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The Chemical Behavior of Low Valence Sulfur Compounds. VIII. The Oxidation of Sodium Thiosulfate with Ozone

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The oxidation of sodium thiosulfate with ozone in an aqueous solution was investigated as a part of a series of studies on the chemical behavior of such low-valence sulfur compounds as thiosulfate and sulfite. The ozone oxidation was carried out by blowing a mixed gas of ozone and oxygen continuously into a 0.3—0.6 mol/l solution of sodium thiosulfate at 10—80 °C. In a neutral solution, thiosulfate is converted to sulfate, sulfite, tri- and tetrathionates, hydrogen sulfide and sulfur dioxide, and finally to sulfate, tri- and tetrathionates. The yield of the sulfate is only 40% of the total sulfur. In an alkaline solution, however, thiosulfate is oxidized to sulfite as an intermediate, and finally to sulfate.

The oxidation of sodium sulfite, and potassium salts of tri- and tetrathionate with ozone was also studied in order to elucidate its mechanism.

The oxidation of sodium thiosulfate with ozone has been studied only by Yamauchi[1] and Riesenfeld *et al.*[2] in the 1910's.

Yamauchi has reported that sodium thiosulfate oxidized to sulfate, sulfite, and elemental sulfur with ozone in a neutral solution according to Eq. (1):

$$3Na_2S_2O_3 + 2O_3 = 2Na_2SO_4 + Na_2SO_3 + 3S + 2O_2 \quad (1)$$

where the formation of sulfate and sulfite is explained as the conversion of the central sulfur atom of the thiosulfate ion. Riesenfeld has proposed that the oxidation of sodium thiosulfate proceeds according to Eqs. (2) and (3) in a neutral solution, which then becomes acidic.

$$Na_2S_2O_3 + O_3 = Na_2S_2O_6 \quad (2)$$

$$Na_2S_2O_3 + O_3 = Na_2SO_4 + SO_2 \quad (3)$$

The number of oxygen atoms consumed in one ozone molecule is three in a neutral solution, but two in an alkaline solution on the addition of sodium carbonate, although the oxidation products are the same in both neutral and alkaline solutions. Dithionate, however, can not be distinguished from other polythionates by qualitative analysis.

Thus, in the early studies there was much doubt about the identification of products. Recently, though, an investigation of the oxidation of ammonium thiosulfate with ozone in an aqueous ammonia solution by one of the present authors[3] has led to the finding that ammonium thiosulfate is oxidized to sulfate, sulfite, sulfamate, and low polythionates.

In the present study, the oxidation of sodium thiosulfate with ozone was investigated as a part of a series of studies on the chemical behavior of low valence sulfur compounds,[4] furthermore, the ozone oxidations of sulfite, tri- and tetrathionates, which are oxidation products of thiosulfate, were studied in order to elucidate the mechanism.

The results may be usefully applied to the treatment of waste water containing thiosulfate and sulfite.

Experimental

Apparatus and Procedure. The apparatus is depicted schematically in Fig. 1. One liter of 0.3—0.6 mol/l sodium thiosulfate solution was put into three-necked round-bottomed flask kept in a water bath at 10—80 °C. Mixed gas of ozone and oxygen was continuously blown into the solution at atmospheric pressure. Every half hour, 10—20 ml aliquots of the solution were withdrawn for analysis. The flow rate, as determined by the orifice meter, was 1—2.9 (mainly 2.1) N.T.P.l/min. The sodium thiosulfate solution used was neutral or alkaline on the addition of sodium hydroxide, the amount of which was equivalent to or in excess of that of the acid produced by the oxidation reaction. An ozonizer with 6 silent discharge tubes of a special construction devised by Kitahara[5] was used with some modification, the center electrode being covered with glass tube to prevent it from being oxidized by ozone.

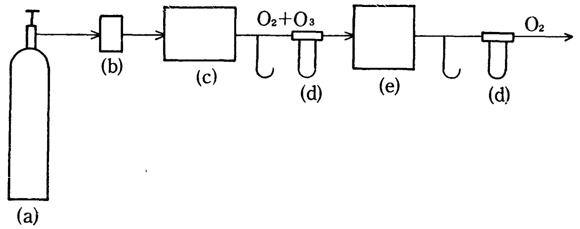

Fig. 1. Apparatus.
(a): O_2 bomb. (b): Drying tube packed with silica gel. (c): Ozonizer. (d): Orifice meter. (e): Reactor.

Sample. The potassium tri- and tetrathionates were prepared by Martin's method.[6]

Analysis. After dilution to a suitable concentration, the sample solution was analyzed for thiosulfate, sulfite, sulfate, tri-, and tetrathionates as follows:

Thiosulfate: Thiosulfate was titrated with a 0.1 N standard solution of iodine after masking sulfite with an aqueous solution of formaldehyde.

Sulfite: The total amount of thiosulfate and sulfite was determined by iodimetry after the neutralization of the sample solution.

Sulfate: After the oxidation of thiosulfate and sulfite with iodine to tetrathionate and sulfate respectively, the sulfate

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[1] Y. Yamauchi, *Amer. Chem. J.*, **50**, 55 (1913).
[2] E. H. Riesenfeld and Th. F. Egidius, *Z. Anorg. Chem.*, **85**, 217 (1914).
[3] K. Naito, M. Yoshida, M. Shieh, and T. Okabe, This Bulletin, **43**, 1365 (1970).
[4] K. Naito and T. Okabe, *ibid.*, **44**, 2434 (1971).
[5] K. Kitahara, *Yakugaku Zasshi*, **81**, 291 (1961).
[6] F. Martin and L. Mets, *Z. Anorg. Allg. Chem.*, **127**, 83 (1923).

was determined to be barium sulfate by gravimetry.

Tri- and Tetrathionates: These polythionates were first identified by paper-chromatography[7,8] and then their quantity was determined by using the sulfide and sulfite methods.[9]

First, the sulfite was removed by the addition of 1 N strontium nitrate, a 4 N aqueous ammonia solution saturated with hydrogen sulfide was then added to the sample solution.

The solution was heated on a water bath for about 10 min, and the thiosulfate released from the following reactions was determined by iodimetry after the removal of the excess hydrogen sulfide with carbon dioxide.

$$S_3O_6^{2-} + S^{2-} = 2S_2O_3^{2-} \qquad (4)$$

$$S_4O_6^{2-} + S^{2-} = 2S_2O_3^{2-} + S \qquad (5)$$

A buffer solution of pH 9.5 and a 1 N sodium sulfite solution were poured into another sample solution and was kept standing for about 10 min, then, an aqueous solution of formaldehyde was added, and the thiosulfate formed by the following reaction was determined by iodimetry after acidification with 1 N acetic acid.

$$S_4O_6^{2-} + SO_3^{2-} = S_3O_6^{2-} + S_2O_3^{2-} \qquad (6)$$

Ozone: A known volume of a mixed gas of ozone and oxygen was passed through a 2% potassium iodide solution. After the acidification of the solution with 6 N sulfuric acid, the iodine liberated was titrated with a 0.1 N standard solution of sodium thiosulfate.

Results and Discussion

Oxidation of Sodium Thiosulfate with Ozone. Different reactions occurred by ozone oxidation depending on the pH of the solutions, whether they were neutral or alkaline. In either solution, however, the ozone supplied was completely consumed throughout the reaction stage except in the terminating period of the reaction.

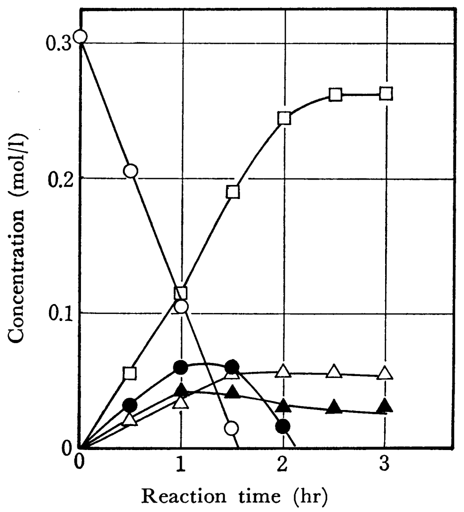

Fig. 2. Oxidation of thiosulfate in neutral solution.
Temp.: 25°C, O_3: 5.16 g/hr, O_3-O_2: 2.1 N. T. P. l/min.
-○-: $S_2O_3^{2-}$, -●-: SO_3^{2-}, -□-: SO_4^{2-},
-▲-: $S_3O_6^{2-}$, -△-: $S_4O_6^{2-}$

In a Neutral Solution. A general view of the reaction at 25 °C is shown in Fig. 2. Thiosulfate was converted into sulfate, sulfite, tri- and tetrathionate, hydrogen sulfide gas, and sulfur dioxide gas. Dithionate was not detected by means of paper-chromatography. Initially, only hydrogen sulfide evolved, and then sulfur dioxide evolved with a lowering of the pH, but their amount as sulfur was less than 5% of the total sulfur. Sulfate and tri- and tetrathionates remained after the complete consumption of the thiosulfate, the amount of sulfate sulfur reached 40% of total sulfur, and the pH of solution decreased to 1—2. The successive oxidation of polythionates proceeded slowly. Although simultaneous and consecutive reactions took place, the amount of thiosulfate decreased linearly, consuming the supplied ozone completely.

The decreasing amount of thiosulfate, R, is proportional to the amount of ozone supplied, R is given as follows:

$$R = kP_{O_3}V_0 \qquad \text{(mol/min)} \qquad (7)$$

$$r = R/V_0 = kP_{O_3} \qquad (8)$$

P_{O_3}: Partial pressure of ozone (atm)
V_0: Flow rate of mixed gas (N.T.P. l/min)
k: Constant (mol/l·atm)

The relation between r and P_{O_3} is shown in Fig. 3.

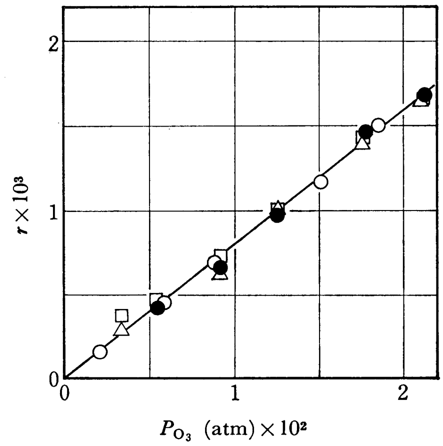

Fig. 3. Plot of r *vs.* P_{O_3}
-●-: 10°C, -○-: 25°C, -△-: 40°C, -□-: 60°C

As is expressed by the straight line which intersects at the point of origin, independently of the reaction temperature, R is shown experimentally as follows:

$$R = 0.080\, P_{O_3}V_0 \qquad (10\text{—}60\ ^\circ\text{C}) \quad \text{(mol/min)} \qquad (9)$$

This equation does not express a stoichiometric relation between thiosulfate and ozone, but it does indicate the relation between the consumed amount of thiosulfate and the supplied amount of ozone. In spite of the perfect consumption of ozone, the reaction was accelerated a little by the addition of 10^{-3}—10^{-4} mol/l of ammonium metavanadate.

In an Alkaline Solution. As is shown in Fig. 4, only sulfite was observed as an intermediate, and thiosulfate was completely oxidized to sulfate. The amount of sulfate formed by the reaction was twice as much as that of the initial thiosulfate. Unlike as a reaction in a neutral solution, the oxidation reaction

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[7] F. H. Pollard, G. Nickless and R. B. Glover, *J. Chromatogr.*, **15**, 518 (1964).

[8] P. A. Trudinger, *J. Bacteriol.*, **93**, 550 (1967).

[9] A. Kurtenacker and E. Goldbach, *Z. Anorg. Allg. Chem.*, **166**, 177 (1927); *ibid.*, **134**, 265 (1924).

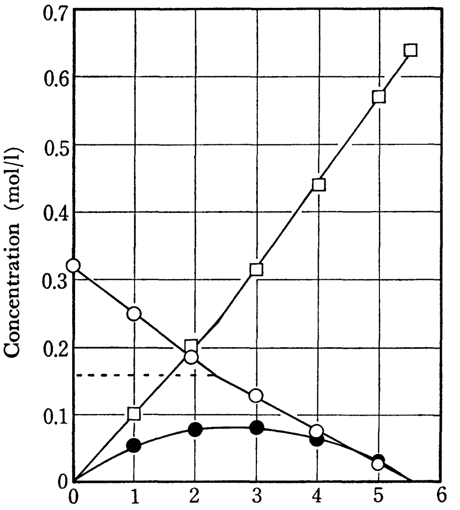

Fig. 4. Oxidation of thiosulfate in alkaline solution.
Temp.: 25°C, O_3: 5.16 g/hr, O_3-O_2: 2.1 N.T.P. l/min.
-○-: $S_2O_3^{2-}$, -●-: SO_3^{2-}, -□-: SO_4^{2-}.

in an alkaline solution was completed as soon as the thiosulfate disappeared. The oxidized amount of thiosulfate, R, decreased gradually with the reaction time, but it may be expressed approximately as follows:

$$C_0 - C_0/2 \quad R = k_1 P_{O_3} V_0 \quad \text{(mol/min)} \tag{10}$$

$$C_0/2 - 0 \quad R = k_2 P_{O_3} V_0 \quad \text{(mol/min)} \tag{11}$$

$$\log k_1 = -170/T - 0.994 \tag{12}$$

$$\log k_2 = -170/T - 1.149 \tag{13}$$

C_0: Initial thiosulfate consentration(mol/l)
T: Reaction temperature (K)
(25—80°C)

These equations are based on the assumption that the relationship between the thiosulfate concentration and the reaction time is expressed by the two straight lines crossing each other at the point indicating one-half of the initial concentration of thiosulfate. The value of R in an alkaline solution is 1/3—1/4 of that in a neutral solution.

Oxidation of Sodium Sulfite with Ozone. The ozone supplied was completely consumed under the present experimental conditions (reaction temperature, 25—60 °C, initial concentration of sodium sulfite, 0.6 mol/l, and flow rate of mixed gas of ozone and oxygen, 2.1 N.T.P-l/min), thus forming sulfate quantitatively. The relation between reaction molar ratio (Na_2SO_3/O_3) and the ozone concentration in the gas phase is shown in Fig. 5. The reaction molar ratio was calculated from Eq. (14):

$$Na_2SO_3/O_3 = \{\text{amount of sulfite oxidized by ozone and oxygen (mol)—amount of sulfite oxidized by oxygen(mol)}\}/\text{ozone supplied (mol)} \tag{14}$$

The molar ratio was not constant, but gradually increased with a rise in the temperature and with a decrease in the ozone concentration. The molar ratio must be less than 3, judging from Eq. (15), but there were actually cases where it was 3 or more, as is shwon in Fig. 5.

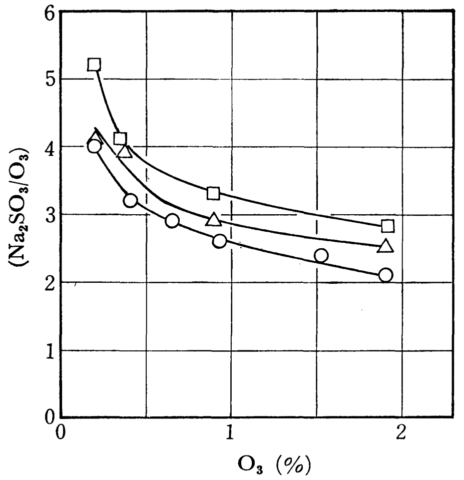

Fig. 5. Plot of (Na_2SO_3/O_3) *vs.* O_3
-○-: 25°C, -△-: 40°C, -□-: 60°C.

$$Na_2SO_3 + 1/3\ O_3 = Na_2SO_4 \tag{15}$$

From the results, it must be considered that the oxidation of sulfite with oxygen is accelerated by the presence of ozone. Under the following conditions:

Reaction temperature:	25—60	(°C)
Partial oxygen pressure P_{O_2}:	0.1—1	(atm)
Partial ozone pressure P_{O_3}:	$(0.1—2) \times 10^{-2}$	(atm)

Flow rate of mixed gas of
O_3-O_2 or O_3-O_2-N_2 V_0: 1—2.8 (l/min at N.T.P.)

the amount of oxidized sulfite, R, may be experimentally expressed as follows:

$$R = kP_{O_3}^{0.5} P_{O_2}^{0.5} V_0 \quad \text{(mol/min)} \tag{16}$$

$$k_{25} = 0.016 \quad \text{(mol/l·atm)}$$

$$k_{40} = 0.018 \quad \text{(mol/l·atm)}$$

$$k_{60} = 0.020 \quad \text{(mol/l·atm)}$$

Oxidation of Potassium Tri- and Tetrathionates with Ozone. In the oxidation of these polythionates, only 16% of the trithionate and 4% of the tetrathionate were converted to sulfate after 4 hr in a neutral solution, and no intermediate was detected under the present experimental conditions (reaction temperature, 25 °C; initial tri- and tetrathionate concentration, 0.1 mol/l; ozone flow rate, 4.75 g/hr).

The rate of the reaction was so slow that most of the ozone passed freely through the solution.

The results obtained from an investigation in an alkaline solution are shown in Figs. 6 and 7. It has previously been shown that tri- and tetrathionates decompose by the following reactions in an alkaline solution.[10]

at pH 13: $$2S_3O_6^{2-} + 6OH^- = S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \tag{17}$$

at pH 11.5: $$4S_4O_6^{2-} + 6OH^- = 2S_3O_6^{2-} + 5S_2O_3^{2-} + 3H_2O \tag{18}$$

partially $$2S_4O_6^{2-} + 6OH^- = 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \tag{19}$$

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[10] K. Naito, M. Shieh and T. Okabe, This Bulletin, **43**, 1372 (1970).

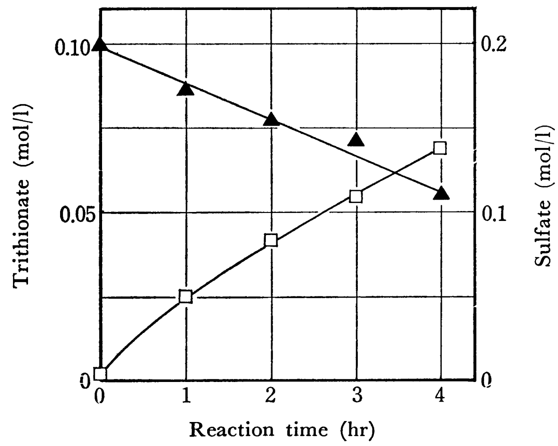

Fig. 6. Oxidation of trithionate in alkaline solution.
Temp.: 25°C, O_3: 4.75 g/hr, O_3-O_2: 2.1 N. T. P. l/min.
NaOH: 0.4 mol/l,
-▲-: $S_3O_6^{2-}$, -□-: SO_4^{2-}.

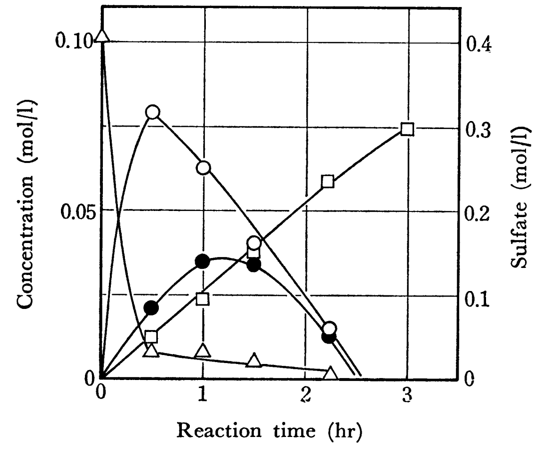

Fig. 7. Oxidation of tetrathionate in alkaline solution.
Temp.: 25°C, O_3: 4.75 g/hr, O_3-O_2: 2.1 N. T. P. l/min.
NaOH: 0.4 mol/l.
-○-: $S_2O_3^{2-}$, -●-: SO_3^{2-}, -□-: SO_4^{2-}, -△-: $S_4O_6^{2-}$.

The changes in degree of the tri- and tetrathionate concentrations in the ozone oxidation were similar to those in their decomposition reaction in an alkaline solution. Therefore, it may be considered that tri- and tetrathionates decompose initially in the manner expressed by Eqs. (17) and (18), and that the thiosulfate and sulfite formed by the decomposition are mainly oxidized by ozone.

The Mechanism of the Oxidation Reaction of Sodium Thiosulfate with Ozone. The reactions expressed by the following equations may be considered to be the oxidation reactions of sodium thiosulfate in a neutral solution.

For the formations of SO_4^{2-} and SO_3^{2-}:

$$S_2O_3^{2-} + O_3 = SO_4^{2-} + SO_2 \tag{3'}$$

$$S_4O_6^{2-} + O_3 \rightarrow SO_4^{2-} \tag{20}$$

$$S_3O_6^{2-} + O_3 \rightarrow SO_4^{2-} \tag{21}$$

$$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} \tag{22}$$

$$SO_3^{2-} + 1/2O_2 = SO_4^{2-} \tag{23}$$

For the formation of $S_3O_6^{2-}$:

$$S_4O_6^{2-} + SO_3^{2-} = S_3O_6^{2-} + S_2O_3^{2-} \tag{6}$$

$$S_2O_3^{2-} + SO_3^{2-} + O_3 \rightarrow S_3O_6^{2-} \tag{24}$$

For the formation of $S_4O_6^{2-}$:

$$2S_2O_3^{2-} + 1/3O_3 + H_2O = S_4O_6^{2-} + 2OH^- \tag{25}$$

$$2S_2O_3^{2-} + 1/2O_2 + H_2O \rightarrow S_4O_6^{2-} \tag{26}$$

If it is assumed that Reactions (3′), (6), (25), and (23) proceed mainly in an early stage of the ozone oxidation, the amounts of thiosulfate and ozone used in the reaction can be calculated also from the amounts of products shown in Fig. 2. The calculated values are tabulated as follows, along with values actually used.

Time range	Thiosulfate (mol)		Ozone (mol)	
(hr)	Calcd	Obsd	Calcd	Suppld
0 —0.5	0.108	0.099	0.065	0.054
0.5—1.0	0.215	0.200	0.132	0.108
1.0—1.5	0.293	0.289	0.172	0.162

The calculated values of the thiosulfate consumed are almost equal to the observed values, therefore, the oxidation of thiosulfate with ozone must proceed mainly *via* the route assumed above.

On the other hand, the amount of ozone actually consumed was less by 20% than that calculated. This discrepancy can be accounted for by the consideration that the oxidation of thiosulfate with oxygen, as expressed by Eq. (26), is induced at atmospheric pressure in the presence of ozone, because thiosulfate is oxidized with compressed oxygen to tetrathionate.[10] In view of the results of the oxidation of sulfite, tri- and tetrathionates with ozone, there is no doubt that Reactions (20), (21), and (22) proceed to some extent.

Furthermore, it is probably reasonable to consider that the formation of trithionate takes place, as is

Table 1. The ozone oxidation of thiosulfate in an alkaline solution

Time range (hr)	$S_2O_3^{2-}$ (mol)	SO_3^{2-} (mol)	SO_4^{2-}		O_3	
			Obsd (mol)	Calcd (mol)	Calcd (mol)	Suppld (mol)
0—1	0.071	0.023	0.099	—	0.078	0.175
1—2	0.063	0.040	0.104	0.103	0.076	0.175
2—3	0.057	0.054	0.113	0.111	0.075	0.175
3—4	0.053	0.069	0.123	0.122	0.076	0.175
4—5	0.049	0.082	0.132	0.131	0.076	0.175

SO_3^{2-}: Amount of sulfite oxidized by Eq. (23). SO_4^{2-} Calcd: SO_3^{2-} + amount of sulfate formed by Eq. (3).
O_3 Calcd: Amount of ozone being required to oxidize $S_2O_3^{2-}$ to SO_4^{2-} and SO_3^{2-}.

expressed not only by Eq. (6), but also by Eq. (24), by means of the oxidation of a complex which consists of thiosulfate and sulfite, because such a complex is easily formed in an acidic solution.[11]

The evolution of hydrogen sulfide may be considered to be result from the decomposition reaction of thiosufate as follows:

$$S_2O_3^{2-} + H_2O = H_2S + SO_4^{2-} \tag{27}$$

$$2S_2O_3^{2-} + 2H^+ = H_2S + S_3O_6^{2-} \tag{28}$$

The acceleration of ammonium metavanadate may be explained by the fact that Reaction (25) or (26) is promoted by a catalytic action of ammonium metavanadate, for these reactions contribute mostly to the consumption of thiosulfate.

In an alkaline solution, the oxidation of thiosulfate must proceed mainly *via* (3′) and (15), as is shown in Table 1.

Although polythionates could not be detected in the alkaline solution, polythionates are possibly responsible for the formation of sulfite as an unstable intermediate.

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[11] C. J. Battaglia and W. J. Miller, *Photogr. Sci. Eng.*, **12**, 46 (1968).