The Chemical Behavior of Low Valence Sulfur Compounds. VII.[1] The Oxidation of Ammonium Sulfide and Ammonium Sulfite with Compressed Oxygen in Aqueous Ammonia Solution

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The oxidation of ammonium sulfide and ammonium sulfite with compressed oxygen in aqueous ammonia soultion was studied in order to confirm the formation of ammonium sulfamate. Ammonium sulfite is easily oxidized to ammonium thiosulfate through polysulfides with oxygen and further to ammonium sulfamate and ammonium sulfate. Suitable conditions for producing ammonium sulfamate were found to be: initial concentration of ammonium sulfide 2.0 mol/*l*, temperature 100°C, concentration of ammonia 12 mol/*l*, concentration of cupric ion 0.1 mol/*l* and oxygen pressure 50 kg/cm^2. Though ammonium sulfite is wholly oxidized to ammonium sulfate under the same conditions, it is partially oxidized to ammonium sulfamate besides sulfate in the presence of cupric ion under high concentration of ammonia. The mode of oxidation might differ from that of ammonium thiosulfate, ammonium sulfide and elemental sulfur because of no formation of polythionate as an intermediate.

In a previous study, the oxidation of ammonium thiosulfate was investigated for the purpose of production of ammonium sulfamate and it was found that the yield was improved by increasing the concentration of ammonia. Ammonium sulfide and ammonium sulfite can be easily obtained as industrial raw materials. If ammonium sulfamate could be produced by aqueous oxidation of these compounds, it would be of interest for industry. The aqueous oxidation of these compounds has been investigated and some results have been applied to the industrial production processes of ammonium sulfate.[2] However, no formation of ammonium sulfamate has been reported. We have studied the oxidation of ammonium sulfide and ammonium sulfite in concentrated aqueous ammonia solutions in order to obtain the suitable conditions for the industrial production of ammonium sulfamate.

Experimental

Apparatus and Procedure. The autoclave shown in a previous paper[3] was used.

An ammoniacal solution of ammonium sulfide was prepared from concentrated aqueous ammonia and hydrogen sulfide controlling the concentration of sulfide to be in the range 1.0—2.0 mol/*l*. A certain amount of cupric oxide as a catalyst, 400 m*l* of the above solution(or about 45 g of crystalline ammonium sulfite and 400 m*l* of concentrated aqueous ammonia) were put in the autoclave and kept in a heated glycerine bath. Temperature was regulated within 0.5°C. When the autoclave was heated to the desired temperature, oxygen was introduced, pressure being kept at a certain value. After the temperature and pressure became constant, about 15 m*l* of the reaction solution was withdrawn every few hours and was analyzed.

Analysis. Concentration of sulfide and free ammonia in the original solution were determined by iodometric and acidimetric titration.

Soluble sulfide, thiosulfate, sulfite, sulfamate, sulfate, and cupric ion were determined as follows.

Soluble Sulfide: Soluble sulfide appearing in the initial stage of the oxidation of ammonium sulfide was determined by iodometric differential titration.

Thiosulfate: In the presence of soluble sulfide, thiosulfate was determined by iodometry after removal of soluble sulfide as cadmium sulfide. In the presence of cupric ion, it was directly titrated with 0.05N standard solution of iodine after adding 0.01M EDTA solution for masking cupric ion, and adding 4N acetic acid until the sample solution became acidic with bromocresol purple.

Sulfite: After pouring the sample solution into 0.05N solution of iodine and then adding 0.01M EDTA solution as a masking reagent of cupric ion and 4N acetic acid, the excess iodine was titrated with 0.05N standard solution of sodium thiosulfate.

Sulfamate: In the oxidation of ammonium sulfide, sulfamate was determined by the same procedure described previously.[4] In the oxidation of ammonium sulfite, sulfamate was determined as follows: 0.1N potassium permanganate was added to the sample solution to oxidize sulfite to sulfate. After being kept standing for 10 min, the excess permanganate was decomposed by adding 2N solution of ammonium formate, and the precipitate formed was removed by filtration. Filtrate was acidified with 4N acetic acid and the barium sulfate precipitated was removed by filtration. After the filtrate was heated on a water bath and concentrated hydrochloric acid and 1M sodium nitrite were added, sulfamate was determined as barium sulfate by gravimetry.

Sulfate: In the oxidation of ammonium sulfide, sulfate was determined by the same procedure previously.[4] In the oxidation of ammonium sulfite, sulfate was determined as follows: After adding an aqueous solution formaldehyde into the sample solution and then acidifying it with 4N acetic acid, sulfate was precipitated as barium sulfate with the addition of 0.5M solution of barium chloride. Barium sulfate was determined by gravimetry.

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[2] Samuel B. Thomas, U. S. 2869844 (1959). Bergwerksverband zur Verwertung von Schutzrechten der Kohlentechnik G. m. b. H., Brit. 718675 (1954); Ger. 905243 (1954); Ger. 925408 (1955); S. Hori and S. Nakagawa, *Tokyo Kogyo Shikensho Hokoku* (Rept. Govt. Chem. Ind. Res. Inst., Tokyo), **37**, 1 (1942); S. Hori, *ibid.*, **46**, 297 (1952).

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

[4] K. Naito, M. C. Shieh, M. Yoshida, and T. Okabe, *ibid.*, **43**, 1365 (1970).

Results and Discussion

Oxidation of Ammonium Sulfide with Compressed Oxygen in Aqueous Ammonia Solution. Ammonium sulfide is rapidly oxidized with oxygen to thiosulfate through polysulfides. At the maximum concentration of thiosulfate, cupric ion once predipitated begins to dissolve in the solution and accelerate the oxidation of thiosulfate to form sulfamate and sulfate. A general view of the oxidation of ammonium sulfide is shown in Fig. 1. A small amount of imidodisulfonate and nitrite were also detected in the final solution.

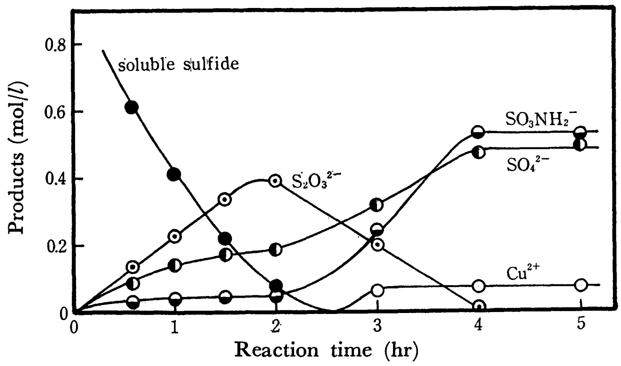

Fig. 1. General view of the whole reaction.
Temp.: 100°C, P_{O_2}: 25 kg/cm², NH_3 concn.: 12 mol/*l*, Cu^{2+} ion concn.: 0.05 mol/*l*, $(NH_4)_2S$ initial concn.: 1.0/mol/*l*

Effect of the Concentration of Cupric Ion: The effect of the concentration of cupric ion was examined in the range 0.05—0.3 mol/*l*. It was found that the proper concentration of cupric ion is 0.1 to 0.2 mol/*l* for the oxidation of ammonium thiosulfate.[4] The results are shown in Figs. 2, 3, and 4. The yield of sulfamate was not affected by the concentration of cupric ion.

Effect of Oxygen Pressure: The effect of oxygen pressure was examined in th range 25 to 75 kg/cm². Pressure is given in terms of total pressure, in which both the vapor pressure of water and ammonia are included in addition of that of oxygen. The yield of sulfamate decreases with the increase of oxygen pressure. It seems that there is an induction period at 25 kg/cm² due to the slow oxidation of thiosulfate under a low oxygen pressure.

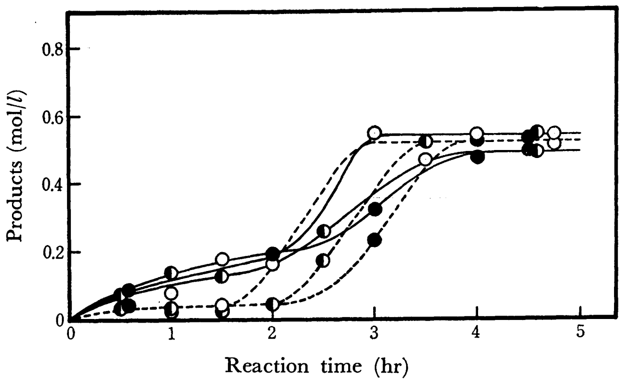

Fig. 2. Effect of the concentration of cupric ion (I).
Temp.: 100°C, P_{O_2}: 25 kg/cm², NH_3 concn,: 12 mol/*l*, $(NH_4)_2S$ initial concn.: 1.0 mol/*l*

Cu^{2+} ion concn.:	0.05 mol/*l*	0.1 mol/*l*	0.2 mol/*l*
SO_4^{2-}	—●—	—◐—	—○—
$SO_3NH_2^-$	--●--	--◐--	--○--

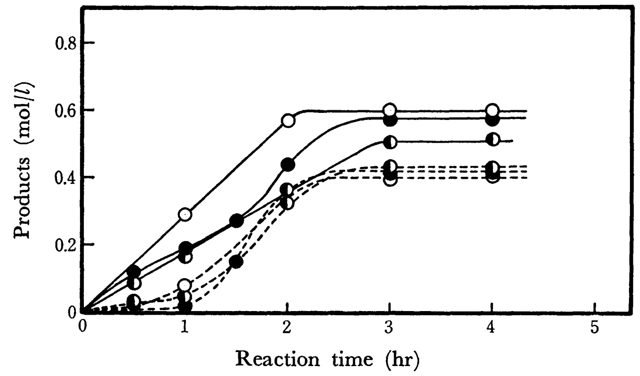

Fig. 3. Effect of the concentration of cupric ion (II).
Temp.: 100°C, P_{O_2}: 50 kg/cm², NH_3 concn.: 12 mol/*l*, $(NH_4)_2S$ initial concn.: 1.0 mol/*l*

Cu^{2+} ion concn.:	0.05 mol/*l*	0.1 mol/*l*	0.2 mol/*l*
SO_4^{2-}	—●—	—◐—	—○—
$SO_3NH_2^-$	--●--	--◐--	--○--

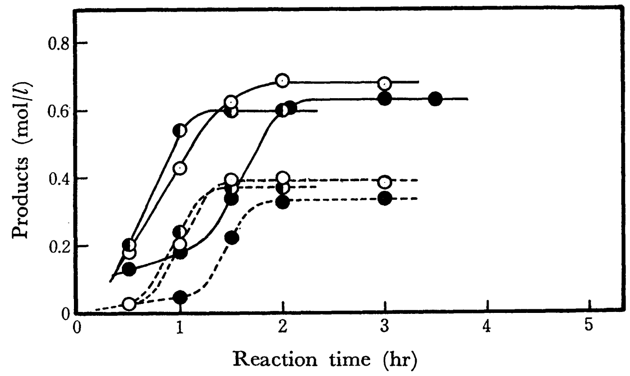

Fig. 4. Effect of the concentration of cupric ion (III).
Temp.: 100°C, P_{O_2}: 75 kg/cm², NH_3 concn.: 12 mol/*l*, $(NH_4)_2S$ initial concn.: 1.0 mol/*l*,

Cu^{2+} ion concn.:	0.05 mol/*l*	0.1 mol/*l*	0.2 mol/*l*
SO_4^{2-}	—●—	—◐—	—○—
$SO_3NH_2^-$	--●--	--◐--	--○--

Effect of the Initial Concentration of Ammonium Sulfide: The yield of sulfamate is affected largely by the concentration of thiosulfate formed as an intermediate. The effect was examined by varying the initial concentration of ammonium sulfide from 1.0 to 2.0 mol/*l*. The results are shown in Fig. 5. It was found that the yield of sulfamate increases with the increase of initial concentration of ammonium sulfide, but the reaction time is hardly affected.

From the results, it seems that ammonium sulfide is oxidized to thiosulfate through polysulfides, and thiosulfate is further oxidized to sulfamate and sulfate.

Suitable conditions for the preparation of ammonium sulfamate in the highest yield are: initial concentration on ammonium sulfide 2.0 mol/*l*, reaction temperature 100°C, concentration of ammonia 12 mol/*l*, concentration of cupric ion 0.1 mol/*l* and oxygen pressure 50 kg/cm².

Oxidation of Ammonium Sulfite with Compressed Oxygen in Aqueous Ammonia Solution. The oxidation of ammonium sulfite, whose initial concentration was 1.0 mol/

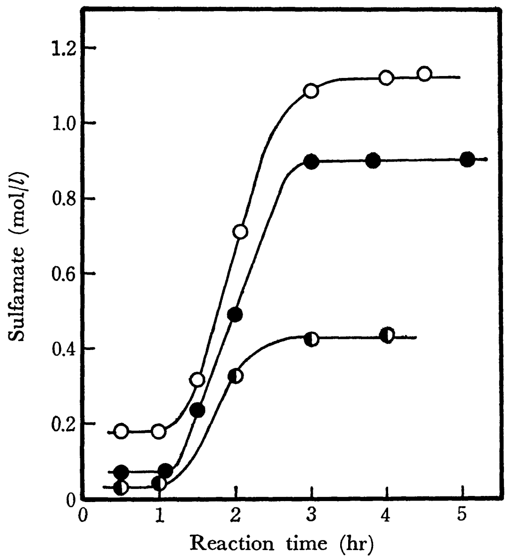

Fig. 5. Effect of the initial concentration of ammonium sulfide.
Temp.: 100°C, P_{O_2}: 50 kg/cm^2, NH_3 concn.: 12 mol/*l*, Cu^{2+} ion concn.: 0.1 mol/*l*
$(NH_4)_2S$ initial concn.:
○ 2.0 mol/*l*, ● 1.7 mol/*l*, ◐ 1.0 mol/*l*

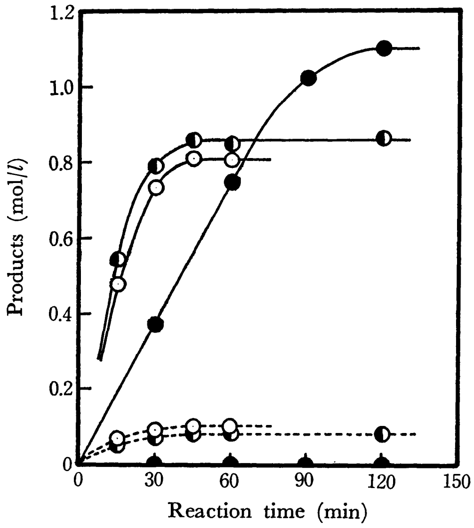

Fig. 6. Effect of the concentration of cupric ion.
Temp.: 100°C, P_{O_2}: 25 kg/cm^2, NH_3 concn.: 16 mol/*l*, $(NH_4)_2SO_3$ initial concn.: 1.0 mol/*l*

Cu^{2+} ion concn.:	0.2 mol/*l*	0.1 mol/*l*	0 mol/*l*
SO_4^{2-}	—○—	—◐—	—●—
$SO_3NH_2^-$	--○--	--◐--	--●--

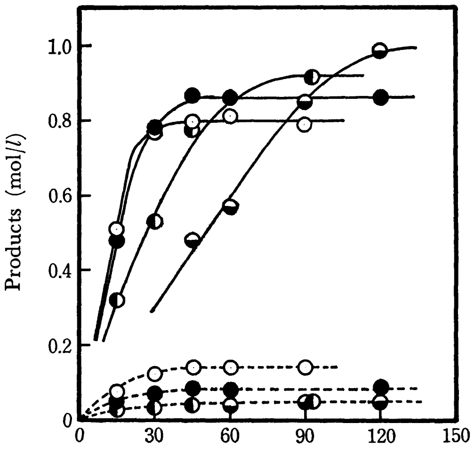

Fig. 7. Effect of temperature.
P_{O_2}: 25 kg/cm^2, NH_3 concn.: 16 mol/*l*, Cu^{2+} ion concn.: 0.1 mol/*l*, $(NH_4)_2SO_3$ initial concn.: 1.0 mol/*l*

Temp:	60°C	80°C	100°C	120°C
SO_4^{2-}:	—◒—	—◐—	—●—	—○—
$SO_3NH_2^-$	--◒--	--◐--	--●--	--○--

l, was carried out in a concentrated aqueous solution of ammonia containing 0 to 0.2 mol/*l* of cupric ion at 60—120°C and under the pressure of 25 kg/cm^2. The results are shown in Figs. 6 and 7. The formation of ammonium sulfamate was observed in the oxidation of ammonium sulfite, and a small amount of dithionate was detected also in the final solution. Thiosulfate and polythionates which exist as intermediates in the oxidation of elemental sulfur, ammonium thiosulfate and ammonium sulfide were not detected during the course of oxidation. This suggests that the oxidation mechanism of ammonium sulfite differs from that of elemental sulfur, ammonium thiosulfate and ammonium sulfide.

The presence of cupric ion accelerates remarkably the oxidation, but makes the yield of sulfate decrease. The sulfite corresponding to the decrement of sulfate may be converted into dithionate, for a small amount of dithionate is detected in the final solution.

The elevation of temperature accelerates fairly the oxidation at temperature below 100°C, and improves the yield of sulfamate. This differs from that on the oxidation of ammonium thiosulfate and elemental sulfur. Though the formation of ammonium sulfamate has been achieved, its low yield makes the industrial application process still difficult.