BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1365—1372 (1970)

The Chemical Behavior of Low Valence Sulfur Compounds. III.*[1] Production of Ammonium Sulfamate by the Oxidation of Ammonium Thiosulfate

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(Received August 1, 1969)

The oxidation of ammonium thiosulfate with compressed oxygen in aqueous ammonia solution was examined. It was found that ammonium sulfamate and ammonium sulfate are mainly produced and a small amount of nitrite and imidodisulfonate obtained in the final solution. The most suitable conditions to produce ammonium sulfamate from ammonium thiosulfate industrially are as follows: reaction temperature 100°C, oxygen pressure 50 kg/cm^2, concentration of ammonia 16 mol/l, concentration of cupric ion 0.1—0.2 mol/l. The electrolytic oxidation, hydrogen peroxide oxidation and ozone oxidation of ammonium thiosulfate were also examined.

The authors, in their studies on the chemical behavior of low valence sulfur compounds, have investigated the oxidation of elemental sulfur with compressed oxygen in aqueous ammonia solution.[1)] It was found that oxidation proceeds through thiosulfate and some low polythionates as intermediates, and under a suitable condition, a large amount of ammonium sulfamate is formed by the oxidation. The oxidation of thiosulfate may be said to be the rate determining step of the overall reaction and has an important effect upon the yield of sulfamate.

The air-oxidation of thiosulfate is a very slow reaction under normal pressure. Under atmospheric pressure and normal temperature, a trace of sodium tetrathionate was detected in the air-oxidation of sodium thiosulfate by Schulek and Koros,[2)] and ammonium thiosulfate was observed to be oxidized very little in a neutral or alkaline solution by Koseki.[3)]

The oxidation of thiosulfate with compressed air or oxygen has been rarely investigated. In Gluud's work,[4)] elemental sulfur and sodium sulfate were detected in a neutral solution, but only sodium sulfate in an alkaline solution at 100°C under an air-pressure of 10 kg/cm^2. The formation of ammonium trithionate was confirmed by Forward[5)] in the oxidation of ammonium thiosulfate with compressed air. The oxidation of ammonium thiosulfate with compressed oxygen in aqueous ammonia solution has been investigated in the author's laboratory, and Kanematsu[6)] found that the oxidation is almost a zero order reaction and that metal ions such as copper, nickel and cobalt extremely accelerate the oxidation reaction, although the products were not sufficiently confirmed.

In the present study, effort was made to clarify the chemical behavior of thiosulfate in oxidation and to obtain the most suitable conditions for industrial production of ammonium sulfamate from ammonium thiosulfate.

Experimental

Apparatus and Procedure. In the oxidation with oxygen, two autoclaves, one the same as shown in a previous paper,[1)] and the other a Shin-Sakashita Seisakusho Model SR-100 with 1 l capacity lined with Hastelloy-F, were used for the reaction.

On addition of crystalline ammonium thiosulfate, aqueous ammonia and cupric sulfate as a catalyst, the autoclave was kept in a heated glycerine bath at temperatures regurated within 0.5°C. When the autoclave was heated to fixed temperature, oxygen was introduced and kept at a constant pressure. After the introduced oxygen showed the fixed pressure, 15 ml of the solution was withdrawn every few hours and was analyzed.

Electrolytic oxidation was carried out by keeping the anode potential constant with Yanagimoto Controlled Potential Electrolyser Model VE-3. The cell was a 300 ml closed glass vessel with platinum plates as electrodes and with a Soxlay filter paper (Toyo No. 84) as a diaphragm. A saturated calomel electrode (SCE) was used as a reference electrode, and concentrated aqueous ammonia was used as an intermediate solution and they were coupled with a salt bridge. The cell and electrode were kept at 0°C in an ice bath. Ammo-

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[1] Preceding Paper: II. K. Naito, S. Takei and T. Okabe, This Bulletin, **43**, 1360 (1970).

[2] Present address: Idemitsu Kōsan Co., Ltd., Chiba.

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

2) E. Schulek and E. Koros, *Magy. Chem. Folyoirat*, **56**, 426 (1950); *Chem. Abstr.*, **46**, 1380 (1952).

3) K. Koseki, unpublished data.

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

5) F. A. Forward, *Trans. Can. Inst. Min. Met.*, **66**, 191 (1957).

6) T. Okabe, and K. Kanematsu Lecture argument of the 4th Symposium on High Pressure, Japan (1962).

nium thiosulfate and aqueous ammonia were added into the cell and electrolyzed. The quantity of electricity was roughly calculated from the current and time.

Hydrogen peroxide oxidation was carried out by adding C.P. grade hydrogen peroxide solution to thiosulfate solution drop by drop from a buret at a constant temperature with constant stirring.

Analysis. The final solution contained sulfamate, sulfate, cupric ion, sometimes traces of nitrite and imidodisulfonate. When nitrite is present in the solution, it is necessary to determine these ions by avoiding the interference of nitrite, because nitrite decomposes sulfamate and imidodisulfonate to sulfate. The determination of sulfur compounds such as sulfamate, sulfate and imidodisulfonate was successfully carried out by the method proposed by Sisler and Audrieth,[7] and the determination of nitrite and cupric ion was performed by an improved iodimetric method proposed originally by Kolthoff and Abeledo.[8]

The sample solution was diluted to a suitable concentration and then analyzed.

SO_4^{2-}: After the addition of an equal volume of 4 mol/*l* aqueous ammonia to one portion of the sample solution, it was heated on a water bath. Barium salts of sulfate, imidodisulfonate and carbonate were precipitated by the addition of 0.5 mol/*l* solution of barium chlorid in excess. The precipitate was filtered and washed with 4 mol/*l* aqueous ammonia making the filtrate within 200 m*l*. It was washed with 4 mol/*l* acetic acid and a small amount of 0.1 mol/*l* hydrochloric acid to decompose and remove barium imidodisulfonate and barium carbonate making the filtrate within 200 m*l*, and was determined as barium sulfate by the usual method.

$SO_3NH_2^-$: The filtrate obtained by washing with aqueous ammonia was evaporated to 100 m*l*, and acidified with concentrated hydrochloric acid. Sulfamate was decomposed with sodium nitrite. The precipitate of barium sulfate was determined by the usual method.

$HN(SO_3)_2^{2-}$: The filtrate obtained by washing with acetic acid and hydrochloric acid was evaporated and acidified with 4 mol/*l* hydrochloric acid. Imidodisulfonate was decomposed with sodium nitrite as follows. Imidodisulfonate was determined as barium sulfate

$$HN(SO_3)_2^{2-}+NaNO_2+HCl = 2HSO_4^-+N_2+NaCl$$

by the gravimetric method.

Total Amount of Sulfur: One portion of the sample solution was evaporated nearly to dryness. Potassium chlorate and concentrated hydrochloric acid were added in order to oxidize all sulfur compounds to sulfate. After evaporation to near dryness again, the sulfate in the solid was extracted with 4 mol/*l* hydrochloric acid and determined as barium sulfate.

Cu^{2+}: After the addition of potassium carbonate and urea, one portion of the sample solution was acidified with concentrated hydrochloric acid. When the generation of carbon dioxide ceased, potassium iodide was added and the iodine liberated was titrated with a standard solution of sodium thiosulfate.

NO_2^-: After addition of potassium carbonate and urea to one portion of the sample solution, nitrogen gas was passed through it for 15—20 min, and for additional 5—10 min after the addition of potassium iodide. It was acidified with hydrochloric acid and iodine liberated was titrated with a standard solution of sodium thiosulfate. The nitrite was obtained by subtraction of cupric ion from the total.

The solution taken out during the course of the reaction contains thiosulfate and traces of polythionates in addition to the above-mentioned compounds. For determination of thiosulfate by the iodimetric method, it is necessary to remove cupric ion previously added as a catalyst. When the concentration of cupric ion is low, it can be easily removed by passing the solution through ion-exchange resin column, but when the cupric ion concentration is higher than 0.1 mol/*l*, it is difficult to be removed with the resin because of the complex formation of cupric ion with thiosulfate. In this case, therefore, sulfate and sulfamate are determined as follows:

SO_4^{2-}: One portion of the sample solution was controlled at $pH=5$ with 4 mol/*l* acetic acid by using bromocresol purple. By adding iodine solution, thiosulfate in the sample solution was oxidized to tetrathionate. Sulfate was precipitated as barium sulfate by adding 0.02 mol/*l* solution of barium chloride and determined.

$SO_3NH_2^-$: By adding 1 mol/*l* solution of silver nitrate to one portion of the sample solution heated on a water bath, thiosulfate and some low polythionates in the solution were decomposed and converted into silver sulfide, sulfate and elemental sulfur. After the addition of barium chloride solution, insoluble matters such as silver sulfide, barium sulfate and silver chloride were removed by filtration. Sulfamate remained in the filtrate and was determined by the above method.

Results and Discussion

Oxidation of Ammonium Thiosulfate with Compressed Oxygen in Aqueous Ammonia Solution. In the present study, the formation of nitrite and imidodisulfonate were observed for the first time. Nitrite was ascertained by the Peter-Griess reaction, and imidodisulfonate was identified by X-ray diffraction of barium salt. During the cource of preliminary experiments, the composition of the products seemed to differ somewhat with autoclave made of SUS 32 stainless steel and that lined with Hastelloy-F alloy. In order to clarify the effect of reactor materials, several materials were tested for the reaction. However, no remarkable results were obtained as shown in Table 1.

The Effect of the Concentration of Cupric Ion. It has been found that cupric ion is the most suitable catalyst to increase the reaction rate and the yield of sulfamate in the oxidation of elemental sulfur. Although a similar effect was expected in the present study, the reaction was examined in the presence of 10^{-3} to 1.0 mol/*l* cupric ion.

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[7] H. H. Sisler and L. F. Audrieth, *J. Amer. Chem. Soc.*, **61**, 3392 (1931).

[8] C. A. Abeledo and I. M. Kolthoff, *ibid.*, **53**, 2893 (1939).

TABLE 1. EFFECT OF REACTOR MATERIAL

Reactor material	Reaction time(hr)	$[Cu^{2+}]$ (mol/*l*)	Yield of products(mol%) $SO_3NH_2^-$	SO_4^{2-}	$NH(SO_3)_2^{2-}$	$[NO_2^-]$ (mol/*l*)
SUS 32	6.0—6.5	0.5	62.70	35.90	1.40	—
Ti	5.0—5.5	0.2	63.84	33.48	1.19	0.0549
	5.0—5.5	0.5	59.86	39.96	0.78	0.0137
	5.0—5.5	0.7	62.85	34.24	2.20	0.0183
10 g of* Hastelloy	6.0—6.5	0.5	63.86	35.81	trace	0.0194
20 g of* Hastelloy	6.0—6.5	0.5	60.47	42.37	2.48	0.0057
30 g of* Hastelloy	6.0—6.5	0.5	61.03	38.51	1.12	0.0034

Reaction temperature: 100°C
Oxygen pressure: 50 kg/cm^2
Concn. of ammonia: 16 mol/*l*
Concn. of total sulfur: 2 S-g atom/*l*

* Small tip of Hastelloy-F was added into the autoclave made of SUS 32 stainless steel.

TABLE 2. EFFECT OF CUPRIC ION ON THE COMPOSITION OF THE FINAL SOLUTION

$[Cu^{2+}]$ (mol/*l*)	Yields of products (mol%) $SO_3NH_2^-$	SO_4^{2-}	$HN(SO_3)_2^{2-}$	$[NO_2^-]$ (mol/*l*)
0.0992	63.09	34.03	2.88	—
0.1873	67.60	37.85	1.76	0.0215
0.3003	64.96	37.04	3.86	0.0386
0.5022	62.69	35.88	—	0.0057
0.6189	60.64	39.16	—	0.0069
0.8225	60.57	40.39	—	0.0028

Reaction temperature: 100°C
Oxygen pressure: 50 kg/cm^2
Ammonia concn.: 16 mol/*l*
Concn. of total sulfur: 2 S-g atom/*l*

The results obtained are shown in Table 2 and Figs. 1, 2 and 3. It is obvious that the reaction time is shortened with the increase of the concentration of cupric ion, but the yield of sulfamate has its maximum at 0.1—0.2 mol/*l* of cupric ion. The formation of sulfamate shows a zero order reaction in the concentration higher than 0.1 mol/*l* of cupric ion. The catlytic oxidation of thiosulfate has been explained by Abel[9] as

$$2Cu^{2+} + 2S_2O_3^{2-} = 2Cu^+ + S_4O_6^{2-} \quad \text{(fast)}$$
$$2Cu^+ + \tfrac{1}{2}O_2 = 2Cu^{2+} + O^{2-} \quad \text{(slow)}$$
$$O^{2-} + 2H^+ = H_2O \quad \text{(fast)}$$

But it is supposed that cupric ion exists as an ammine complex in aqueous ammonia solution and in the presence of thiosulfate, forms further a thio-

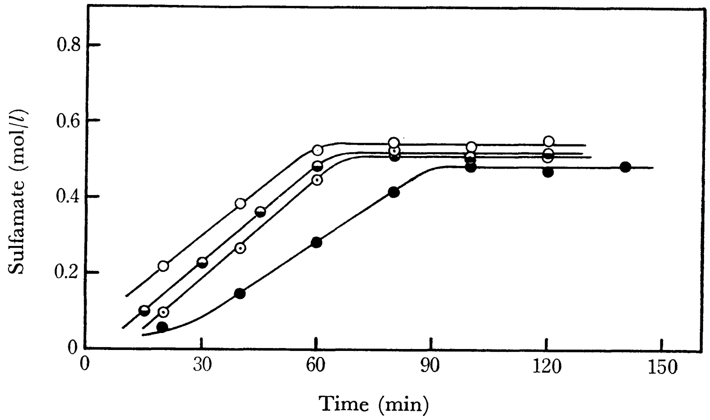

Fig. 1. Effect of the concentration of cupric ion with the yield of sulfamate on the oxidation of ammonium thiosulfate.
Reaction temp.: 100°C, Oxygen press.: 75 kg/cm^2, $(NH_4)_2S_2O_3$ concn.: 0.5 mol/*l*, NH_3 concn.: 16 mol/*l*
Cu^{2+} ion concn.: ○ 0.3 mol/*l* ◒ 0.1 ⊙ 0.01 ● 0.001

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[9] E. Abel, *Ber.*, **56**, 1076 (1923).

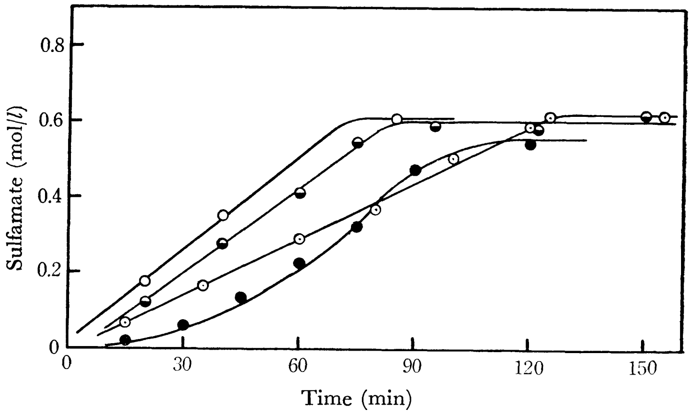

Fig. 2. Effect of the concentration of cupric ion with the yield of sulfamate on the oxidation of ammonium thiosulfate.
Reaction temp.: 100°C, Oxygen press.: 50 kg/cm^2,
$(NH_4)_2S_2O_3$ concn.: 0.5 mol/l, NH_3 concn.: 16 mol/l
Cu^{2+} ion concn.: ○ 0.5 mol/l ◒ 0.1 ⊙ 0.01 ● 0.001

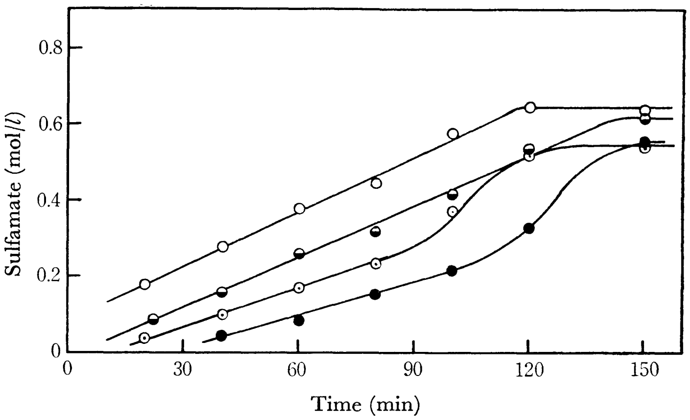

Fig. 3. Effect of the concentration of cupric ion with the yield of sulfamate on the oxidation of ammonium thiosulfate.
Reaction temp.: 100°C, Oxygen press.: 25 kg/cm^2,
$(NH_4)_2S_2O_3$ concn.: 0.5 mol/l, NH_3 concn. 16 mol/l,
Cu^{2+} ion concn.: ○ 0.5 mol/l ◒ 0.1 ⊙ 0.01 ● 0.001

sulfate complex. Abel's mechanism, therefore, can not be easily accepted. The formation of complexes between cobalt ammine[10)] or cupric ethylenediamine[11)] and thiosulfate has been actually known to take place.

The Effect of Oxygen Pressure. The effect of oxygen pressure, in which the vapor pressure of the solution was included, was examined in the range of 25—75 kg/cm^2. As shown in Figs. 4, 5 and 6, the reaction time is shortened with the increase of presure. The yield of sulfamate has its maximum at 50 kg/cm^2, while in the presence of 0.1 to 0.5 mol/l of cupric ion, it decreases with the increase of the pressure.

The Effect of the Ammonia Concentration. The ammonia concentration was varied from 4 to 16 mol/l. The results are shown in Fig. 7. An increase in the ammonia concentration improves the yield of sulfamate, and accelerates the reaction slightly. This tendency for the yield of sulfamate to increase in a high concentration of ammonia is quite similar to that of the oxidation of elemental sulfur and the decomposition of potassium trithionate in aqueous ammonia solution.

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10) H. Yoneda, This Bulletin, **28**, 125 (1955). Y. Shimura and R. Tsuchida, *ibid.*, **28**, 572 (1955).

11) H. Yoneda, *ibid.*, **29**, 68 (1956).

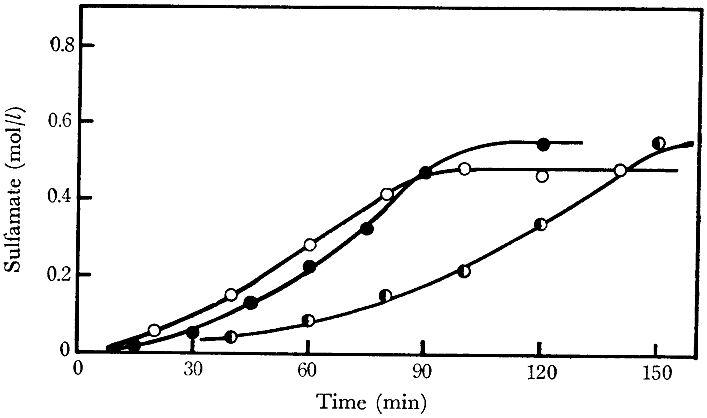

Fig. 4. Effect of the oxygen pressure with the yield of sulfamate in the oxidation of ammonium thiosulfate.

Reaction temp.: 100°C, Cu^{2+} concn.: 10^{-3} mol/*l*,
$(NH_4)_2S_2O_3$ concn.: 0.5 mol/*l*, NH_3 concn.: 16 mol/*l*,
Oxygen pressure: ○ 75 kg/cm^2 ● 50 ◐ 25

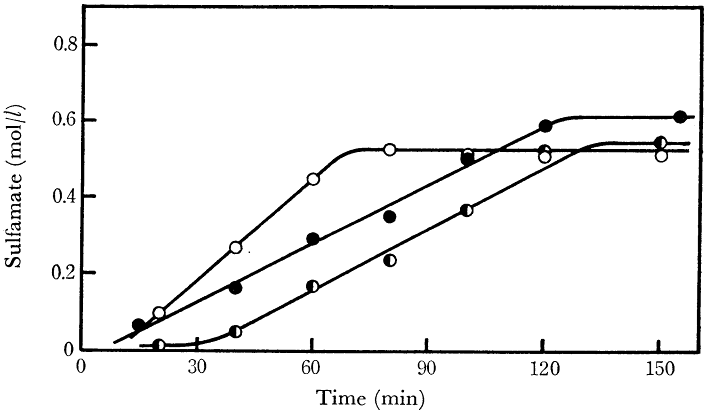

Fig. 5. Effect of the oxygen pressure with the yield of sulfamate in the oxidation of ammonium thiosulfate.

Reaction temp.: 100°C, Cu^{2+} concn.: 10^{-2} mol/*l*,
$(NH_4)_2S_2O_3$ concn.: 0.5 mol/*l*, NH_3 concn.: 16 mol/*l*,
Oxygen pressure: ○ 75 kg/cm^2 ● 50 ◐ 25

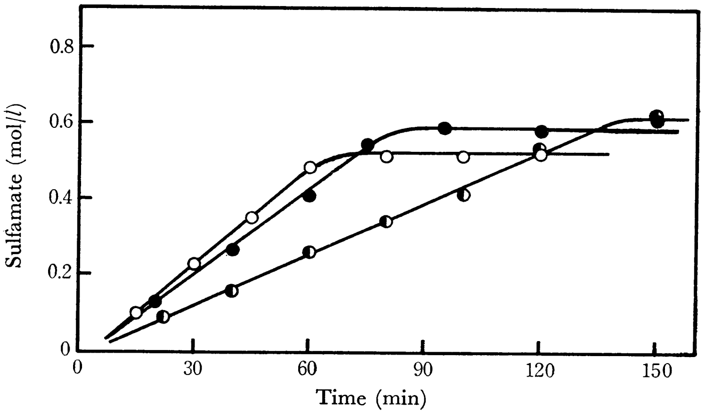

Fig. 6. Effect of the oxygen pressure with the yield of sulfamate in the oxidation of ammonium thiosulfate.

Reaction temp.: 100°C, Cu^{2+} concn.: 0.1 mol/*l*,
$(NH_4)_2S_2O_3$ concn.: 0.5 mol/*l*, NH_3 concn.: 16 mol/*l*,
Oxygen pressure: ○ 75 kg/cm^2 ● 50 ◐ 25

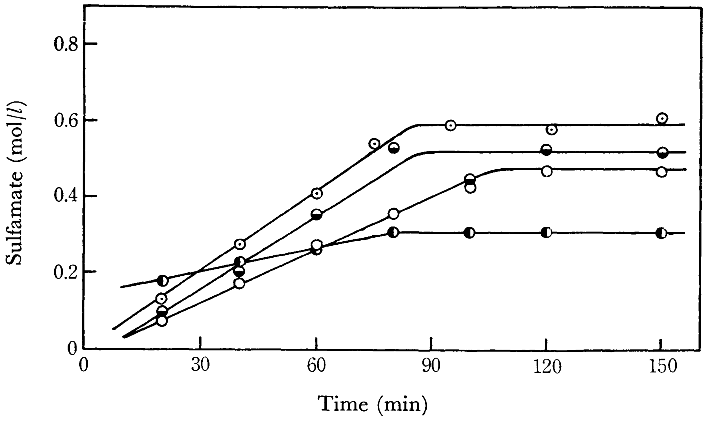

Fig. 7. Influence of the ammonia concentration with the yields of sulfamate in the oxidation of ammonium thiosulfate in aqueous ammonia.
Reaction temp.: 100°C, Oxygen press.: 50 kg/cm^2,
$(NH_4)_2S_2O_3$ concn.: 0.5 mol/*l*, Cu^{2+} ion concn.: 0.1 mol/*l*,
$[NH_3]$: ⊙ 16 mol/*l* ◒ 12 ○ 8 ◐ 4

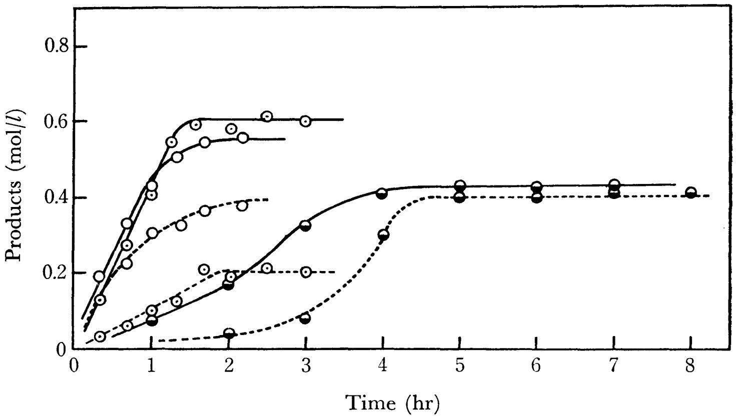

Fig. 8. Influence of the reaction temperature in the oxidation of thiosulfate in aqueous ammonia.
$(NH_4)_2S_2O_3$ concn.: 1 mol/*l*, Oxygen press.: 50 kg/cm^2,
NH_3 conc.: 16 mol/*l*, Cu^{2+} ion concn.: 0.1 mol/*l*,
$SO_3NH_2^-$: ---○--- 120°C ---⊙--- 100 ---◒--- 80

Table 3. Results obtained in the electrolytic oxidation of ammonium thiosulfate in aqueous ammonia solution

Quantity of electricity (C)	Concn. of reactant and products (S-g atom/*l*)					
	$S_2O_3^{2-}$	$S_2O_6^{2-}$	$S_3O_6^{2-}$	$S_4O_6^{2-}$	SO_4^{2-}	$SO_3NH_2^-$
0	1.052	0	0	0	0	0
10,500	0.428	0	0.481	0.054	0.036	0.034
19,800	0.013	0	0.748	0.096	0.079	0.091
36,700	0.018	0.108	0.747	0	0.152	0.108
77,000	0.021	0.284	0.446	0	0.306	0.184

Reaction temperature:	0°C
Ammonia concn.:	12.25 mol/*l*
Amounts of ammonium thiosulfate:	0.145 mol
Anode potential:	1.5 V (*vs.* SCE at 30°C)

The Effect of Reaction Temperature. The reaction temperature was varied from 80 to 120°C. The results are shown in Fig. 8. The reaction time is shortened with the rise in reaction temperature, while the yield of sulfamate has its maximum at 100°C. It seems that an induction period appears at 80°C in the beginning of the reaction.

From the above results, the suitable conditions to prepare ammonium sulfamate by the oxidation of ammonium thiosulfate with compressed oxygen in aqueous ammonia solution are as follows: the concentration of cupric ion 0.1—0.2 mol/*l*, the ammonia concentration 16 mol/*l*, oxygen pressure 50 kg/cm^2 and reaction temperature 100°C.

The Electrolytic Oxidation of Ammonium Thiosulfate in Aqueous Ammonia Solution. Ammonium thiosulfate was dissolved in 12.25 mol/*l* aqueous ammonia to make 0.145 mol/*l* solution, and oxidized by means of anodic oxidation at 0°C and 1.5 V of the anode potential (*vs.* SCE at 30°C). The results are shown in Table 3.

The oxidation was carried out in a high concentration solution of ammonia at a low temperature, because the yield of sulfamate increases with the increase of the concentration of ammonia and with the lowering of temperature. As the oxidation was carried out at a high potential to improve the reactivity, some known reactions took place simultaneously. From the results, it may be said that thiosulfate is oxidized to tetrathionate or trithionate and converted finally to sulfate, sulfamate and dithionate.

The electrolytic oxidation of sodium thiosulfate has been studied by several investigators.12-14) It has found that the electrolytic oxidation of sodium thiosulfate proceeds as follows:

$$S_2O_3{}^{2-} = S_2O_3{}^{-} + e$$
$$2S_2O_3{}^{-} = S_4O_6{}^{2-}$$
$$S_2O_3{}^{2-} + H_2O = SO_4{}^{2-} + S + 2H^+ + 2e$$

The first reaction takes place mainly at the low voltage in a neutral solution. From the present results, it is not clear whether tetrathionate or trithionate is first formed from thiosulfate. However, it might be certain that the final products such as sulfamate and sulfate are formed from the low polythionates. The formation of sulfamate in the electrolytic oxidation of ammonium thiosulfate seems to be new.

The Oxidation of Ammonium Thiosulfate with Hydrogen Peroxide and Ozone in Aqueous Ammonia Solution. Hydrogen peroxide and ozone were tested as stronger oxidants than oxygen for the production of sulfamate. The results are shown in Tables 4 and 5. The oxidation of thiosulfate with hydrogen peroxide, an exothermic reaction, is one which accompanies simultaneous decomposition of hydrogen peroxide because of the alkalinity. Kurtenacker and Benson reported that thiosulfate is completely oxidized to sulfate with hydrogen peroxide in an alkaline solution and the oxidation is useful for the determination of thiosulfate.15) The formation of sulfamate in this reaction is new information. As the presence of trithionate in the reaction solution was confirmed by thinlayer chromatography, the formation of sulfamate should proceed through the course of trithionate decomposition in an aqueous ammonia solution.

TABLE 4. RESULTS OBTAINED FROM THE HYDROGEN PEROXIDE OXIDATION OF AMMONIUM THIOSULFATE IN AQUEOUS AMMONIA

Sample No.	Concn. of the products (mol/*l*)	
	sulfamate	sulfate
1	0.0602	0.2107
2	0.0977	0.2176
3	0.0716	0.2208

Reaction temperature: 0—10°C
Concn. of ammonia: 12 mol/*l*
28% Solution of H_2O_2: 40 m*l*
3N (f=0.8740) solution of $Na_2S_2O_3$: 76 m*l*

TABLE 5. RESULTS OBTAINED FROM THE OZONE OXIDATION OF AMMONIUM THIOSULFATE IN AQUEOUS AMMONIA SOLUTION

Reaction time (hr)	Composition of the reaction solution (mol/*l*)			
	$S_2O_3{}^{2-}$	$SO_3{}^{2-}$	$SO_3NH_2{}^{-}$	$SO_4{}^{2-}$
0	0.900	0.103	0.049	0.044
2	0.641	0.245	0.044	0.505
7	0.003	0.000	0.084	2.001

Reaction temperature: 0—4°C
Ammonia concn.: 12 mol/*l*
flow rate of ozone: 5.02 g/hr

The ozone oxidation differes extremely from the above-mentioned oxidation in which the yield of sulfamate is very low, and, traces of sulfite and low polythionates appear. In a previous work by B. C. Brodie,16) it was found that sodium thiosulfate is oxidized to dithionate, sulfate and sulfur

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12) C. J. Thatcher, *Z. Phys. Chem.*, **47**, 641 (1904); *Trans. Electrochem. Soc.*, **45**, 157 (1924).

13) S. Glasstone and A. Hickling, "Electrolytic Oxidation and Reduction," Chapman & Hall, Ltd., London (1935), pp. 248—251.

14) W. D. Bancroft, *Trans. Electrochem. Soc.*, **71**, 195 (1937).

15) A. Kurtenacker, "Analytische Chemie der Sauerstoffsauren des Schwefels," Ferdinand Enke Verlag Stuttgart (1872), pp. 118; A. A. Besson, *Chem. Z.*, **37**, 926 (1913).

16) B. C. Brodie, *Phil. Trans.*, **162**, 435 (1872); A. Kotowski, "Gmelins Handbuch der Anorganischen Chemie," Schwefel Teil-B, Weinheim, Bergstrass (1960), p. 895.

dioxide with ozone in a weak alkaline solution according to the following schema.

$$Na_2S_2O_3 + O_3 = Na_2S_2O_3\cdot O_3 \begin{array}{l} \nearrow Na_2S_2O_6 \\ \searrow Na_2SO_4 + SO_2 \end{array}$$

Because of the presence of sulfite, which is not detected in the oxidation with oxygen, thiosulfate must be oxidized with ozone through a different mechanism from those of other oxidations.

Consequently, by the oxidation of ammonium thiosulfate with compressed oxygen in aqueous-ammonia solution, 55—65 mol% of thiosulfate-sulfur is converted to sulfamate and the remainder to sulfate. The oxidation proceeds forming some low polythionates as intermediates.

Sulfamate and sulfate are formed by electrolytic oxidation or hydrogen peroxide oxidation, but the yield of sulfamate is lower than that by oxidation with compressed oxygen. By ozone oxidtaion, a large amount of sulfate is finally formed with sulfite as an intermediate, but the yield of sulfamate is extremely small.