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The Chemical Behavior of Low Valence Sulfur Compounds. V. Decomposition and Oxidation of Tetrathionate in Aqueous Ammonia Solution

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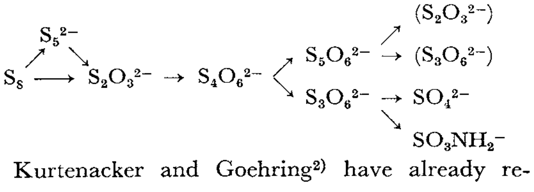
The decomposition and oxygen oxidation of tetrathionate in aqueous ammonia solution have been investigated. In the decomposition, thiosulfate, sulfate and sulfamate were formed through penta- and trithionate as intermediate compounds. The molar ratio of the products $(SO_4^{2-}+SO_3NH_2^-)/S_2O_3^{2-}$ was roughly equal to 2/7, where 0.1N ammonia solution was used. The deficient use of ammonia made the solution neutral or weakly acidic and the precipitation of sulfur and the formation of higher polythionates were observed. The polythionate was detected by means of TLC (Thin Layer Chromatography). In the oxidation, tetrathionate was supposed to go through the following three sequent steps. 1) Decomposition of tetrathionate to form thiosulfate, tri- and pentathionate, and further decomposition of pentathionate to thiosulfate. 2) Oxidation of thiosulfate to tetrathionate and partly to sulfate. 3) Decomposition of trithionate to form sulfate, sulfamate and thiosulfate.

During the course of an investigation of the chemical behavior of low valence sulfur compounds, the oxidation of sulfur in aqueous ammonia was studied and the main process of the reaction was briefly proposed in the preceding paper.[1] It seemed reasonable to assume that tetrathionate is first formed as an intermediate in the oxidation of thiosulfate and disintergrates into pentathionate and trithionate as follows:



Kurtenacker and Goehring[2] have already reported that the decomposition of tetrathionate proceeds diversely, depending on the alkalinity of the solution as follows:[3-6]

pH = 8.9

$$2S_4O_6^{2-} = S_3O_6^{2-} + S_5O_6^{2-} \quad (1)$$

pH = 11.5

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

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[1] Preliminary report: M. C. Shieh, H. Otsube and T. Okabe, This Bulletin, **38**, 1596 (1965).

[2] M. Goehring, *Fortschr. Chem. Forsch.*, **2**, 444 (1952).

[3] A. Kurtenacker and M. Kaufmann, *Z. Anorg. Allg. Chem.*, **148**, 43 (1925); A. Kurtenacker, A. Mutschin and F. Stastny, *ibid.*, **224**, 399 (1935).

[4] F. Haber, *Naturwiss.*, **19**, 452 (1931); A. Kurtenacker and M. Kaufmann, *Z. Anorg. Allg. Chem.*, **148**, 369 (1925).

[5] F. Foerster, *Z. Anorg. Allg. Chem.*, **144**, 337 (1925); A. Hornig, *ibid.*, **176**, 423 (1928).

[6] J. Fordos and A. Gelis, *J. Prakt. Chem.*, **50**, 86 (1850); V. Lewes, *Ber.*, **15**, 2222 (1882); E. H. Riesenfeld, *Z. Anorg. Allg. Chem.*, **119**, 225 (1921).

pH = 12

$$S_3O_6^{2-} + 2OH^- = S_2O_3^{2-} + SO_4^{2-} + H_2O \quad (3)$$

pH = 13

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

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

When tetrathionate is stood for a long time in a strong alkaline solution, sulfite and thiosulfate are finally formed by the following reaction[7]

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

In this reaction, sulfamate is not formed, but a great deal of sulfite is observed. The discrepancy of the products in each case is not due to the presence of compressed oxygen, but might dependent on the reaction medium which controls the first step of the decomposition of tetrathionate. In the present investigation, the decomposition and the oxidation of tetrathionate were studied to clarify the chemical behavior of sulfur compounds in aqueous ammonia solution.

Experimental

Materials. Potassium tetrathionate was prepared according to the method of Martin.[8] An alcoholic solution of iodine was added drop by drop into a potassium thiosulfate solution with stirring. The crude crystals of potassium tetrathionate obtained were then recrystallized from an alcoholic solution. Its purity was 99%, and was free from thiosulfate and sulfur.

Methods. The oxidation and decomposition reactions were carried out in the same autoclave and by the same procedure described in a previous paper.[1] The decomposition reaction in a diluted ammonia solution at low temperature was carried out in a 50 m*l* flask, which contained 20 m*l* of reactant. A portion of the solution in the flask was withdrawn at regular intervals and analyzed in the same manner as described previously, and chromatograph in ethanol-*n*-butanol-1 mol/*l* solution of NH_4Ac-conc. NH_4OH=75 : 75 : 40 : 10. The concentration of potassium tetrathionate in the decomposition and in the oxidation reaction were 0.02 and 0.25 mol/*l*, respectively.

Results

Decomposition of Tetrathionate. The decomposition of potassium tetrathionate was carried out in ammonia solution of various concentrations at 50—80°C. The results obtained are shown in Figs. 1—7. Under these conditions tetrathionate decomposed rapidly, and trithionate and thiosulfate were formed unless ammonia was deficiently used. Since trithionate also decomposed, thiosulfate remained in the final solution with small amounts of sulfate and sulfamate. The general view of the whole reaction is shown in Fig. 1.

The behavior of these sulfur compounds may be qualitatively supported from TLC as shown in Fig. 2. That is, the spots of tetrathionate, trithionate and thiosulfate appeared on the TLC plate at the beginning, but the first two faded away successively, the spot of thiosulfate remaining till the last.

The decomposition of tetrathionate was largely influenced by concentration of ammonia as shown in Figs. 3 and 4. The increase of ammonia concentration accelerated the decomposition. The largest amount of thiosulfate was produced in around 0.4N solution of ammonia. When an

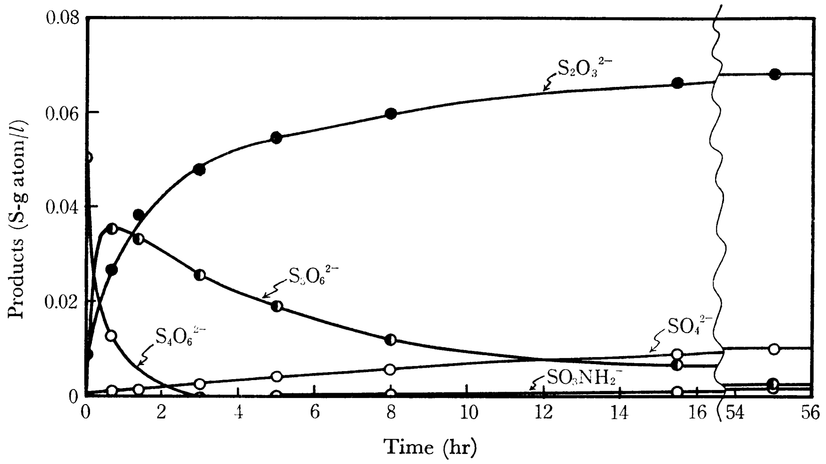

Fig. 1. The decomposition of tetrathionate in aqueous ammonia solution.
Reaction temp.: 60°C
Ammonia concn.: 0.416N
$K_2S_4O_6$ concn.: 0.020 mol/*l*

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[7] A. Gutmann, *Ber.*, **39**, 509 (1906); *ibid.*, **40**, 3614 (1907); E. H. Riesenfeld, *Z. Anorg. Allg. Chem.*, **141**, 109 (1924).

[8] F. Martin and L. Metz, *Z. Anorg. Allg. Chem.*, **127**, 83 (1923).

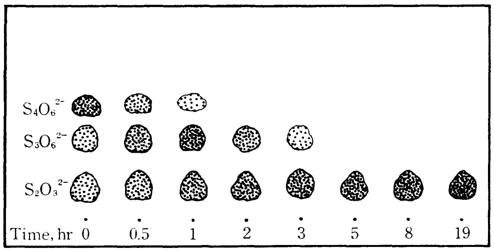


Fig. 2. TLC spot changes of $K_2S_4O_6$ on the aqueous ammonia solution with reaction time.
Reaction temp.: 80°C
Ammonia concn.: 1.64N
$K_2S_4O_6$ concn.: 0.020 mol/*l*
Solvent: Ethenol 75 m*l*, *n*-butanol 75 m*l*, 1 mol/*l*, of NH_4Ac 40 m*l*, concn. NH_4OH 10 m*l*

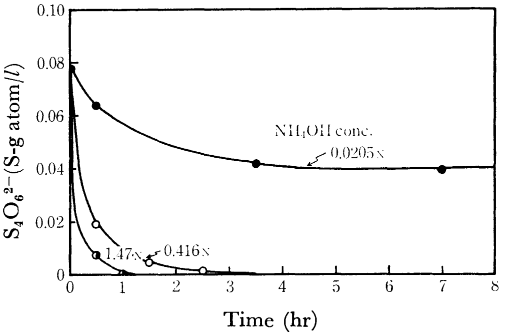


Fig. 3. Influence of ammonia concentration on the decomposition of $K_2S_4O_6$.
Reaction temp.: 60°C
$K_2S_4O_6$ concn.: 0.020 mol/*l*

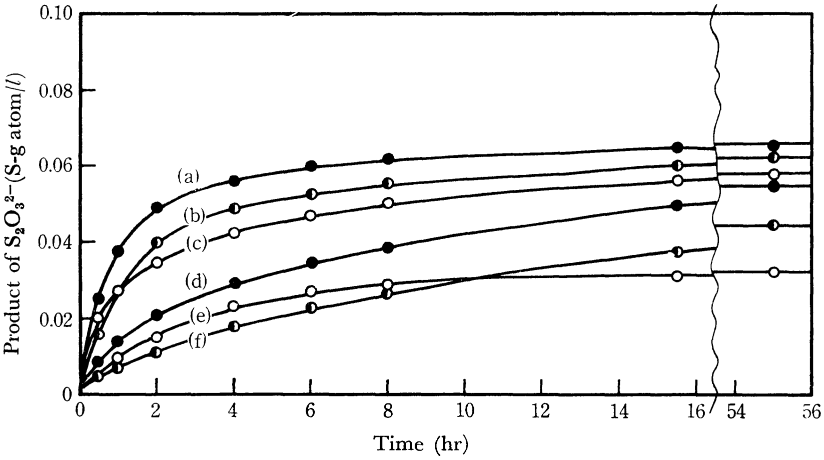


Fig. 4. Effect of ammonia concn. with the product of $S_2O_3^{2-}$ on the decomposition of $K_2S_4O_6$.
Reaction temp.: 60°C
$K_2S_4O_6$ concn.: 0.020 mol/*l*
NH_4OH concn.: (a) 0.416N (b) 0.105N (c) 2.057N
(d) 5.120N (e) 0.0207N (f) 9.64N

extremely dilute ammonia such as 0.017N was used, the pH of the solution gradually decreased from 11.2 to 7.9, where elemental sulfur, pentathionate and hexathionate appeared as indicated by Figs. 5 and 6. The rise of temperature also accelerated the rate of decomposition as shown in Fig. 7.

Oxidation of Tetrathionate. The oxidation of potassium tetrathionate was carried out in 12N solution of ammonia at 90°C with compressed oxygen of 75 kg/cm². The results obtained are shown in Figs. 8 and 9. The difference of introduction time of oxygen made the reaction rate somewhat vary, but no remarkable change in the composition of the final solution was observed.

Discussion

It is apparent from this study that the mechanism of the decomposition of tetrathionate in aqueous ammonia solution is partly in conformity with Eqs. (1) and (2) suggested by the previous investigators. Therefore, the first products which depend on ammonia concentration are trithionate, pentathionate and thiosulfate. Then pentathionate and trithionate decompose as:

$$2S_5O_6^{2-} + 6OH^- = 5S_2O_3^{2-} + 3H_2O \quad (7)$$

$$S_3O_6^{2-} + 2OH^- = SO_4^{2-} + S_2O_3^{2-} + H_2O \quad (8)$$

$$S_3O_6^{2-} + NH_3 + OH^- = SO_3NH_2^- + S_2O_3^{2-} + H_2O \quad (9)$$

Equations (8) and (9) are in competition with each other. Sulfamate is formed through Eq. (9), which is different from tetrathionate decomposition in caustic soda solution.

It is obvious from the experiments that the yield of sulfamate depends on the ammonia concentration.

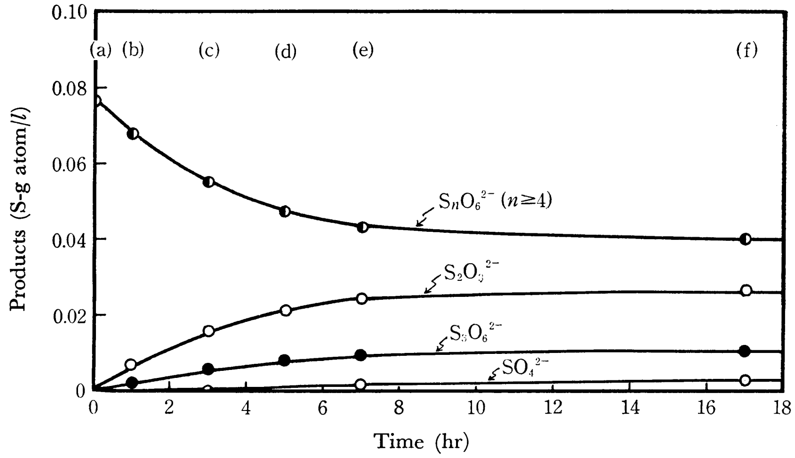


Fig. 5. The decomposition of $K_2S_4O_6$ on the dilute ammonia aqueous solution.
Reaction temp.: 50°C
Ammonia concn.: 0.017N
$K_2S_4O_6$ concn.: 0.020 mol/l

pH change with time:	(a)	(b)	(c)	(d)	(e)	(f)
pH	11.19	10.48	10.12	9.71	9.52	7.92

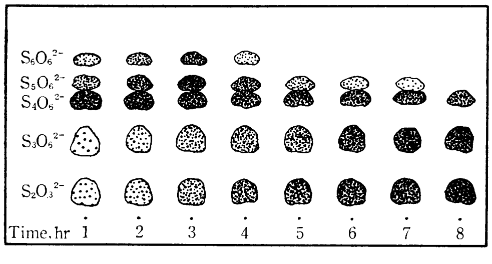


Fig. 6. TLC spot change of $K_2S_4O_6$ on the aqueous ammonia solution with reaction time.
Reaction temp.: 50°C
Ammonia concn.: 0.017N
$K_2S_4O_6$ concn.: 0.020 mol/l
Solvent: Ethenol 75 ml, n-butanol 75 ml, 1 mol/l of NH_4Ac 40 ml, conc. NH_4OH 10 ml

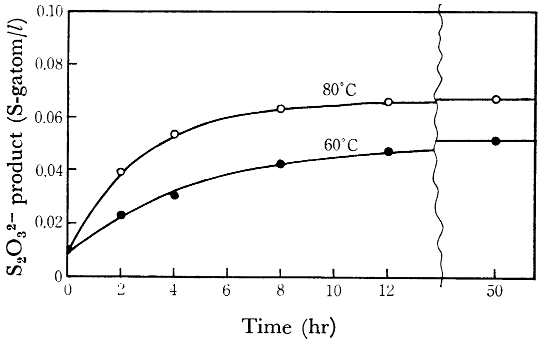


Fig. 7. Influence of the reaction temperature with $S_2O_3^{2-}$ yield on the decomposition of $K_2S_4O_6$.
Ammonia concn.: 5.0N
$K_2S_4O_6$ concn.: 0.020 mol/l

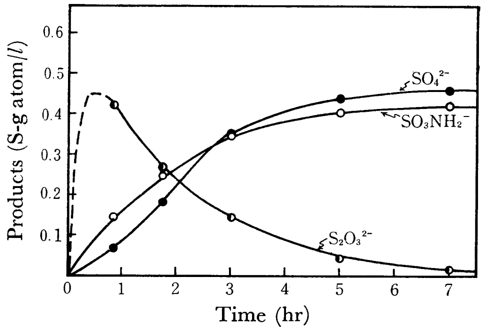


Fig. 8. Oxygen oxidation of $K_2S_4O_6$.
Oxygen was introduced at the beginning.
$K_2S_4O_6$ concn.: 0.25 mol/l, Oxygen pres.: 75 kg/cm², Ammonia concn.: 12N, Reaction temp.: 90°C

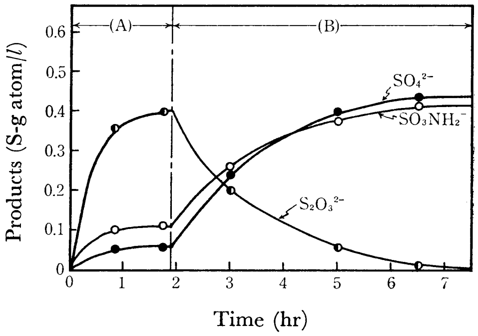


Fig. 9. Oxygen oxidation of $K_2S_4O_6$.
(A) Decomposition reaction
(B) Oxidation reaction under oxygen pressure
$K_2S_4O_6$ concn.: 0.25 mol/l, Oxygen press.: 75 kg/cm², Ammonia concn. 12N,: Reaction temp.: 90°C

TABLE 1. EFFECT OF AMMONIA CONCENTRATION ON THE DECOMPOSITION OF POTASSIUM TETRATHIONATE

Ammonia concn. (N)	$K_2S_2O_6$ concn. mol/*l*	Yield of product (S-g atom/*l*) $S_2O_3^{2-}$	SO_4^{2-}	$SO_3NH_2^-$	molar ratio $(SO_4^{2-}+SO_3NH_2^-)/S_2O_3^{2-}$
0.11	0.020	0.0688	0.011	—	0.32
0.52	0.020	0.0658	0.0126	0.0013	0.42
1.92	0.020	0.0541	0.0208	0.0064	1.01
5.91	0.020	0.0525	0.0159	0.0113	1.04
9.65	0.020	0.0509	0.0153	0.0129	1.10

When the ammonia concentration is below 2N, sulfamate is hardly formed. If ammonia is deficiently used, the solution will become neutral or weakly acidic leading to the precipitation of sulfur and the formation of higher polythionates. In this case sulfite is also produced because trithionate and tetrathionate should react with excess thiosulfate to form higher polythionates, *viz*:

$$S_3O_6^{2-} + H^+ + S_2O_3^{2-} = S_4O_6^{2-} + HSO_3^- \quad (10)$$

$$S_4O_6^{2-} + H^+ + S_2O_3^{2-} = S_5O_6^{2-} + HSO_3^- \quad (11)$$

$$S_5O_6^{2-} = S_4O_6^{2-} + S \quad (12)$$

In the presence of excess free ammonia, the details of the reaction are not clear, but the overall reaction may be expressed as follows:

$$4S_4O_6^{2-} + 10OH^- = 7S_2O_3^{2-} + 2SO_4^{2-} + 5H_2O \quad (13)$$

$$4S_4O_6^{2-} + 2NH_3 + 8OH^- = 7S_2O_3^{2-} + 2SO_3NH_2^- + 5H_2O \quad (14)$$

The above equations indicate that the molar ratio of $(SO_4^{2-}+SO_3NH_2^-)/S_2O_3^{2-}$ should be equal to 2/7, even if the ammonia concentration or the temperature may change. When the ammonia concentration is about 0.1N, the experimental results obtained agree with the theoretical values within about 10% error. However, the molar ratio of $(SO_4^{2-}+SO_3NH_2^-)/S_2O_3^{2-}$ becomes about 1.01—1.10 in the ammonia concentration 2N or higher than 2N as shown in Table 1. This large discrepancy may be explained by the fact that tetrathionate is easily oxidized to sulfate in alkaline solution. That is, tetrathionate is easily oxidized to sulfate and sulfamate by air remaining in the flask. The overall equation may be considered as follows:

$$3S_4O_6^{2-} + 10OH^- + 2\tfrac{1}{2}O_2 = 4S_2O_3^{2-} + 4SO_4^{2-} + 5H_2O \quad (15)$$

$$3S_4O_6^{2-} + 4NH_3 + 6OH^- + 2\tfrac{1}{2}O_2 = 4S_2O_3^{2-} + 4SO_3NH_2^- + 5H_2O \quad (16)$$

Consequently, the oxidation of tetrathionate in the presence of excess free ammonia may be represented by the following three sequent steps.

1) At first, tetrathionate is decomposed to trithionate and pentathionate, or trithionate and thiosulfate according to Eq. (1) or (2), respectively. Pentathionate is further decomposed to thiosulfate.

2) Oxidation of thiosulfate occurs as:

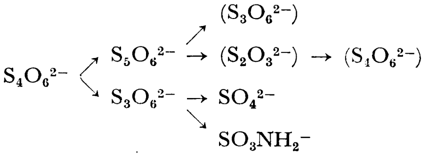
$$2S_2O_3^{2-} + \tfrac{1}{2}O_2 + H_2O = S_4O_6^{2-} + 2OH^- \quad (17)$$

Decomposition of tetrathionate is repeated until all thiosulfate is consumed and, in these consecutive steps, this oxidation step of thiosulfate seems to be rate-determining. However, a small part of thiosulfate is considered to be oxidized to sulfate as:

$$S_2O_3^{2-} + 2O_2 + 2OH^- = 2SO_4^{2-} + H_2O \quad (18)$$

3) The final step is the decomposition of trithionate as shown in Eqs. (8) and (9).

From the above results, the oxidation of potassium tetrathionate in ammonia solution may be considered to proceed *via* the following course:



$$\begin{tikzcd}
 & & (S_3O_6^{2-}) & \\
 & S_5O_6^{2-} \arrow[r] \arrow[ur] & (S_2O_3^{2-}) \arrow[r] & (S_4O_6^{2-}) \\
S_4O_6^{2-} \arrow[ur] \arrow[dr] & & & \\
 & S_3O_6^{2-} \arrow[r] \arrow[dr] & SO_4^{2-} & \\
 & & SO_3NH_2^- &
\end{tikzcd}$$