V. Summary

1. The conductance of the following salts has been measured in pyridine at 25°: tetrabutylammonium nitrate, acetate and triphenylborofluoride; tetramethylammonium, ethyltrimethylammonium, hydroxyethyltrimethylammonium, bromoethyltrimethylammonium, bromomethyltrimethylammonium, phenyldimethylhydroxyammonium, ammonium, lithium, sodium, potassium and silver picrate; ammonium, sodium and potassium iodide; and pyridonium and piperidonium nitrate.

2. The conductance has also been determined for solutions of tetrabutylammonium picrate in the presence of ammonia; sodium picrate in the presence of ammonia and of water and potassium picrate in the presence of methanol.

3. The experimental results have been analyzed by the usual graphical methods and values of Λ_0 and of the dissociation constant K have been obtained for all the systems investigated. Ion conductances have been evaluated by the method of Fowler.

4. The effect of various interactions on ion conductances and dissociation constants are discussed.

5. It has been shown that the addition of polar molecules to the solvent medium usually causes little change in ion conductance of salts having large ions. With salts of smaller ions, the dissociation constant is often increased. In the case of sodium picrate, the addition of ammonia causes a very large change in Λ_0, up to as much as 33%, with only a small increase in the dissociation constant.

PROVIDENCE, R. I. RECEIVED JUNE 20, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thallous Sulfoxylate Isomerism[1]

BY J. FENTRESS AND P. W. SELWOOD

The fact that thallous sulfide, Tl_2S, is easily oxidized when exposed to air was first pointed out by Lamy.[1a] At that time it was postulated that the final product of this oxidation was thallous sulfate, Tl_2SO_4. More recent investigation of the oxidation by Iskoldsky[2] has served to confirm much of Lamy's work. It is found that at 720° in air, thallous sulfide is oxidized 90% to thallous sulfate in two and a half hours. Further, the oxidation of the sulfide proceeds step-wise with the intermediate compounds, Tl_2SO_2 and Tl_2SO_3, being identified. Although one might expect to find a compound with the formula Tl_2SO, Iskoldsky was unable to prepare such a compound.

With Case's[3] discovery of the photo-sensitivity of oxidized thallous sulfide, and the more recent improvements on "Thalofide" photo-cells by Cashman[4] and several others,[5–9] new interest has developed in the actual oxidation of thallous sulfide, and the products formed.

The percentage of oxygen in various photosensitive cells[10] varies up to as much as a nearly 1:1 mole ratio of $Tl_2:O_2$, corresponding to the formula Tl_2SO_2. Thus, our interest in thallous sulfide oxidation products, from the point of view of identifying the composition of the photo-sensitive material, only extends as far as Tl_2SO_2 and is not concerned with the complete oxidation to thallous sulfate.

This present study is concerned with the two forms of thallous sulfoxylate[11] that we were able to obtain.

Preparation of Thallous Sulfide.—Thallous sulfide may be prepared either by precipitation at ordinary temperatures, or by direct reaction of thallium metal and sulfur at high temperatures. We selected the former method because early experiments indicated that oxidation proceeds more rapidly with thallous sulfide prepared by precipitation methods.

All the thallous sulfide used in our experiments was prepared by precipitation from alkaline thallous sulfate solution. The thallous sulfate starting material was originally 99% pure commercial material, which was purified by three recrystallizations from aqueous solution. This procedure yielded thallous sulfate which when analyzed by the standard chromate method gave results of satisfactorily high purity, *i. e.*, more than 99.9% of the theoretical thallium content.

A dilute solution of thallous sulfate, under nitrogen atmosphere, was made alkaline with ammonium hydroxide and the thallous sulfide precipitated at 50° with hydrogen sulfide in the pre-

---

(1) This investigation was carried under Contract Nobs. 45068, Bureau of Ships, U. S. Navy. Our thanks are due to Dr. R. J. Cashman at whose suggestion this research was undertaken.

(1a) A. Lamy, *Compt. rend.*, **54**, 1255 (1862); **57**, 442 (1863); *Ann. chim. phys.*, [3] **67**, 385 (1862); [4] **5**, 410 (1865); *Bull. soc. chim.*, [2] **11**, 210 (1869).

(2) I. I. Iskoldsky, *Mineralnoje Syrye*, No. 4, 404 (1931).

(3) T. W. Case, *Phys. Rev.*, **15**, 289 (1920).

(4) R. J. Cashman, N. D. R. C. Report No. 16.4–6 (1943).

(5) R. Sewig, *Tech. physik*, **11**, 269 (1930).

(6) W. Leo and C. Mueller, *Physik. Z.*, **36**, 113 (1935).

(7) Q. Majorana and G. Tedesco, *Atti accad. Lincei*, **8**, 9 (1928).

(8) F. Micheissen, *Tech. physik*, **11**, 511 (1930).

(9) A. A. Sivkov, *J. Tech. Phys. U. S. S. R.*, **8**, 11 (1938).

(10) A. von Hippel, F. G. Chesley, H. S. Denmark, P. B. Ulin and E. S. Rittner, *J. Chem. Phys.*, **14**, 355 (1946).

(11) Both of these compounds were prepared in this Laboratory early in 1943. The publication of parts of this paper has been delayed owing to the war.

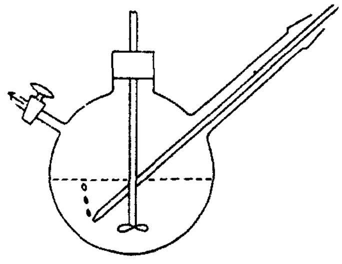


Fig. 1.

cipitation flask (Fig. 1) The filter tube (Fig. 2) was then attached and the thallous sulfide filtered under nitrogen atmosphere. The filter tube was then connected to the sample tube (Fig. 3) which was in place in the vacuum apparatus. While the filter tube was being put in place, a stream of nitrogen was passed through the sample tube to insure that no oxygen was present. The sample tube was evacuated and the sample pumped out until it appeared to be completely dry, two to three days, and then several taps on the side of the filter tube served to dislodge the sample causing it to fall into the sample tube. The sample was evacuated and pumped to a high vacuum, 10^{-3} mm., as measured by a McLeod gage incorporated in the vacuum system. The pumping was continued until the sample was brought to constant weight.

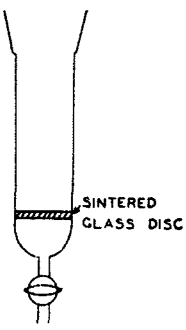


Fig. 2.

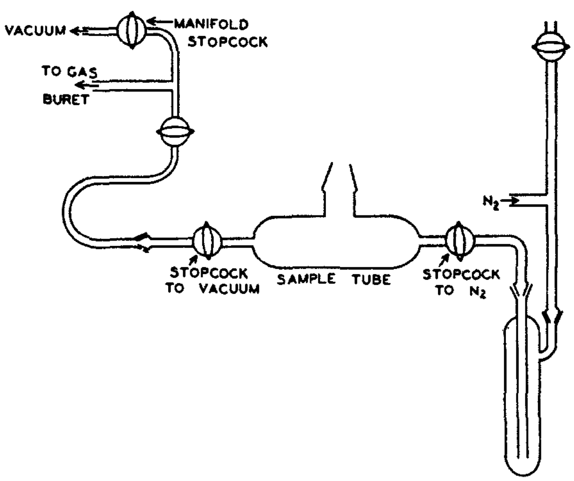


Fig. 3.

In order to carry out an analysis of the thallous sulfide without exposing the sample to the air the sampler (Fig. 4) was attached. The sample was taken by rotating the sample tube 180°, allowing some thallous sulfide to enter the sampler. Then the sample tube was rotated back to its original position leaving a small sample, 0.25–0.50 g., in the sampler. The end of the sampler containing the small sample of thallous sulfide was then sealed off. Once the weight was determined the sealed tube containing the sample was placed in a beaker of sulfuric acid and the tube broken, allowing the thallous sulfide to dissolve. This solution was boiled to remove all the hydrogen sulfide, then made alkaline with ammonium hydroxide, and the thallium determined by precipitation as the chromate. The results of the analyses on a series of thallous sulfide samples gave values from 99.5 to 99.75% pure thallous sulfide. The impurity in these samples was small amounts of water vapor that are not removed by evacuating the sample at room temperature. However, since the reaction between thallous sulfide and oxygen must be catalyzed by water vapor, or some other common catalyst, no attempt was made to remove these last traces of water.

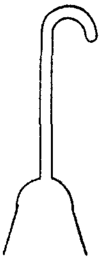


Fig. 4.

Oxidation of Thallous Sulfide.—The bulk of the thallous sulfide which was left in the sample tube was thoroughly pumped out at room temperature and its weight determined. After replacement of the sample tube in the vacuum line the whole system was completely evacuated and the stopcocks to the manifold and nitrogen lines closed. Pure oxygen gas was then introduced into the closed system from a gas buret and the rate at which the oxygen reacted with the thallous sulfide was measured.

In preliminary experiments the oxygen was generated by heating a mixture of potassium chlorate with small amounts of manganese dioxide. Any dust particles of manganese dioxide were filtered out by a sintered glass disc and the gas was stored in a reservoir bulb until it was drawn into the buret. In later experiments the oxygen was generated by direct heating of potassium permanganate. This change in procedure was made because it was felt that small amounts of chlorine gas might be present in the oxygen prepared by the first method.

The nitrogen gas used in these experiments was standard tank nitrogen which was passed over reduced copper at 300°, through soda lime and phosphorus pentoxide before being brought into contact with the thallous sulfide.

The thallous sulfide, with small amounts of water vapor as a catalyst, reacts moderately rapidly with oxygen until a mole ratio of $1:1/\mathrm{Tl_2S}:\mathrm{O_2}$ is reached. At this point the black thallous sulfide phase has completely disappeared and an olive-brown compound with the formula $\mathrm{Tl_2SO_2}$ is formed. This compound will be designated as *alpha* thallous sulfoxylate, α-$\mathrm{Tl_2SO_2}$. This compound is stable in air at room temperature and thus may be removed from the vacuum system without any decomposition.

The oxidation curves showed no break when a composition corresponding to the formula $\mathrm{Tl_2SO}$ was reached, which is in agreement with the observation of Iskoldsky.[2] In order to characterize the *alpha* thallous sulfoxylate the X-ray powder pattern was obtained, and the basic chemistry of the compound was investigated.

Conversion of Alpha Thallous Sulfoxylate to the Beta Form.—Since the *alpha* form of thallous sulfoxylate did not correspond to the greenish yellow compound reported by Iskoldsky,[2] nor to the yellow compound reported by von Hippel[10] as Tl_2SO_2, experiments were undertaken to prepare this yellow form. Since both workers had obtained their compound by oxidation of thallous sulfide at elevated temperatures small samples of the *alpha* form were heated in vacuum in hopes of obtaining the *beta* form. Approximately 1 g. of the *alpha* form in a sample tube was thoroughly evacuated at room temperature. An open-end manometer was included in the system to measure any pressure changes. After the sample was evacuated the stopcock to the vacuum line was closed and the sample was slowly heated in an oil-bath to 250°. In order to get good results the heating must be done slowly and a temperature of 250° must not be exceeded. If the heating is carried out too fast, or if too high a temperature is reached, a grayish powder results which is a mixture of the sulfoxylate with thallous sulfide. If the conversion is carried out as indicated the greenish-yellow form is obtained as a single phase. The small pressure changes noted on the manometer may be satisfactorily explained on the basis of the small amounts of water vapor impurity. This greenish-yellow compound, which also has the formula Tl_2SO_2, will be designated as *beta* thallous sulfoxylate, β-Tl_2SO_2. This compound is also stable in air at room temperatures, and under ordinary conditions shows no tendency to revert back to the *alpha* form. The X-ray powder pattern and basic chemistry of this compound were also investigated.

X-Ray Study of the Two Forms of Thallous Sulfoxylate.—The X-ray patterns of the two forms of thallous sulfoxylate, thallous sulfide and patterns of mixtures of these compounds were taken. These patterns were obtained using the North American Philips Company X-Ray Spectrometer Type No. 12021. In this instrument the conventional camera is replaced by a Geiger counter. A Brown recorder was used in connection with the counting unit to make the machine self-recording. For all the data given a copper target was used, thus all calculations are based on the CuKα line.

A series of patterns of thallous sulfide samples were taken and found to agree closely with the structure of thallous sulfide as proposed by Ketelaar and Gorter.[12] In Fig. 5 a diagram giving the positions and relative intensities of diffraction lines from samples of Tl_2S, α-Tl_2SO_2 and β-Tl_2SO_2 are given. In Table I are given the exact positions of the diffraction lines for *alpha* and *beta* thallous sulfoxylate as determined from the X-ray patterns. Values of d corresponding to measured values of the angle θ are calculated from the expression

$$d = 0.77/\sin\theta$$

for CuKα radiation. It should be noted that the angles given in Table I are equal to 2θ.

TABLE I

X-RAY POWDER DIFFRACTION DATA ON THALLOUS SULFOXYLATE

	Alpha Thallous Sulfoxylate			Beta Thallous Sulfoxylate		
	Line position $2\theta \pm$ 0.1°	Rel. int.	d, Å.	Line position $2\theta \pm$ 0.1°	Rel. int.	d, Å.
1	19.63	0.1	4.51 ± 0.04	20.50	0.3	4.32 ± 0.04
2	20.75	0.1	4.28 ± .04	24.34	.1	3.65 ± .03
3	22.75	.1	3.91 ± .03	25.25	.6	3.52 ± .03
4	24.34	.2	3.65 ± .03	27.48	.7	3.24 ± .03
5	26.95	.3	3.31 ± .03	28.56	1.0	3.12 ± .03
6	28.63	.3	3.11 ± .03	29.32	1.0	3.05 ± .03
7	29.43[a]	1.0	3.03	30.12	0.6	2.96 ± .02
8	33.01	0.1	2.71 ± .02	32.25	.2	2.77 ± .02
9	34.03	.4	2.64 ± .02	34.13	.1	2.63 ± .02
10	36.19	.1	2.48 ± .01	35.38	.2	2.53 ± .02
11	39.38	.1	2.28 ± .01	36.65	.2	2.46 ± .01
12	39.98	.1	2.25 ± .01	38.98	.1	2.31 ± .01
13	43.75	.1	2.06 ± .01	41.37	.1	2.18 ± .01
14	44.44	.1	2.03 ± .01	41.91	.2	2.16 ± .01
15	46.25	.1	1.96 ± .01	44.06	.1	2.04 ± .01
16	48.81[a]	.1	1.86	46.56	.1	1.95 ± .01
17	52.56	.1	1.75 ± .01	47.25	.1	1.92 ± .01
18	53.62	.1	1.71 ± .01	49.83	.1	1.83 ± .01
19	54.44	.1	1.69 ± .01	51.43	.2	1.78 ± .01
20	56.50	.1	1.62 ± .01	52.87	.1	1.74 ± .01
21	57.95	.3	1.59 ± .01	54.55	.1	1.68 ± .01
22	59.41	.1	1.56 ± .01	59.35	.1	1.56 ± .10
23	60.88	.1	1.52 ± .01	62.91	.1	1.48 ± .01
24	71.40	.1	1.32	65.45	.1	1.42 ± .01
25	72.69	.1	1.30	69.50	.1	1.35
26	77.75	.1	1.23	79.90	.1	1.20
27	79.00	.1	1.21			
28	81.38	.1	1.18			

[a] The positions of these two lines were found by manually moving the Geiger tube until a maximum counting rate was obtained, and thus may be considered accurate to ±0.05°.

The patterns of the two forms of thallous sulfoxylate clearly show that we are dealing with two different structural forms. Further, comparison with the powder pattern of thallous sulfide indicates that both forms are significantly different from thallous sulfide itself.

The data given for *beta* thallous sulfoxylate, although not in exact agreement with the pattern given by von Hippel[10] for the yellow phase that he obtained in oxidized cells, is certainly in satisfactory enough accord to warrant the assumption that *beta* thallous sulfoxylate and von Hippel's yellow phase are one and the same compound. The pattern of the *beta* form was checked by comparison of three samples of β-Tl_2SO_2 prepared from three separate samples of α-Tl_2SO_2. Attempts to change the pattern by further heating of the *beta* form gave negative results. This heating only resulted in decomposition of the compound and the appearance of characteristic Tl_2S lines. Von Hippel[10] has proposed a face-centered cubic structure for the *beta* form. It appears that

---

(12) J. A. A. Ketelaar and E. W. Gorter, *Z. Krist.*, **101**, 367 (1939).

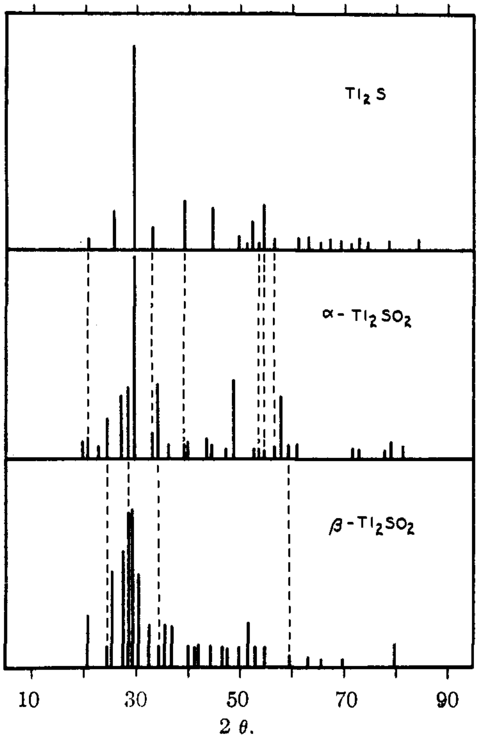


Fig. 5.

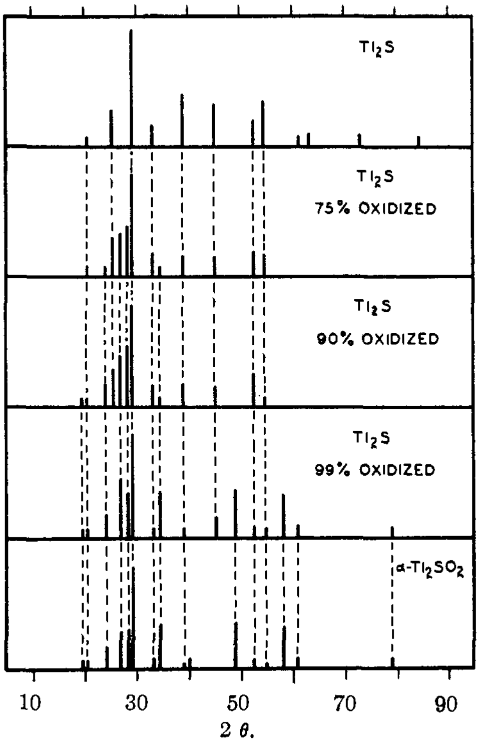


Fig. 6.

the *alpha* form may retain the layer lattice structure of thallous sulfide, but as yet we have failed to obtain sufficient data definitely to give the complete structure of this form, as all attempts to obtain crystals have been unsuccessful.

In Fig. 6 patterns showing different stages of oxidation in the preparation of the *alpha* form are given. These patterns indicate that partially oxidized samples of thallous sulfide do not represent mixtures of Tl_2S and α-Tl_2SO_2. Although some of the characteristic lines of α-Tl_2SO_2 are present in the 75% oxidized samples, at least two of the most intense lines given by the *alpha* form, 48.81° and 57.95°, do not appear until the oxidation is practically complete. This datum is in agreement with our observation that the characteristic brown phase of the *alpha* form does not appear until the reaction is nearly finished These patterns serve to give further evidence for the nonexistence of Tl_2SO at room temperature.

Our inability to obtain evidence of a Tl_2SO phase seems to cast some doubt on the theory advanced by von Hippel and Rittner[13] as to the position of the oxygen atoms in the photo-sensitive phase. These authors state that the most likely sites for the oxygen atoms are in spaces interleaving the Tl–Tl layers in the normal Tl_2S structure. Since the unit cell in the thallous sulfide structure contains twenty-seven Tl_2S units, and the number of possible oxygen positions is equal to the number of sulfur positions, based on the sites proposed by Von Hippel and Rittner, there will be twenty-seven possible locations for the oxygen atoms. If the oxygen atoms actually occupied these proposed sites the saturated structure would be Tl_2SO. The fact that Tl_2SO is so difficult to prepare may indicate that these sites are not as easily available as would at first appear. Calculations indicate that there are fifty-four equivalent positions in the Tl_2S unit cell available to oxygen atoms. Occupation of these would lead to the Tl_2SO_2 arrangement. However, the exact positions of the oxygen atoms cannot be determined without a more detailed X-ray study.

Basic Chemistry of the Thallous Sulfoxylates.—In attempting to elucidate the basic chemistry of the two forms of thallous sulfoxylate two early experiments led us to assign both forms as univalent thallium salts of sulfoxylic acid. Firstly, all evidence indicated that the oxidation of thallous sulfide had not served to oxidize either thallous ion to the thallic valence state. Secondly, all attempts to demonstrate the existence of sulfide ion in either form gave negative results.

Although sulfoxylic acid, H_2SO_2, is not known as the free acid, several inorganic salts have been prepared. The zinc salt $ZnSO_2$ may be prepared either by the action of sulfuryl chloride on zinc dust in absolute ether solution,[14] or by the reaction of

$$SO_2Cl_2 + 2Zn \longrightarrow ZnCl_2 + ZnSO_2$$

zinc metal with sulfur dioxide in absolute alcohol

$$SO_2 + Zn \longrightarrow ZnSO_2$$

---

[13] A. von Hippel and E. S. Rittner, *J. Chem. Phys.*, **14**, 370 (1946).

[14] E. Fromm and J. de S. Palma, *Ber.*, **39**, 3317 (1906).

The cobalt salt, $CoSO_2$, has been prepared by Scholder and Denk[15] by treating cobalt chloride with sodium hyposulfite in ammoniacal solution. Finally, Vogel and Partington[16] have prepared sodium sulfoxylate, Na_2SO_2, by treating sodium ethyl sulfoxylate with sodium hydroxide. In addition to these inorganic derivatives many organic compounds are known which may be considered as organic sulfoxylates.

Modifications of the above methods were attempted to prepare thallous sulfoxylate. Thallium metal turnings were added to a solution of pure sulfuryl chloride in absolute ether. But after prolonged stirring no reaction was observed. The speed with which thallium metal forms a protective oxide film may have been responsible for the failure to obtain any results.

The reaction between several different thallous salts and sodium hyposulfite was attempted under varying conditions. By adding thallous sulfate slowly to a solution of sodium hyposulfite an immediate white precipitate began to form which, however, could not be removed from the solution before it had turned dark gray. Repeated attempts to obtain the white compound which was believed to be $Tl_2S_2O_4$ failed and only Tl_2S and Tl_2SO_4 could be identified in the end-product.

The most satisfactory reaction was that between thallium metal shavings and sulfur dioxide in absolute alcohol. The reaction proceeded slowly yielding a white precipitate. This compound which was rather insoluble in alcohol could be obtained from the solution, and was found on analysis to be $Tl_2S_2O_4$. This compound appeared fairly stable in air, and was found to be rather highly soluble in water. Repeated attempts to convert this salt to thallous sulfoxylate failed to give any results.

However, it was found that *alpha* thallous sulfoxylate prepared from thallous sulfide, readily reacted with sulfur dioxide in alcoholic suspension to give a compound with the formula $Tl_2S_2O_4$ which seemed to be identical with the compound obtained above. It should be noted that *beta* thallous sulfoxylate would not react with sulfur dioxide under the same conditions.

Both forms of the sulfoxylate are only slightly soluble in water, but are quite soluble in dilute sulfuric acid. In the presence of concentrated acids both compounds appear to be decomposed, but concentrated bases have little effect on either compound. Solutions of both compounds containing 10 g. per liter of thallous ion were prepared and subjected to the standard tests for thallous ion. In all cases both compounds reacted as expected yielding both thallium ions immediately in the thallous state. Some difficulty was encountered in oxidizing these solutions to trivalent thallium with mild oxidizing agents, which suggested the presence of some reducing action in the solution.

In more dilute solution, less than 1 g. per liter of thallium, significant differences from normal thallous ion reactions may be noted. Attempts to precipitate the insoluble thallous halides from dilute acid solution gave precipitates only after several minutes, while attempts to precipitate the chromate from ammoniacal solution resulted in failure in most cases. However, it can be stated that there is very little difference in the two forms of the sulfoxylate as regard to the availability of the metal ions.

It was mentioned above that solutions of both forms appear to have a certain degree of reducing action. This fact coupled with the observation that both compounds on treatment with 5 *N* sulfuric acid gave precipitation of sulfur led us to postulate the existence of the thiosulfate ion as an intermediate product of the hydrolysis of sulfoxylic acid. This idea has already been suggested by Foerster[17] who considers sulfoxylic acid as an intermediate product in the formation of polythionates. He suggested that sulfoxylic acid is hydrolyzed according to the equation

$$2H_2SO_2 \longrightarrow H_2S_2O_3 + H_2O$$

The fact that we were able to demonstrate the presence of thiosulfate ion in aqueous solution of both forms lends support to the reaction as given above.

The thiosulfate ion was detected as an intermediate in the hydrolysis of both forms of thallous sulfoxylate by the characteristic reaction given with silver and mercuric ion. In the case of the *alpha* form 5 ml. of 10% solution of silver nitrate added to a saturated aqueous solution of the sulfoxylate gave the expected formation of a series of bright colored precipitates finally going to black silver sulfide. In the case of the ***beta*** form the reaction did not proceed as far as silver sulfide, but stopped with the formation of an intermediate brown precipitate, which was in part silver sulfite.

The following reactions were carried out in order to more fully investigate any difference in the course of hydrolysis of the two compounds. An aqueous solution containing 10 mg. of β-Tl_2SO_2 was made slightly acid with 2 *N* sulfuric acid. Before any sulfur began to appear this solution was treated with 0.5 ml. of potassium cyanide solution and 5 drops of ferric sulfate solution. The appearance of the familiar red color of the ferric thiocyanate complex indicated the presence of thiocyanate ion. A similar test with α-Tl_2SO_2 gave no color.

This formation of the thiocyanate ion is indicative of the presence of tetra- and pentathionic acid which may react with potassium cyanide according to the reaction

$$S_4O_6^{=} + 3CN^- + H_2O \longrightarrow SO_4^{=} + 2CN^- + S_2O_3^{=} + SCN^- + 2H^+$$

---

(15) R. Scholder and G. Denk, *Z. anorg. allgem. Chem.*, **222**, 17 (1935).

(16) I. Vogel and J. R. Partington, *J. Chem. Soc.*, **127**, 1514 (1925).

(17) F. Foerster, F. Lange, O. Drossbach and W. Seidel, *Z. anorg. allgem. Chem.*, **128**, 268 (1923).

$$S_5O_6^{=} + 4CN^- + H_2O \longrightarrow SO_4^{=} + 2CN^- + S_2O_3^{=} + 2SCN^- + 2H^+$$

Direct treatment of the two forms of thallous sulfoxylate with highly concentrated sulfuric acid gave different results in the two cases. When treated with 18 *N* acid the *beta* form gave off hydrogen sulfide as a decomposition product, and the solution remained clear, *i. e.*, no precipitation of sulfur. As opposed to this the *alpha* form gave no hydrogen sulfide, and sulfur began to precipitate immediately.

The formation of hydrogen sulfide may have been due to direct decomposition of the β-Tl_2SO_2, or may be a result of the hydrolysis of thiosulfate ion in strong acid according to the equation

$$2H_2S_2O_3 \longrightarrow H_2S + H_2S_3O_6$$

Bassett and Durrant[18] suggested the above reaction as one of three possible hydrolysis reactions of thiosulfate. These authors state that the above reaction would be favored in very strong acid.

In view of these results it should be mentioned that our inability to obtain thallous chromate precipitates from dilute solutions of the sulfoxylates in ammonium hydroxide may have been due to the formation of stable thiosulfate complexes in alkaline solution. Strongly complexed salts of this type are well known.

Goehring[19] has proposed that sulfoxylic acid may exist in two isomeric forms: the normal or sulfoxylic form reacting as if it were $S(OH)_2$, while the sulfinic form seems to react as HS(:O)OH. It is proposed by Goehring that the sulfoxylic form may react with thiosulfate ion according to the reaction

$$S(OH)_2 + 2S_2O_3^{=} + 2H^+ \longrightarrow S_5O_6^{=} + 2H_2O$$

and react with the bisulfite ion

$$S(OH)_2 + 2HSO_3^- \longrightarrow S_3O_6^{=} + 2H_2O$$

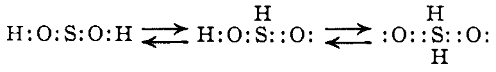
while the sulfinic form does not undergo reactions of this type.

To the present authors such marked differences seem difficult to understand when one realizes that if the sulfoxylate ion is involved the two forms given by Goehring are merely two possible resonance forms and thus could not be distinguished.

$$\mathrm{^-O{:}S{:}O^-} \rightleftarrows \mathrm{^-O{:}\underset{-}{S}{::}O}$$

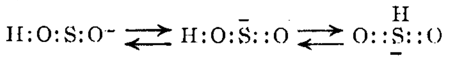
While if the postulated reactions involve the undissociated acid or bisulfoxylate ion it seems highly probable that a labile equilibrium between the two forms will exist.

Such an equilibrium between the two forms proposed by Goehring plus a third possible form could be represented by the equation



$$\mathrm{H{:}O{:}S{:}O{:}H} \rightleftarrows \mathrm{H{:}O{:}\overset{H}{S}{::}O{:}} \rightleftarrows \mathrm{{:}O{::}\overset{H}{\underset{H}{S}}{::}O{:}}$$

for the undissociated acid and



$$\mathrm{H{:}O{:}S{:}O^-} \rightleftarrows \mathrm{H{:}O{:}\bar{S}{::}O} \rightleftarrows \mathrm{O{::}\overset{H}{\underset{-}{S}}{::}O}$$

for the bisulfoxylate ion.

From the data obtained it is evident that the primary step in the hydrolysis of both forms of thallous sulfoxylate proceeds according to the equation

$$2Tl_2SO_2 + H_2O \longrightarrow Tl_2S_2O_3 + 2TlOH$$

The noted differences in the end-products of the hydrolysis in each case would then most probably be due to the reaction of the thiosulfate ion, or some further hydrolysis product, with undissociated thallous sulfoxylate.

Summary

Two different forms of thallous sulfoxylate have been prepared and X-ray diffraction patterns of the two forms obtained. The pattern of *beta* thallous sulfoxylate indicates that this compound is identical with a compound obtained by von Hippel and independently by Iskoldsky. No previous reference has been found concerning the *alpha* thallous sulfoxylate.

Conditions are given for converting the *alpha* form into the *beta* form by careful heating *in vacuo* to 250°.

The chemistry of both forms has been investigated and both compounds have been shown to be thallous salts of the hypothetical sulfoxylic acid.

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED JUNE 9, 1947

---

[18] H. Bassett and R. G. Durrant, *J. Chem. Soc.*, 1416 (1927).

[19] M. Goehring, *Ncturwiss.*, **32**, 42 (1944).