The Chemical Behavior of Low Valence Sulfur Compounds. I. Oxidation of Elemental Sulfur with Compressed Oxygen in Aqueous Ammonia Solution

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Recently, the chemistry of sulfane (hydrogen sulfide), sulfane monosulfonic acid (the family of the derivatives of thiosulfuric acid formulated as $H_2S_{x+1}O_3$ or $H_2S_x \cdot SO_3$) and sulfane disulfonic acid (polythionic acids formulated as $H_2S_{x+2}O_6$ or $H_2S_x \cdot 2SO_3$) has been splendidly systematized, as a series of sulfane derivatives, by the excellent work of Feh'er[1] and Schmidt[2]. Nevertheless, the details of the mechanisms by which these compounds react are still obscure, because of the lack of reliable methods of chemical analysis and because of the complexity of the reactions. Knowledge of these mechanisms has, in fact, so far been based mainly on speculation.

In the well-known work of Forward[3] on the hydrometallurgy of nonferrous metals, which involves the leaching of complex sulfide ores containing nickel, cobalt and copper with ammonia solution and compressed air, it has yet been reported that the metal sulfides can be easily converted into sulfate through thiosulfate trithionate and sulfamate as intermediates, but no concrete evidence for their mechanism has been provided. The formation of sulfate by the oxidation of thiosulfate has been observed by Glund[4] in the high pressure oxidation of sodium thiosulfate, but the reaction mechanism has not yet been reported.

The intention of this paper is to clarify the reaction mechanism of the oxidation of sulfide to sulfate, when elemental sulfur suspended in aqueous ammonia is used as the starting material. This study will show that, under optimum conditions, 50% or more of the sulfur can be converted into ammonium sulfamate, a compound which is expected to become an important raw material for various products, as weed killers, fire-proofing agents, and sweetening agents. This oxidation can, therefore, profitably be applied to the manufacture of sulfamate-form sulfur-bearing materials.

Experimental

Apparatus.—A Sakashita Seisakusho Model SR-50 autoclave with a 500-ml. capacity and made of SUS 32 stainless steel, which is the same as alloy AISI 316 or V4A, was used for the reaction. The apparatus is depicted schematically in Fig. 1.

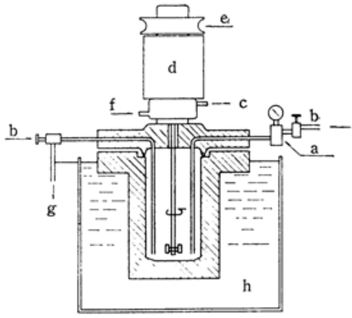

Fig. 1. Experimental apparatus.

(a) Oil trap
(b) Needle valve
(c) Ammonia gage
(d) Magnetic stirrer
(e) Pulley
(f) Cooling water
(g) Sampling pipe
(h) Glycerine bath

Procedure.—After the addition of the sulfur and aqueous ammonia, the autoclave was kept in a heated glycerine bath regulated within 1°C. After one hour the disproportionation reaction had been completed; oxygen was then introduced through a control valve and carefully kept at a constant pressure. Every few hours, 10 ml. aliquots of the solution were withdrawn for analysis.

Analysis.—The sample solution did not contain any sulfite or dithionate. Although the presence of polythionates, such as 3-, 4-, and 5-thionate, was proved by the the paper chromatography proposed by Pollard,[5] their concentrations were too low to permit their determination by chemical analysis. Therefore, after it had been diluted to a suitable concentration, the sample solution was analyzed for sulfides, thiosulfate, sulfate, and sulfamate as follows:

S_x^{2-} : a 1N cadmium acetate solution was added to the diluted solution; the cadmium sulfide precipitated, after being separated by filtration, was oxidized to sulfate with nitric acid and potassium chlorate and weighed as barium sulfate.

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[1] F. Feh'er, W. Laue and G. Winkhaus, *Z. anorg. u. allgem. Chem.*, **288**, 113 (1956); ibid., **290**, 52 (1957).

[2] M. Schmidt, "Sulfur Polymer," in "Inorganic Polymer," Vol. 2, Ed. by F. G. A. Stone and W. A. G. Graham, Academic Press Inc., New York (1962), p. 98.

[3] F. A. Forward, *Trans. Canad. Inst. Min. Metall.*, **66**, 191 (1957).

[4] W. Gluud, *Ber.*, **54**, 2425 (1921).

[5] F. H. Pollard, *Brti. Med. Bull.*, **10**, 187 (1954).

$S_2O_3^{2-}$: One portion of the sample solution was directly titrated with a 0.02 N iodine solution.

$SO_3NH_2^-$: After the addition of a 1 N silver nitrate solution, the sample solution was heated on a water bath in order to convert $S_2O_3^{2-}$ into SO_4^{2-} by the following reaction:

$$S_2O_3^{2-} + 2Ag^+ + 2OH^- = Ag_2S + SO_4^{2-} + H_2O$$

The silver sulfide was then removed by filtration, and the sulfate ions and excess silver nitrate in the filtrate were precipitated, as barium sulfate and silver chloride respectively, by the addition of a barium chloride solution. Then the filtered solution was acidified with dilute hydrochloric acid and heated to boiling, after a sufficient amount of sodium nitrite had been added to decompose the $SO_3NH_2^-$ as follows:

$$SO_3NH_2^- + NO_2^- = SO_4^{2-} + N_2 + H_2O$$

The sulfate ion formed was determined by the ordinary method as barium sulfate, and the amount of sulfamate was estimated.

Results

General View of the Entire Reaction.—When elemental sulfur is heated in aqueous ammonia at about 100°C, the solution gradually becomes reddish brown and is found to contain polysulfide and thiosulfate, as is shown in Table I and II. Although these results are not completely accurate, as the result of a poor sampling, the molar ratio, $S_x^{2-}/S_2O_3^{2-}$, seems to indicate that the value of x has a tendency to decrease from about 8 to 5 during the course of the reaction. This fact can be explained by assuming the successive formation of S_8^{2-} and S_5^{2-}. When oxygen is introduced into a solution in which the sulfur has been entirely disproportionated, the red color of the solution rapidly fades away and the temperature of the solution rises; at the same time a large amount of thiosulfate is formed. The oxidation of polysulfide which proceeds faster than that of thiosulfate, appears to be the rate-determining step for the over-all reaction; thus thiosulfate temporarily reaches a maximum concentration and then gradually changes into sulfate and sulfamate, the final products. If oxygen is introduced at the beginning of the reaction, both the disproportionation and the oxidation will occur in the early stages. These aspects are shown schematically in Fig. 2. The kinetics of these reactions could not be determined, because free ammonia is continuously consumed in the course of the reaction and, consequently, the partial pressure of oxygen increases under a constant pressure. These relations become even more complicated when the changes in temperature are taken into account.

The Effect of the Ammonia Concentration.—The ammonia concentration varied from 4 N to 16 N. An increase in the concentration of ammonia caused a remarkable increase in the reaction rate and improved the yield of sulfamate.

The Effect of the Oxygen Pressure.—The effect of the oxygen pressure was examined in the 20—100 kg./cm² range. This pressure includes the vapor pressure of the solution. As is shown in Fig. 3, the increase in the reaction rate is proportional to the oxygen pressure, but only at pressures below 50 kg./cm². On the other hand, while high oxygen pressures cause a small improvement in the yield of sulfamate, this enhancement of the yield of sulfamate is not as great as that due to a decrease in the temperature or that due to an increase in the ammonia concentration.

TABLE I. COMPOSITION OF THE DISPROPORTIONATE SOLUTION OF SULFUR

Reaction temp., °C	90	110	110	110	110	130	130	150
Ammonium concn., N	8.30	4.16	7.88	12.14	15.97	8.16	8.16	8.30
Reaction time, hr.	1	1	1	1	1	1	1	1
S_x^{2-} (S-g. atom/l.)	0.42	0.69	1.34	1.89	1.92	1.78	1.79	1.75
$S_2O_3^{2-}$ (S-g. atom/l.)	0.12	0.12	0.25	0.55	0.35	0.32	0.29	0.32
Total S (S-g. atom/l.)	0.54	0.81	1.57	2.40	2.27	2.10	2.08	2.07
$S_x^{2-}/S_2O_3^{2-}$	3.5	5.8	5.4	3.4	5.5	5.6	6.2	5.5

$S_x^{2-}/S_2O_3^{2-}$: Sulfur atom ratio of polysulfide ion to thiosulfate ion.

TABLE II. COMPOSITION OF THE DISPROPORTIONATE SOLUTION OF SULFUR

Reaction time, hr.	0	3	6	12	18	24
S_x^{2-} (S-g. atom/l.)	3.95	3.74	3.92	3.89	3.90	3.93
$S_2O_3^{2-}$ (S-g. atom/l.)	0.51	0.63	0.67	0.61	0.72	0.73
Total S (S-g. atom/l.)	4.46	4.37	4.59	4.50	4.62	4.66
$S_x^{2-}/S_2O_3^{2-}$	7.7	5.9	5.8	6.4	5.4	5.4

Reaction temp., 130°C Stirring speed, 500 r. p. m. Ammonium concn., 16.9 N
Partial pressure of NH_3, 16.0 kg./cm²

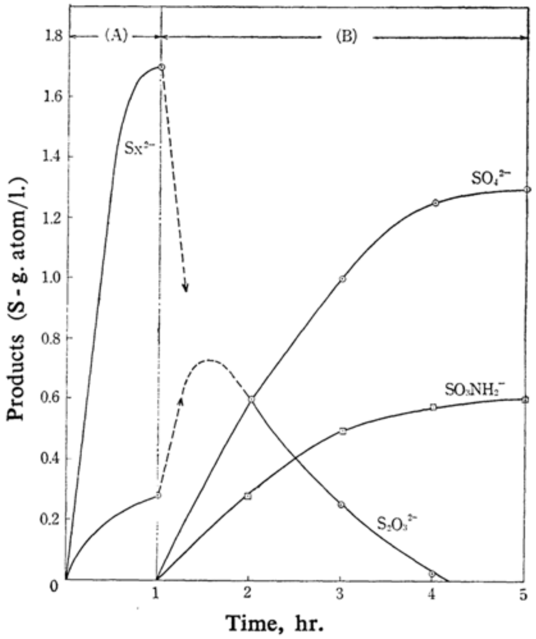

Fig. 2. General view of the whole reaction Disproportionation and oxidation of sulfur.
(A) Disproportionation reaction
(B) Oxidation reaction under oxygen pressure

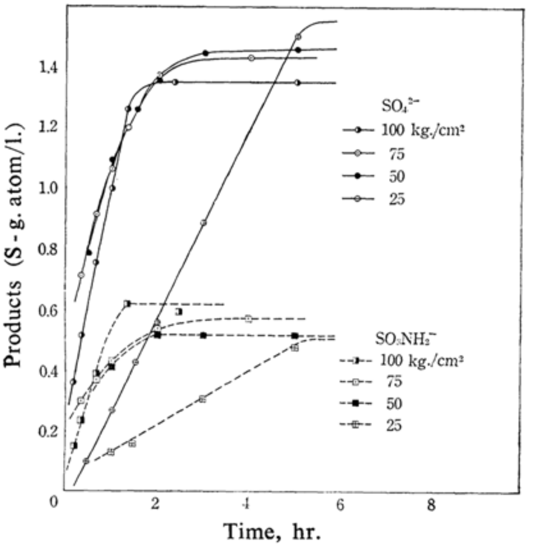

Fig. 3. Effect of oxygen pressure on the reaction of sulfur oxidation.
Temperature 130°C
Ammonia concentration 8 N

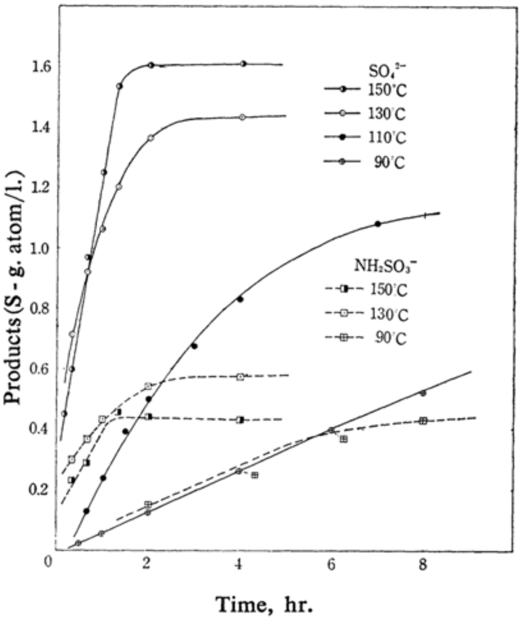

Fig. 4. Effect of temperature on the reaction of sulfur oxidation.
Oxygen pressure 75 (kg./cm²)
Ammonia concentration 8 N

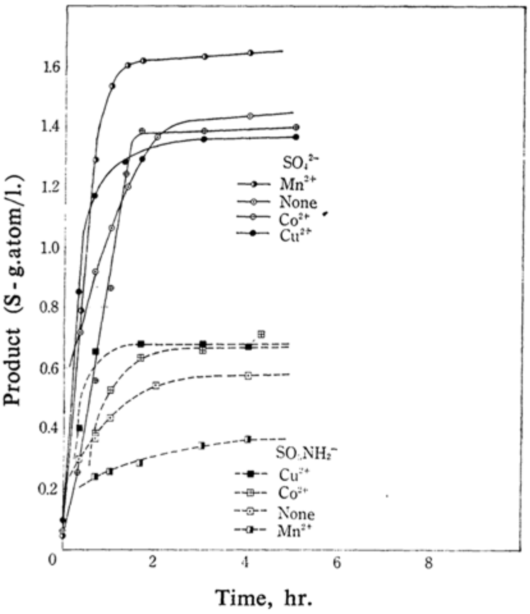

Fig. 5. Effect of metal ion on the reaction of sulfur oxidation.
Temperature 130°C
Oxygen pressure 75 (kg./cm²)
Ammonia concentration 8 N

The Effect of the Reaction Temperature.—The reaction rate is increased by raising the reaction temperature, but the yield of sulfamate is thus decreased, probably because of the decomposition of trithionate into sulfate by the hydrolysis. The results are shown in Fig. 4.

The Catalytic Effect of Metal Ions.—The transition metals, such as cobalt, nickel, and

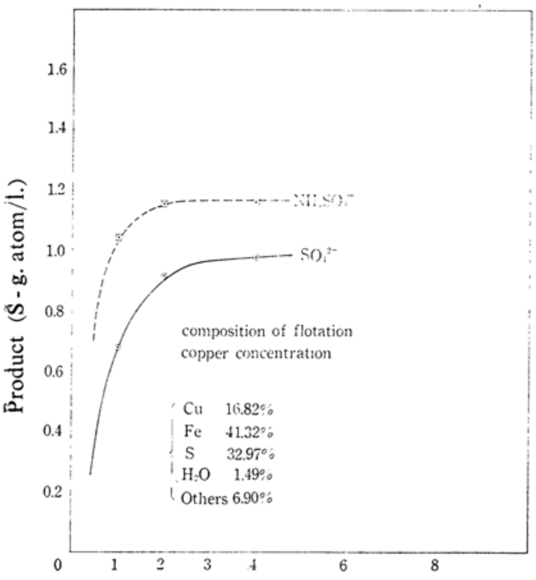

Fig. 6. Effect of flotation copper concentrate on the reaction of sulfur oxidation.

Temperature	110°C
Oxygen pressure	75 (kg./cm²)
Ammonia concentration	11.74 N

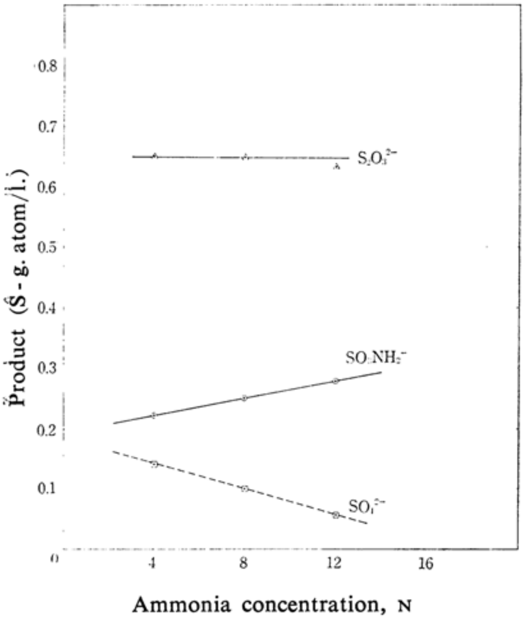

Fig. 7. Effect of ammonia concentration on the decomposition of trithionate.

Reaction temperature 110°C

copper, are known to accelerate remarkably the oxidation of sulfite with oxygen. The expected catalytic effects of these metals on the above oxidation of sulfur are shown in Figs. 5 and 6. The reaction rate is significantly affected by the presence of these metals, but the effect is not as large as that in the sulfite oxidation. However, the yield of sulfamate can be remarkably increased by the addition of copper sulfide ores. Since most of the dissolved copper is precipitated as sulfide in the course of the reaction, there are very few copper ions to serve as catalysts.

The Decomposition of Trithionate.—Related experiments were made on trithionate; the results, shown in Fig. 7, indicate that the yield of sulfamate ions increases with the concentration of ammonium hydroxide, while that of sulfate ions shows a reverse tendency.

Discussion

Although the reaction mechanism has not yet been fully established, the main course of the reaction is roughly disclosed by this study. The oxidation of sulfur does not occur as a series of simultaneous reactions; Rather, it proceeds through the following series of consecutive steps:

The Disproportionation of Sulfur.—According to Pryor's review,[6] the most widely-accepted mechanisms of the disproportionation of sulfur in an alkaline solution are as follows;

$$\frac{1}{2}S_8 + 4NaOH = Na_2S_2O_3 + 2NaHS + H_2O \qquad (100-200°C)$$

$$\frac{1}{2}S_8 + 5NH_4OH = (NH_4)_2SO_4 + 3NH_4SH + H_2O \qquad (250—350°C)$$

However, the present study, at 100°C, revealed that unstable ammonium octasulfide forms at the beginning and that this polysulfide gradually degrades to pentasulfide. This behavior can be understood easily by assuming that the eight-membered ring of the sulfur molecule is broken open to form an octasulfide by the attack of the ammonia, and that the octasulfide is then converted into the stable pentasulfide by the step-by-step elimination of three sulfur atoms. Consequently, the disproportionation can be represented as follows:

$$\frac{3}{2}S_8 + 6NH_4OH = 2(NH_4)_2S_5 + 2(NH_4)_2S_2O_3$$

The Oxidation of Sulfide.—Bloxam[7] reported

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[6] W. A. Payor, "Mechanisms of Sulfur Reaction," McGraw-Hill Inc., New York (1962), p. 12.

[7] W. P. Bloxam, *J. Chem. Soc.*, **67**, 277 (1895), see also E. Schulek and E. Koros, *Acta Chim. Acad. Sci. Hung.*, **3**, 125 (1953); *Chem. Abstr.*, **47**, 10390 (1953).

the formation of thiosulfate in the oxidation of ammonium sulfide under atmospheric pressure at room temperature, but the reaction velocity must be very small under such conditions. It has been found that, if compressed oxygen is employed, the oxidation of sulfide to thiosulfate is almost instantaneous. The rise in the temperature of the reaction mixture must be due to a strongly exothermic reaction, such as the following:

$$2(NH_4)_2S_5 + 6NH_4OH + 6O_2 = 5(NH_4)_2S_2O_3 + 3H_2O + 640\ \text{kcal.}^{8)}$$

The Oxidation of Thiosulfate.—Most thiosulfates can hardly be oxidized at all with oxygen under ordinary pressures. The oxidation of thiosulfate by air was first studied by Gluud,4) who employed a pressure of 10 atm. at 100°C for the sodium salt. The thiosulfate was found to afford only sulfate in alkaline solutions, but in neutral solutions it was converted into free sulfur and sulfate. Moreover, Forward3) reported that ammonium thiosulfate is first oxidized to trithionate with compressed air at 175—300°C. From the fact that thiosulfate is usually oxidized to tetrathionate with iodine and other mild oxidants, it is most reasonable to regard tetrathionate as the product first formed from thiosulfate. The decomposition of the tetrathionate produces trithionate, pentathionate and thiosulfate; the pentathionate then further decomposes, thus forming both trithionate and thiosulfate. Therefore, it now remains to clarify the behavior of trithionate in an aqueous ammonia solution. Its yield is improved by an increase in the ammonia concentration, as Fig. 7 shows. The decomposition of trithionate must, therefore, proceed mainly as:

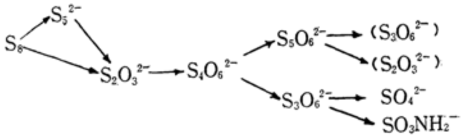
$$S_3O_6^{2-} + NH_3 + OH^- = SO_3NH_2^- + S_2O_3^{2-} + H_2O$$

but partly as:

$$S_3O_6^{2-} + 2OH^- = SO_4^{2-} + S_2O_3^{2-} + H_2O$$

When these reactions are considered, the reason for the increase in the yield of the sulfamate with the increase in the ammonia concentration becomes obvious.

Consequently, although further studies are required, the oxidation of sulfur in an aqueous ammonia solution may be considered to proceed via the following course:



Summary

1) The oxidation of sulfur with compressed oxygen proceeds through the following sequence of steps: (a) The disproportionation of sulfur to both pentasulfide and thiosulfate. (b) The oxidation of pentasulfide to thiosulfate. (c) The oxidation of thiosulfate to sulfate and sulfamate through a series of complicated intermediates.

2) Sulfamate forms only in the decomposition of trithionate.

3) The over-all reaction of the oxidation is prompted by a rise in the temperature, an increase in the ammonia concentration, and the addition of transition metal ions, especially copper ions.

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8) F. D. Rossini "Selected Values of Chemical Thermodynamic Properties. Part 1. Tables," Department of Commerce, U. S. A. (1961).