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The Chemical Behavior of Low Valence Sulfur Compounds. VI. Decomposition of Tetrasulfur Tetranitride in Aqueous Ammonia Solution

Mu-Chang SHIEH, Kenichi KATABE and Taijiro OKABE

Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai

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The decomposition of tetrasulfur tetranitride in an aqueous ammonia solution has been investigated. Ammonolysis of tetrasulfur tetranitride gives thiosulfate, sulfite, sulfate and sulfamate through the intermediate compound of trithionate. An increase in the concentration of ammonia raises the yield of sulfamate and lowers that of sulfate, but gives no remarkable change in the yield of thiosulfate. Besides this, in a concentration of ammonia higher than 15 N at 100°C an explosive reaction takes place. Addition of copper ion improves the yield of sulfamate, and the sulfite ion reacts with tetrasulfur tetranitride in an ammonia aqueous solution to form sulfate and sulfamate ion quantitatively.

In a previous paper[1] describing the reaction of low valence sulfur compounds, such as elemental sulfur, thiosulfate, sulfide, tetrathionate and trithionate in aqueous ammonia solution, it was shown that sulfate and sulfamate were finally formed in the oxidation of sulfur under oxygen pressure through polythionates as intermediate compounds, when the concentration of ammonia was restricted to about 16 N. On the other hand, it was reported[2] that the reaction of sulfur in an anhydrous ammonia gives tetrasulfur tetranitride:

$$10S + 4NH_3 = S_4N_4 + 6\,H_2S^{*1} \qquad (1)$$

In this reaction, if a highly concentrated solu-

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

[2] F. W. Bergstrom, *J. Amer. Chem. Soc.*, **48**, 2319 (1926).

[*1] The reaction is reversible, and the following reaction can take place according to the molar ratio of ammonia to sulfur.

$$H_2S + 2NH_3 = (NH_4)_2S$$
$$S_4N_4 + 2NH_3 = 2\,S(NH)_2 + S_2(NH)_2$$
$$(NH_4)_2S + xS = (NH_4)_2S_{x+1}$$
$$(NH_4)_2S_{x+1} = (NH_4)_2S_x + S$$

tion of ammonia is used for sulfur oxidation, tetrasulfur tetranitride can be regarded as an important intermediate compound. Thus we studied the decomposition of tetrasulfur tetranitride in aqueous ammonia solution in order to clarify the behavior of tetrasulfur tetranitride in the solution.

The decomposition of tetrasulfur tetranitride in aqueous sodium hydroxide solution has been studied by Meuwsen,3) Goehring,4) and Nair,5) and it was revealed that the reactions depend on the alkalinity of solution as follows.

In a weak alkaline solution:

$$2S_4N_4 + 6OH^- + 9H_2O = S_2O_3^{2-} + 8NH_3 + 2S_3O_6^{2-} \quad (2)$$

In a strong alkaline solution:

$$S_4N_4 + 6OH^- + 3H_2O = S_2O_3^{2-} + 4NH_3 + 2SO_3^{2-} \quad (3)$$

Thiosulfate, trithionate and ammonia were formed in the former, and thiosulfate and ammonia in the latter. When the reaction, however, was carried out in aqueous ammonia, sulfite, sulfate, thiosulfate and sulfamate were produced through trithionate.

Experimental

Materials. Tetrasulfur tetranitride was prepared by the reaction of ammonia with sulfur chloride as described by Meuwsen.3)

$$6S_2Cl_2 + 16NH_3 = S_4N_4 + 8S + 12NH_4Cl \quad (4)$$

The crude product was recrystallized from benzene, washed with carbon disulfide and dried over silica gel. The final product has a 99.5% purity and is free from sulfur.

Procedure. Known weights of finely ground tetrasulfur tetranitride and ammonium hydroxide were put into a 100 m*l* flask at 50°C or in a 30 m*l* pressure glass tube at 100°C. The flask or tube was kept in a heated glycerol bath regulated within ±0.5°C, withdrawn at regular intervals and the contents were analyzed in the same manner as described previously. Since the solubility of tetrasulfur tetranitride in the aqueous ammonia solution is low and the rate of reaction is determined merely by the dissolution of tetrasulfur tetranitride, no kinetic research was undertaken.

Results

When aqueous ammonia is added to finely ground tetrasulfur tetranitride, the solution gradually becomes slightly yellowish brown. Colora-

TABLE 1. DECOMPOSITION OF TETRASULFUR TETRANITRIDE AT 50°C

React. time (hr)	S_4N_4 taken (g)	Ammonia concn. (N)	Ammonia taken (m*l*)	Products (S-g·atom %) SO_3^{2-}	$S_2O_3^{2-}$	SO_4^{2-}	$SO_3NH_2^-$	$S_3O_6^{2-}$
24	0.4439	0.1	100.0	1.89	49.62	17.57	2.06	28.86
	0.8572	0.5	100.0	3.87	53.80	15.70	3.44	23.19
	1.0015	1.0	100.0	3.53	56.28	15.91	4.15	20.13
	1.1910	3.0	100.0	3.75	60.24	11.35	8.08	16.58
	1.4734	6.0	40.0	3.21	56.48	8.70	12.08	18.81
	1.2988	15.0	20.0	1.25	62.22	6.65	15.80	14.17
96	0.9848	0.5	80.0	1.65	75.25	20.73	3.52	
	0.9985	1.0	60.0	0.51	74.80	19.58	6.24	
	1.0267	3.0	50.0	0.77	75.38	14.01	10.88	
	1.0081	6.0	40.0	0.55	73.60	10.01	14.17	
	1.0034	12.0	30.0	0.06	75.90	6.03	19.26	
	1.0024	15.0	20.0	0.05	76.62	4.91	19.31	

TABLE 2. DECOMPOSITION OF TETRASULFUR TETRANITRIDE AT 100°C

React. time (hr)	S_4N_4 taken (g)	Ammonia concn. (N)	Ammonia taken (m*l*)	Products (S-g·atom %) SO_3^{2-}	$S_2O_3^{2-}$	SO_4^{2-}	$SO_3NH_2^-$
1/3	0.9766	3.0	20.0	1.88	75.74	12.51	8.53
1	0.9856	3.0	20.0	2.17	77.64	11.93	9.02
3	0.9761	3.0	20.0	1.53	76.38	12.18	9.02
5	0.9765	3.0	20.0	2.09	77.43	12.58	9.22
1	0.9681	12.0	10.0	1.30	78.79	5.03	15.91
3	0.9989	12.0	10.0	1.03	78.96	5.16	17.11
5	0.9936	12.0	10.0	0.88	78.18	4.97	16.02

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3) A. Meuwsen, *Ber.*, **62**, 1959 (1929).

4) W. L. Jolly and M. Goehring, *Inorg. Chem.*, **1**, 76 (1961).

5) C. G. R. Nair and A. R. V. Murthy, *J. Inorg. Nucl. Chem.*, **25**, 453 (1963).

tion is caused by a slight dissolution of tetrasulfur tetranitride and fades away to a colourless state in less than 10 min, producing a large amount of thiosulfate. The results of the decomposition of tetrasulfur tetranitride at 50°C and 100°C are presented in Tables 1 and 2, respectively. The products of the reaction are thiosulfate, sulfite, sulfate and sulfamate and the conversions of sulfur in tetrasulfur tetranitride are $S_2O_3^{2-}$ 50—80 mol%, $SO_3NH_2^-$ 2—19 mol%, SO_4^{2-} 20—5 mol%, and SO_3^{2-} 1—4%.

Figs. 1 and 2 show the effect of ammonia concentration on the yield. An increase in the concentration of ammonia raises the yield of sulfamate and lowers that of sulfate, but gives no remarkable effect on the yield of thiosulfate.

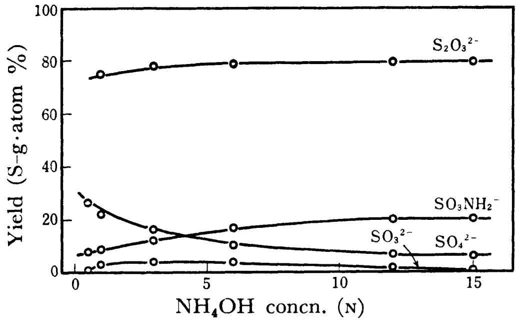

Fig. 1. Effect of ammonia concentration on the yeild of products.
React. temp.: 15°C React. time: 17 hr

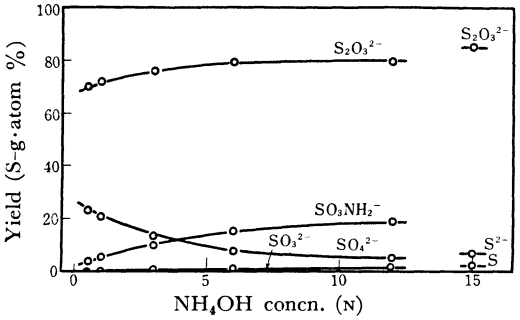

Fig. 2. Effect of ammonia concentration on the yield of products.
React. temp.: 100°C React. time: 3 hr

The effect of reaction temperature on the yield of products is slight as is shown in Fig. 3 and Fig. 4. When the concentration of ammonia is greater than 15 N, an explosive reaction occurs at 100°C with a flash producing a large amount of thiosulfate, a small amount of elemental sulfur and sulfide, and traces of sulfate and sulfamate.

Figs. 5 and 6 give the results of the decomposition of tetrasulfur tetranitride in the presence of sulfite ion and copper ion, respectively. Sulfite reacts with tetrasulfur tetranitride in an aqueous ammonia solution to form sulfate and sulfamate ion, quantitatively.

Addition of copper ion improves the yield of sulfamate but depresses that of thiosulfate. Fig. 7 shows the results of thin layer chromatographic analyses of tetrasulfur tetranitride in aqueous

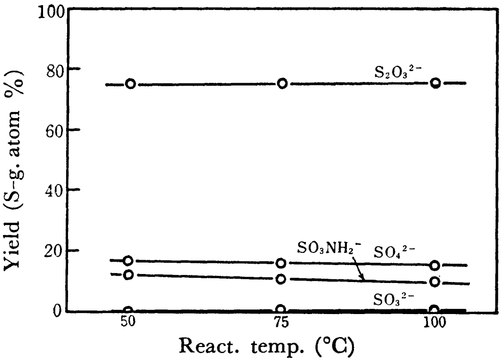

Fig. 3. Effect of reaction temperature on the yield of the products.
Ammonia concn.: 3 N

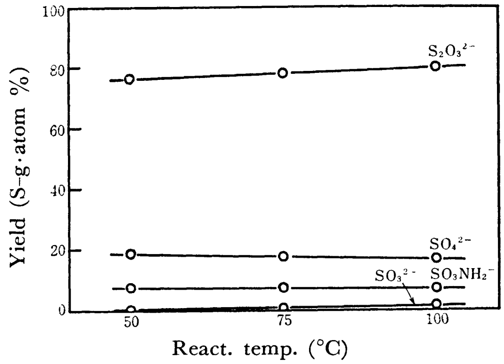

Fig. 4. Effect of reaction temperature on the yield of products.
Ammonia concn.: 12 N

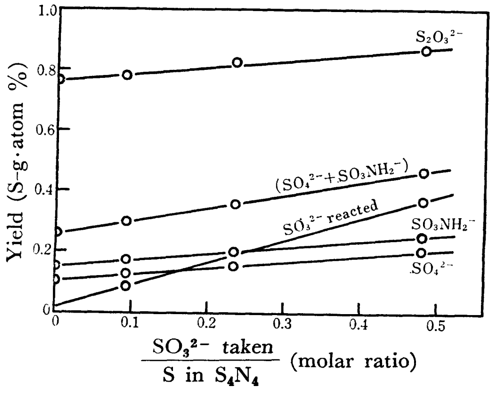

Fig. 5. Decomposition of tetrasulfur tetranitride in the presence of an excess sulfite ion.
React. temp.: 75°C React. time: 17 hr

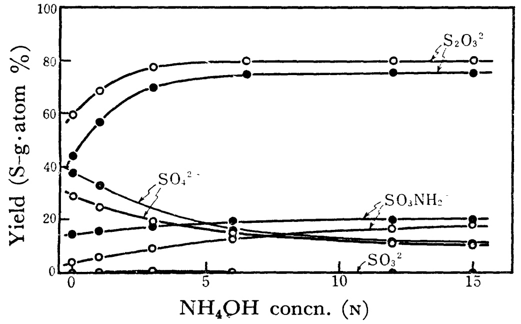

Fig. 6. Decomposition of tetrasulfur tetranitride in the presence of copper ion.
React. temp.: 75°C React. time: 17 hr

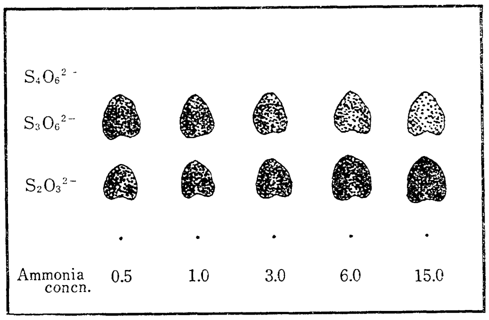

Fig. 7. Thin layer chromatographic analysis of the solution of tetrasulfur tetranitride ammonolysis.
React. temp.: 50°C React. time: 24 hr
Elution solvent: Ethanol—*n*-Butanol—1 mol/*l* of ammonium acetate—conc. ammonia solution =75 : 75 : 40 : 10
Adsorbent: Silica gel (Wako gel B-O)
Thin layer chromatographic analysis following the improved method of Seiler and Erlenmeyer.[6]

ammonia solution. Thiosulfate and trithionate were present in the decomposition of tetrasulfur tetranitride, but no higher polythionate was observed.

Discussion

From the reactions

$$S_4N_4 + 20HI = 4H_2S + 4NH_3 + 10I_2 \quad (5)$$

$$S_4N_4 + 6(O) + 10H_2O = 4H_2SO_4 + 4NH_3 \quad (6)$$

we see that the oxidation states of sulfur and nitrogen in tetrasulfur tetranitride are +3 and −3, respectively. The electropositive nature of sulfur in tetrasulfur tetranitride is in agreement with Pauling's electro-negativity scale (N 3.0, S 2.5).

Nair and Murthy[5] assumed the derivative of S^{3+} *viz.* "sulfur trihydroxide" $S(OH)_3$ to be a primary product in the alkaline hydrolysis of tetrasulfur tetranitride. Such a compound will be extremely unstable and will have only a transient existence, being transformed into sulfoxylic acid and sulfurous acid:

$$S_4N_4 + 12H_2O = 4S(OH)_3 + 4NH_3 \quad (7)$$

$$4S(OH)_3 = 2S(OH)_4 + 2S(OH)_2 \quad (8)$$

$$S(OH)_4 = H_2SO_3 + H_2O \quad (9)$$

Sulfoxylic acid which is not isolated in a pure state or in solution, is known to be a highly reactive species as is seen from studies on its derivatives.[7] Formation of various compounds in the hydrolysis of tetrasulfur tetranitride can be easily explained by the secondary reactions as follows:

$$S(OH)_2 + 2H_2SO_3 = H_2S_3O_6 + 2H_2O \quad (10)$$

$$2S(OH)_2 = H_2S_2O_3 + H_2O \quad (11)$$

$$2S(OH)_2 = H_2S + H_2SO_4 \quad (12)$$

$$3S(OH)_2 = H_2S + 2H_2SO_3 \quad (13)$$

$$S_3O_6^{2-} + OH^- = S_2O_3^{2-} + SO_4^{2-} + H^+ \quad (14)$$

$$2S_3O_6^{2-} + 6OH^- = S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \quad (15)$$

From results obtained so far, it is apparent that the mechanism of the decomposition of tetrasulfur tetranitride in an aqueous ammonia solution is partly in conformity with the above reaction except for the explosive reaction which occurs at high temperature and high ammonia concentration. The result differs in the following aspects as compared with alkaline hydrolysis: no formation of sulfide ion, formation of trace sulfite ion and formation of sulfamate ion in the reaction of tetrasulfur tetranitride ammonolysis. Thus, we might conclude that the reactions (12) and (13) do not occur in tetrasulfur tetranitride ammonolysis.

Formation of sulfamate is caused by the ammonolysis of trithionate:

$$\begin{aligned} &S_3O_6^{2-} + NH_3 + OH^- \\ &\quad = S_2O_3^{2-} + SO_3NH_2^- + H_2O \end{aligned} \quad (16)$$

Trithionate is known to be hydrolysed in the presence of sodium hydroxide in two ways as shown in Eqs. (14) and (15) depending upon the concentration of hydroxyl ion, but in an aqueous ammonia solution Eq. (16) will take place instead of Eq. (14).

The abundant presence of sulfite increases the yields of thiosulfate, sulfate and sulfamate. This can be explained by the fact that the formation of trithionate is improved by the addition of sulfite as indicated by Eq. (10), and that trithionate decomposes to thiosulfate, sulfate and sulfamate according to Eq. (16).

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[6] H. Seiler and H. Erlenmeyer, *Helv. Chem. Acta*, **47**, 264 (1964).

[7] M. Goehring, *Z. Anorg. Allg. Chem.*, **253**, 304 (1947).