-}$, ◒: $S_4O_6^{2-}$, ●: HSO_3^-, ◑: SO_4^{2-},[a] ⦶: pH.
a) The amount of sulfuric acid added was substracted.

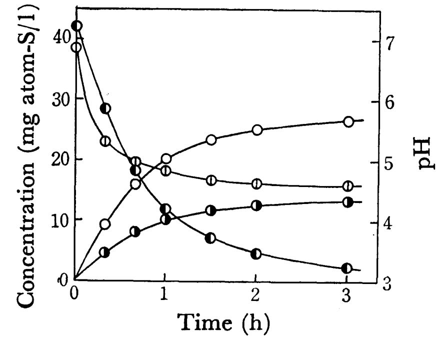


Fig. 6. Disproportionation of trithionate in the presence of acetate buffer solution.

Temp: 90 °C, concn of ammonium acetate: 50 mM. ○: $S_2O_3^{2-}$, ◐: $S_3O_6^{2-}$, ◑: SO_4^{2-}, ⦶: pH.

sulfuric acid concentrations of 20, 30 and 40 mM, respectively (Fig. 2). The only difference is that the amount of sulfate formed is about 20 mM (Fig. 5), which indicates that trithionate decomposes to form equimolar amount of sulfuric acid. Equimolar amounts of thiosulfate and sulfate were exclusively formed from trithionate solution at pH 4.6 (Fig. 6). It seems that trithionate decomposes to thiosulfate, sulfate and hydrogen ions according to Eq. (6), and that the formation of elemental sulfur, tetrathionate and sulfite (Fig. 5) are related to the acid decomposition of thiosulfate thus formed.

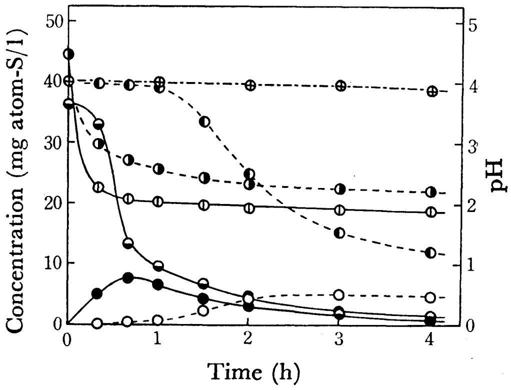
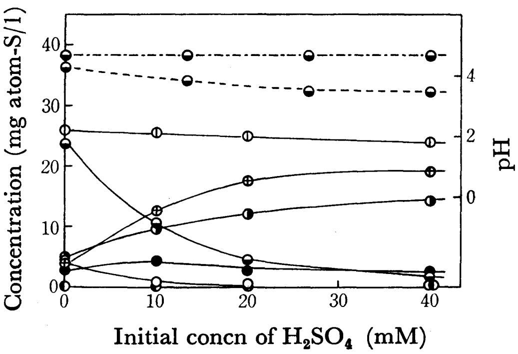


Fig. 7. Disproportionation of potassium tetrathionate solution.

--⊕--: $S_4O_6^{2-}$ (130 °C), ---○---: $S_2O_3^{2-}$ (150 °C), ---◐---: $S_4O_6^{2-}$ (150 °C), ---◑---: pH (150 °C), —●— $S_2O_3^{2-}$(170 °C), —◒—: $S_4O_6^{2-}$ (170 °C), —⦶—: pH (170 °C).

The numbers in parentheses represent reaction temperatures. The amounts of elemental sulfur, sulfite and sulfate formed were not determined.



Figre. 8. Effect of reaction temperature and sulfuric acid concentration on the disproportionation of tetrathionate solution.

Initial concn of $S_4O_6^{2-}$: 9.7 mM, time: 2 h.

--◒--: $S_4O_6^{2-}$ (110 °C), ---◒---: $S_4O_6^{2-}$ (130 °C), —⊕—: S (150 °C), —○—: $S_2O_3^{2-}$ (150 °C), —◐—: $S_3O_6^{2-}$ (150 °C), —◒—: $S_4O_6^{2-}$ (150 °C), —●—: HSO_3^- (150 °C), —◑—: SO_4^{2-} (150 °C),[a] —⦶—: pH (150 °C).

The numbers in parentheses represent reaction temperatures.

a) The amount of sulfuric acid added was substracted.

Disproportionation of Tetrathionate Solution. Figure 7 shows the results of the disproportionation of potassium tetrathionate solution at various temperatures. It is seen that tetrathionate scarcely undergoes thermal decomposition at 130 °C, while it decomposes at temperature above 150 °C after an induction period, forming thiosulfate as an intermediate. The reason why the pH of the solution decreases to 3.0 after 20 min of the initiation of experiment is that a small amount of sulfuric acid is formed due to disproportionation of tetrathionate.

The results of the disproportionation of tetrathionate solution in the presence of sulfuric acid are shown in Fig. 8. The decomposition degree is fairly high at 150 °C and increases with increasing sulfuric acid concentration. The molar ratio of elemental sulfur to sulfate reaches 1.34 when the initial concentration of sulfuric acid is 40 mM. Accordingly, the decomposition reaction of tetrathionate under the acidic conditions can be represented virtually by

$$3S_4O_6^{2-} + 2H_2O = 7S + 5SO_4^{2-} + 4H^+ \tag{7}$$

However, it is evident from the results shown in Figs. 7 and 8 that thiosulfate is also formed as a decomposition product. Some 80% of sulfur atoms was converted into thiosulfate, the remainder of the sulfur atoms being sulfate under the conditions where thiosulfate was not subjected to acid decomposition (Fig. 9). Thus, the first stage of the disproportionation of tetrathionate could be represented by

$$4S_4O_6^{2-} + 5H_2O = 7S_2O_3^{2-} + 2SO_4^{2-} + 10H^+ \tag{8}$$

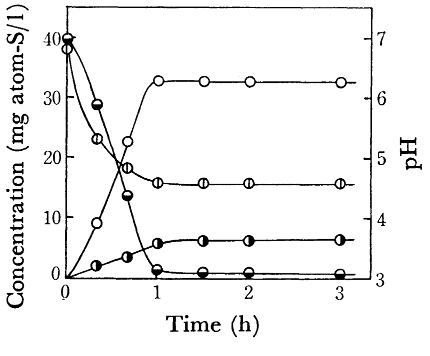


Fig. 9. Disproportionation of tetrathionate in the presence of acetate buffer solution.

Temp: 150 °C, concn of ammonium acetate: 50 mM. ○: $S_2O_3^{2-}$, ◒: $S_4O_6^{2-}$, ◑: SO_4^{2-}, ⦶: pH.

The formation of elemental sulfur and sulfite (Fig. 8) would be attributed to the acid decomposition of thiosulfate thus formed. Sulfite, however, also decomposes easily under the conditions as seen in Fig. 8,[11] resulting in a small amount of sulfite in the final reaction mixtures. From the results, the relation between decomposition degree of tetrathionate at 150 °C and acidity of solution can be summarized as follows: the decomposition degree of tetrathionate at near pH 5—6 (Fig. 9) is higher than that at near pH 2—3 (Fig. 7), although the decomposition degree increases with increasing sulfuric acid concentration (Fig. 8). Tetrathionate solution at 150 °C seems to be the most stable at near pH 2—3. This tendency is similar to the results obtained by Kurtenacker *et al.*[7] that tetrathionate solution at 50 °C is the most stable at near pH 0—3. Thus, the reactions shown by Eqs. (7) and (8) are important in the decomposition of tetrathionate under the acidic conditions. However, the successive occurrence of reactions shown by Eqs. (8) and (1) or (8), (2) and (11) lead to the overall reaction of (7), and the reaction shown by Eq. (7) is not necessarily considered as a separate reaction.

The equation to represent the decomposition of tetrathionate in acidic solutions has been considered to be as follows:[7,8]

$$2S_4O_6^{2-} = S_3O_6^{2-} + S_5O_6^{2-} \quad (9).$$

The decomposition of potassium pentathionate accompanied by the precipitation of elemental sulfur took place under the same conditions (Fig. 9), whereas no elemental sulfur was formed from tetrathionate. The decomosition of tetrathionate is not represented by Eq. (9). By thermodynamical consideration[11,15] the reactions which reasonably proceed under acidic conditions are restrictedly expressed by Eqs. (7) and (8). Reactions such as those given by Eqs. (9) and (10) which are considered to express the occurrence of decomposition of tetrathionate[7] can be ruled out.

$$4S_4O_6^{2-} + 3H_2O = 5S_2O_3^{2-} + 2S_3O_6^{2-} + 6H^+ \quad (10)$$

Disproportionation of Sulfite Solution. It is well known that sulfurous acid is subjected to disproportionation at 150—200 °C to give elemental sulfur and sulfuric acid.[9,10] Acidic sulfite solution also decomposes to elemental sulfur and acidic sulfate accompanied by intermediate formation of thiosulfate. The reaction is largely accelerated by the presence of thiosulfate.[11] The formation of polythionate, however, has not been verified. Experiments were carried out in order to elucidate the role of polythionates participating in the disproportionation of mixed solutions consisting of sodium sulfite, sodium thiosulfate and sulfuric acid. From the results (Fig. 10) it is evident that thiosulfate does not undergo a remarkable change up to a sulfuric acid concentration of 20 mM. The decrease in sulfite concentration below the acid concentration of 20 mM is caused by air oxidation. The increase in thiosulfate concentration at a sulfuric acid concentration of about 25 mM could be related to the formation of another thiosulfate according to the reaction

$$4HSO_3^- = S_2O_3^{2-} + 2SO_4^{2-} + 2H^+ + H_2O \quad (11).$$

It is seen that the formation of tetrathionate becomes predominant under the conditions where sulfite undergoes disproportionation.

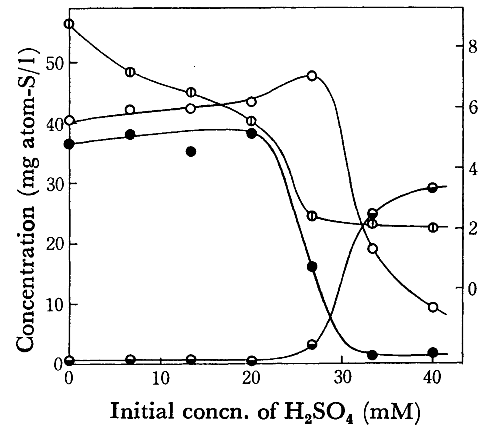


Fig. 10. Disproportionation of mixed solutions of sulfite, thiosulfate and sulfuric acid.
Initial concn of $Na_2S_2O_3$: 21 mM, initial concn of Na_2SO_3: 50 mM, temp: 150 °C, time: 2 h.
○: $S_2O_3^{2-}$, ◒: $S_4O_6^{2-}$, ●: HSO_3^-, ⦶: pH.
The amounts of elemental sulfur and sulfate formed were not determined. When the initial concentration of sulfuric acid is 0, 25, and 40 mM, the initial composition of the solution is given approximately as follows: $Na_2S_2O_3$ (21 mM)—Na_2SO_3 (50 mM), $Na_2S_2O_3$ (21 mM)—$NaHSO_3$ (50 mM), and $Na_2S_2O_3$ (21 mM)—$NaHSO_3$ (20 mM)—H_2SO_3 (30 mM), respectively.

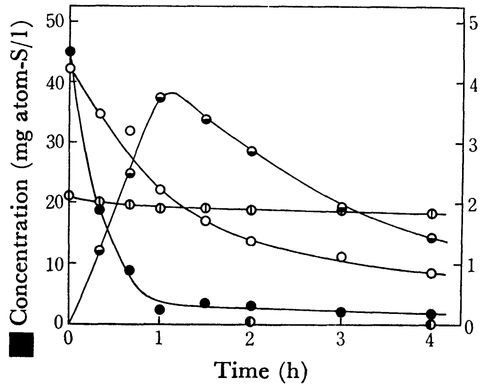


Fig. 11. Time course of the disproportionation of a mixed solution of sulfite, thiosulfate and sulfuric acid.
Initial concn of $Na_2S_2O_3$: 21 mM, initial concn of Na_2SO_3: 45 mM, initial concn of H_2SO_4: 40 mM, temp: 150 °C.
○: $S_2O_3^{2-}$, ◐: $S_3O_6^{2-}$, ◒: $S_4O_6^{2-}$, ●: HSO_3^-, ⦶: pH.
The amounts of elemental sulfur and sulfate formed were not determined.

Figure 11 shows the acid decomposition of a mixed solution of thiosulfate and sulfite with the lapse of time, showing that the decomposition velocity is extremely high, and that the concentration of tetrathionate increases linearly with the lapse of time. The increase in tetrathionate concentration after 1 h from the beginning of experiment is about twice as high as the decrease in thiosulfate concentration, indicating that tetrathionate is formed not only from thiosulfate but also from sulfite. On the other hand, most of the sulfite disappears upon disproportionation within 1 h, and so tetrathionate is not supplied thereafter, which begins to decrease suddenly. The reason why thiosulfate decomposes at a slower speed than that as seen in Fig. 1 is that, under the conditions shown in Fig. 11, the decomposition of thiosulfate is caused by the proton released in the disproportionation of tetrathionate.

It cannot be made clear from the present experiments what kinds of intermediates are formed in the disproportionation of sulfite. It has been concluded that sulfite firstly decomposes according to Eq. (11) to give thiosulfate and sulfate.[11] Thus, the formation of tetrathionate from sulfite may be explained on the basis of reactions (11) and (1).

Pathway of Disproportionation of Low Valence Sulfur Oxyacids. Tetrathionate undergoes sulfite degradation in faintly acidic to alkaline solution, forming thiosulfate and trithionate as shown by

$$S_4O_6^{2-} + HSO_3^- = S_3O_6^{2-} + S_2O_3^{2-} + H^+ \qquad (12).$$

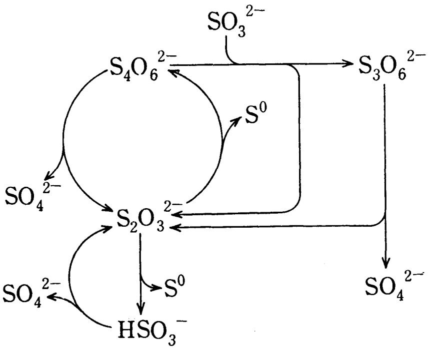


Fig. 12. Pathway of disproportionation of low valence sulfur oxyacids under the acidic conditions.

Taking this reaction into consideration, the pathway of disproportionation of low valence sulfur oxyacids including thiosulfate, trithionate, tetrathionate and sulfite is shown to be as follows (Fig. 12). Tetrathionate is decomposed with sulfite to give thiosulfate and trithionate. Trithionate is subjected to hydrolysis to give thiosulfate and sulfate, only if the temperature is high enough. On the other hand, tetrathionate decomposes to thiosulfate and sulfate at the temperature above 130 °C in the absence of sulfite. The thiosulfate thus formed undergoes disproportionation to elemental sulfur and tetrathionate, or elemental sulfur and sulfite. Sulfite undergoes disproportionation to give thiosulfate and sulfate, and then elemental sulfur and sulfate accompanied by intermediate formation of tetrathionate.

The reaction pathway shown in Fig. 12 has been proposed to explain the species detected in the course of the present experiments, such reactions as shown by Eq. (5) thus being excluded. Further study is necessary to clarify the details of the reactions. The reaction pathway (Fig. 12), however, may be useful in understanding the manner in which low valence sulfur oxyacids decompose and the kinds of intermediates formed in acidic solutions at relatively high temperatures.

References

1) Part IX of this series: T. Mizoguchi and T. Okabe, This Bulletin, **48**, 1799 (1975).

2) J. Janickis, *Z. Anorg. Allg. Chem.*, **234**, 193 (1937).

3) E. Blasium and R. Krämer, *ibid.*, **318**, 113 (1962).

4) F. H. Pollard, G. Nickless, and R. B. Glover, *J. Chromatog.*, **15**, 518 (1964).

5) F. Foerster, *Z. Anorg. Allg. Chem.*, **139**, 246 (1924); *ibid.*, **144**, 337 (1925).

6) A. Kurtenacker and M. Kaufmann, *ibid.*, **148**, 43, 369 (1925).

7) A. Kurtenacker, A. Mutschin, and F. Stastny, *ibid.*, **224**, 399 (1935).

8) E. Blasius and G. Wermbter, *ibid.*, **316**, 251 (1962).

9) T. Marusawa, *Kogyo Kagaku Zasshi*, **20**, 737 (1917).

10) F. Foerster, F. Lange, O. Droßbach, and W. Seidel, *Z. Anorg. Allg. Chem.*, **128**, 245 (1923).

11) T. Okabe, G. Otoshi, and S. Hori, *Kogyo Kagaku Zasshi*, **61**, 662 (1958); T. Okabe, M. Owaku, and S. Hori, *Nippon Kagaku Zasshi*, **81**, 1818 (1960).

12) H. Stamm, M. Goehring, and U. Feldmann, *Z. Anorg. Allg. Chem.*, **250**, 226 (1942).

13) F. Martin and L. Metz, *ibid.*, **127**, 83 (1923).

14) P. A. Trudinger, *J. Bacteriol.*, **93**, 550 (1967).

15) R. M. Garrels and C. L. Christ, "Solutions, Minerals, and Equilibria," Harper and Row, New York (1965).

16) A. Kurtenacker and M. Kaufmann, *Z. Anorg. Allg. Chem.*, **148**, 225 (1925).

17) E. Blasius and W. Burmeister, *Z. Anal. Chem.*, **168**, 1 (1959).

18) C. J. Battaglia and W. J. Miller, *Phot. Sci. Eng.*, **12**, 46 (1968).

19) T. Koh and K. Taniguchi, *Anal. Chem.*, **46**, 1679 (1974).

20) T. Koh, A. Wagai, and Y. Miura, *Anal. Chim. Acta*, **71**, 367 (1974).