

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

**A Study of Complex Dioxalatothiomastannates<sup>1a</sup>**BY HOBART H. WILLARD AND TAFT Y. TORIBARA<sup>1b</sup>

F. W. Clarke<sup>1c</sup> first noticed the unusual phenomenon that hydrogen sulfide will not precipitate stannic tin from an oxalic acid solution. This fact was used as the basis of a separation of tin from arsenic, antimony, molybdenum, lead, bismuth, copper and cadmium by a number of later investigators. Among them Thompson<sup>2</sup> was the first to recognize that hydrogen sulfide was actually absorbed by the solution of the oxalate of tin, and he suggested that a sulfostannate might be formed. Wheeler<sup>3</sup> found that under proper conditions one mole of sulfur was absorbed for every mole of tin present. He was interested in its application as a volumetric method for tin and made no attempt to study the complex. It was the purpose of this work to isolate this complex and to study its properties.

**Experimental**

**Preparation of Dioxalatothiomastannates.**—Tin was dissolved in oxalic acid using hydrogen peroxide<sup>4</sup> as the oxidizing agent. To the solution of oxalatothiomastannic acid, an additional quantity of oxalic acid was added to increase the oxalate to tin ratio to a value greater than 10, following Wheeler's directions, to prevent precipitation of stannic sulfide in the next step. Hydrogen sulfide to saturation was passed into the solution near the boiling temperature. At room temperature, continued passage of hydrogen sulfide caused precipitation of stannic sulfide even from these high oxalate ratios, before the complex apparently could be formed. The excess of the gas was swept out of the cooled solution by passing carbon dioxide or nitrogen through it. By cooling this solution to 0°, a large part of the free oxalic acid but none of the dioxalatothiomastannic acid was precipitated. Attempts to isolate this acid proved unsuccessful because of its instability. Cautious evaporations to deposit a solid phase removed all the hydrogen sulfide along with the water. A number of other schemes were tried in an attempt to precipitate out either the desired acid or oxalic acid, but the properties of the two were found to be quite parallel.

The subsequent studies were made on the potassium salt, which was chosen because it was much less soluble than the impurity of potassium oxalate, and this made separation by crystallization a simple matter. The di-

potassium dioxalatothiomastannate was prepared by neutralizing the excess of oxalic acid in much the same manner as in preparing potassium oxalatothiomastannate. Allowing the one atom of sulfur and one mole of oxalate for each atom of tin, the excess of oxalic acid was neutralized with potassium bicarbonate.

At this stage it is very important that hydrogen sulfide be passed in long enough to give a 1:1 ratio between sulfide and tin. If the ratio is less than unity, part of the tin will be in the form of the more insoluble potassium oxalatothiomastannate. It is also important that the pH after neutralization be high enough to convert all the excess oxalic acid to the neutral oxalate but still low enough to ensure that all the carbonate be present as undissociated carbonic acid. A consideration of the ionization constants of oxalic acid and carbonic acid shows that a pH of 6 will give a ratio  $C_2O_4^{2-}/HC_2O_4^-$  of 61, whereas the same pH will give a ratio  $H_2CO_3/HCO_3^-$  of 30. The most favorable pH is, therefore, somewhat under 6. In one experiment in which a quantity of potassium bicarbonate calculated from the analysis of the solution was gradually added, the pH during the process was followed with a glass electrode. The final pH obtained was 5.64, which agrees with that calculated to be the most favorable.

In order to obtain a good separation by fractional crystallization, it is important that the impurities be more soluble substances. Both potassium oxalatothiomastannate and potassium bioxalate are much less soluble than the desired salt, but potassium oxalate is much more soluble.

An oxalatothiomastannic acid solution was prepared as previously described,<sup>4</sup> and an additional 100 g. of oxalic acid was added to the solution. After heating the solution to about 80°, hydrogen sulfide was passed into the hot solution for 1.5 hours. The excess of hydrogen sulfide was swept out at room temperature by passing nitrogen or carbon dioxide through the solution for forty minutes. A sample of the solution was taken at this point and titrated with iodine to determine the sulfide content in order to ensure the equality of the tin and sulfur present. When this had been established, the solution was cooled to 0° to freeze out most of the excess of oxalic acid. After removing this oxalic acid, the solution was allowed to warm up to room temperature. Solid potassium bicarbonate was added cautiously until a pH of 5.6 was attained. Upon cooling this solution to 0°, it was found that most of the salt crystallized out in pure form. It was recrystallized from water by dissolving the solid at 50-60° and cooling to 0°. Prolonged standing at the higher temperature was avoided because of the relative instability of the salt. The solid was filtered off and vacuum-dried over sulfuric acid, then kept in a desiccator in an atmosphere of nitrogen. Of a theoretical quantity of 93 g., a total of 81 g. of the recrystallized salt was obtained, a yield of 87%.

It was found much more convenient to use concentrated solutions of oxalatothiomastannic acid for the preparation because the relative losses due to solubility at 0° were small. Although concentration of a dilute solution is not possible,

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(1b) Florence Fenwick Memorial Fellow, 1939-1942.

(1c) Clarke, *Am. J. Sci.*, **49**, 48-51 (1870).

(2) Thompson, *J. Soc. Chem. Ind.*, **15**, 179-181 (1896).

(3) Wheeler, *Analyst*, **63**, 883-4 (1938).

(4) Willard and Toribara, *This Journal*, **64**, 1759 (1942).

it is still possible to obtain almost complete recovery by adding 3 volumes of ethyl alcohol to precipitate the solids in solution. Alcohol also precipitates all the potassium oxalate, but this can be removed by fractional crystallization. The use of more dilute solutions necessitates an extra recrystallization to obtain a very pure salt.

Since the compound was dried immediately after preparation to prevent decomposition, the amount of water of hydration varied with the time of drying. For this reason the samples for the analyses of the several constituents were all weighed at one time and after a short period of drying to remove surface moisture. The analyses gave the ratio of the components in the compound.

*Anal.* Found (moles  $\times 10^3$  per gram): K, 4.532, 4.528; Sn, 2.265, 2.270; S, 2.265, 2.267;  $C_2O_4$ , 4.537, 4.531;  $H_2O$  (by difference), 4.50. Indicated formula:  $K_2SnS(C_2O_4)_2 \cdot 2H_2O$ .

**Hydration and Stability of Dipotassium Dioxalatothiometastannate.**—Water was determined directly on a salt which had been crystallized by cooling a solution saturated slightly above room temperature and which had been centrifuged at 1600 r. p. m. for thirty minutes. Analysis showed 9.11% of water, including surface moisture, or 2.25 moles of water per mole of salt. Some of this salt was dried at 95° for four hours without any decomposition. An analysis showed 8.30% of water, or 2.03 moles of water of crystallization. Continued drying at 60° for two weeks left only 0.6 molecule of water. Continued desiccation over sulfuric acid in a vacuum was also found to remove most of the water. A drastic process of desiccation, using the best vacuum obtainable from a Cenco Megavac pump and phosphorus pentoxide as the desiccant at a temperature of 60° for ten days, was found to remove all the water of hydration. No odor of hydrogen sulfide was evident when the flask was opened; such was not the case when the compound was decomposed by strong heating. The results indicate that the dihydrate is the phase which crystallized out of the solution and that it is quite stable. The stability of the compound to drastic drying was quite unexpected, especially in view of its behavior when wet.

The wet compound and the compound in solution were found to be unstable for two reasons: because of hydrolysis and because of atmospheric oxidation of the sulfide. A saturated solution of the compound remained clear for several weeks; a 0.1 *M* solution became tinged with yellow stannic sulfide within a few days; and more dilute solutions became tinged in even shorter periods of time. Boiling a solution of the compound caused separation of stannic sulfide, and prolonged heating at somewhat lower temperatures had the same effect. For this reason the process of recrystallization was accomplished in the shortest time possible. If the wet solid were allowed to remain in contact with air for any appreciable length of time, the sulfide was partially oxidized to free sulfur. When the compound had been dried, contact with air had no deleterious effects.

Reduction of the pressure above a solution of the salt at room temperature caused the liberation of hydrogen sulfide sufficient to precipitate stannic sulfide, making it impossible to use a low pressure evaporation to recover the salt. Complete removal of the water by such a process did not remove all the sulfur as in the case of the dioxalatothiometastannic acid.

**Solubility of Dipotassium Dioxalatothiometastannate in Water.**—The solubility of the salt at 25° was determined by saturating a solution at a slightly higher temperature in contact with the solid and then allowing it to come to equilibrium in the thermostat at the desired temperature. The average values obtained (based on oxalate, tin and sulfur analyses; the first two as already described<sup>4</sup> and sulfur by a titration with iodine) were: at 0°, 2.87% ( $\pm 0.015$ ); at 25°, 10.31% ( $\pm 0.01$ ); at 50°, about 30%, no exact determination being possible because of the instability of the solution.

**pH of Water Solutions.**—A solution 0.1 *M* in dipotassium dioxalatothiometastannate, kept free from oxygen, was prepared, and the first pH was determined with a glass electrode as soon after solution as possible. It was found that the pH of this solution did not change definitely in a period of one week, the readings varying in the range of 3.38 to 3.31. After two days the solution started to take on a tinge of yellow from small amounts of stannic sulfide. The quantity of stannic sulfide formed was sufficient to impart a yellowish tint to the solution but was not an appreciable quantity. This seems to indicate that all the time-change of pH must have occurred in the first few minutes while the solid was being dissolved.

The 0.1 *M* solution was then diluted to make solutions approximately 0.025 *M* and 0.01 *M*. The initial pH for the 0.025 *M* solution was 3.48, dropping to 2.38 in twenty-five minutes and returning to 3.48 as a steady value. For the 0.01 *M* solution, the initial pH was 3.40, dropping to 2.33 in fifteen minutes and increasing to 3.52 on long standing. Noticeable formation of colloidal stannic sulfide took place during these changes. It appears from these results that an equilibrium pH between 3.3 and 3.5 exists for solutions of dipotassium dioxalatothiometastannate. The fact that the neutral salt gives an acid solution indicates hydrolysis of the tin. The decrease in pH with dilution suggests a dissociation of the complex with further hydrolysis of the tin, and the subsequent rise in pH with the precipitation of stannic sulfide a reversal of the hydrolysis.

**Reactions in Solution.**—Different cations were added to an approximately 0.1 *M* solution of dipotassium dioxalatothiometastannate. The metals giving sulfide precipitates in acid solution with hydrogen sulfide gave an interesting set of reactions. The metals forming the more insoluble sulfides as silver, bivalent copper, bismuth, pentavalent antimony and bivalent mercury precipitated immediately as sulfides when added to the solution of dipotassium dioxalatothiometastannate. Bivalent lead and cadmium produced white precipitates which gave a test for sulfur, indicating that oxalatothiometastannate precipitates of those metals were formed. Zinc gave no precipitate. From these data a rather qualitative estimation may be made of the concentration of the sulfide ion. Lead and cadmium did not give sulfide precipitates, but it may be reasoned that this might be caused by the lesser solubilities of their oxalatothiometastannates. In the case of zinc, the fact that no precipitate was formed may serve as a limit for the concentration of sulfide ion, for zinc can be completely precipitated by hydrogen sulfide from a solution in which the pH is between 2 and 3. Although zinc forms a complex in an oxalate solution, the introduction of hydro-

gen sulfide in such a solution ( $pH$  about 3) causes precipitation of zinc sulfide.

The alkaline earths gave precipitates of a complex oxalatothiomastannate in all cases when the concentration of dipotassium dioxalatothiomastannate was made sufficiently large. The qualitative order of decreasing solubility was found to be magnesium, strontium, calcium and barium. In the case of magnesium, it was necessary to use a saturated solution of the potassium salt and allow it to stand for some time after solid magnesium chloride had been dissolved in it. The strontium and calcium precipitates formed rather slowly. Solid lithium chloride and solid sodium sulfate were added to saturated solutions of the potassium salt. The lithium salt dissolved and then gave a dense precipitate of an oxalatothiomastannate salt, but the sodium salt caused no precipitation.

**E. m. f. Measurements with Silver-Silver Sulfide Electrodes.**—An attempt was made to determine the sulfide ion concentration by means of e. m. f. measurements, using a  $Ag-Ag_2S$  electrode. The silver-silver sulfide electrodes were prepared according to Noyes and Freed,<sup>5</sup> but the value of  $E$  did not agree with their value. Several other sets of electrodes were prepared in an attempt to check their value, but no two identical sets of electrodes could be prepared. It was found that consistent results could be obtained by using the same electrodes in different solutions of the same strength. For this reason one set of electrodes was used for all the measurements.

The standard potential,  $E_0$ , of this electrode was determined on the cell

$Ag, Ag_2S, H_2S (0.0685) HCl (0.1) ||$  satd. calomel electrode, using the apparatus shown in Fig. 1. This cell gave 0.0780 v. for  $E$  at  $25^\circ$ , based on the value 0.2448 v. for the calomel electrode. Calculating the sulfide ion activity through the usual ionization constants for hydrogen sulfide ( $7.4 \times 10^{-8}$  for  $K_1$  and  $1.2 \times 10^{-16}$  for  $K_2$ ),  $E_0$  was then derived through the Nernst equation

$$E = E_0 - \frac{RT}{2F} \ln \frac{1}{a_{S^{2-}}}$$

giving  $E_0 = 0.7051$  v.

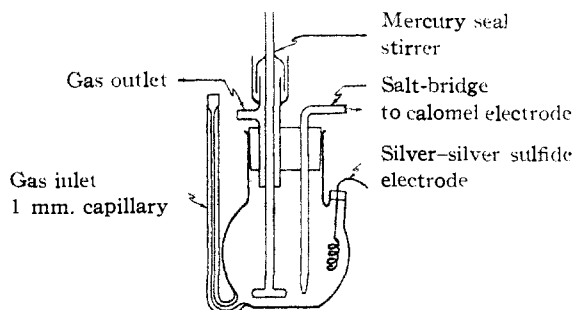


Fig. 1.—Electrode vessel.

Having found the value for  $E_0$ , e. m. f. measurements on solutions of different concentrations

of dipotassium dioxalatothiomastannate were made. The solutions were made with water which had been freed of dissolved air by bubbling through it nitrogen for a sufficient length of time. After removing air from the apparatus, both the gas inlet and outlet were closed off. The results obtained are shown in Table I.

TABLE I  
SULFIDE ACTIVITIES BY E. M. F. MEASUREMENTS AT  $25^\circ$

$K_2SnS(C_2O_4)_2$ concn., $M$	$E$ , volt	$a_{S^{2-}}$ , moles per liter
0.2458	0.0692	$3.1 \times 10^{-22}$
.2189	.0698	$3.2 \times 10^{-22}$
.0914	.1014	$3.8 \times 10^{-21}$
.0906 <sup>a</sup>	.0936	$2.1 \times 10^{-21}$
.1000	.0889	$1.4 \times 10^{-21}$
.0466 <sup>a</sup>	.1110	$8.0 \times 10^{-21}$

In the results marked  $a$  the maximum value of the e. m. f. was used. The e. m. f. was found to rise to a maximum and then to decrease. The solutions were examined and found to be colored with a yellow tinge from colloidal stannic sulfide. The other e. m. f. values were all steady, indicating equilibrium conditions, and the solutions were not colored by colloidal stannic sulfide. Equilibrium as evidenced by steady readings for eight hours or more was reached in about twelve hours.

The behavior of the solutions which showed the maximum e. m. f. values may be explained by stating that the hydrolysis of the salt proceeded to the point where the sulfide ion concentration built up sufficiently to produce a stannic sulfide precipitate. Since the electrode followed the concentration of the sulfide ion, the e. m. f. would rise to this point and then start to diminish as precipitation removed the sulfide ions. This point is probably the same point as that indicated by the minimum  $pH$  value noticed in the study of the  $pH$  of solutions of different concentrations.

The sulfide ion concentrations of the solutions of dipotassium dioxalatothiomastannate are in accord with the more qualitative observations on the addition of different metallic ions. In a solution of  $pH$  2, the sulfide ion concentration in a saturated hydrogen sulfide solution would be approximately  $6 \times 10^{-20}$ . This is about the lower limit of  $pH$  at which zinc can be precipitated. Comparing this value with that of an approximately 0.1  $M$  solution of dipotassium dioxalatothiomastannate as shown in Table I, it can be seen readily why zinc does not precipitate as a sulfide when added to a solution of the salt. Both lead and cadmium can be precipitated as

(5) Noyes and Freed, *THIS JOURNAL*, **42**, 476 (1920).

sulfides in a solution with such a sulfide ion concentration, but the complexes are precipitated instead probably because of their greater insolubility.

### Summary

1. Dipotassium dioxalatothiomastannate was isolated for the first time and proved to have the formula  $K_2SnS(C_2O_4)_2 \cdot 2H_2O$ .

2. The compound was stable enough to permit removal of all of the water of hydration.

3. The solubilities of dipotassium dioxalatothiomastannate in water at 25 and 0° were determined.

4. The pH of water solutions of varying concentrations of dipotassium dioxalatothiomastannate was studied.

5. The reactions of a water solution of dipotassium dioxalatothiomastannate with various cations were studied.

6. E. m. f. measurements in solutions of dipotassium dioxalatothiomastannate with a silver-silver sulfide electrode were made in an attempt to determine the concentration of the sulfide ion.

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## The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. I. Phenyl Substituted Olefins and Acetylenes

BY H. A. LAITINEN AND S. WAWZONEK

Isolated ethylenic and acetylenic linkages are not reducible at the dropping mercury electrode. However, double bonds which are either conjugated with carbonyl groups or present in heterocyclic nuclei like pyridine and quinoline can be reduced.<sup>1</sup> We have found that other types of unsaturated linkage are electroreducible. In the present paper the results of a polarographic study of phenyl substituted olefins and acetylenes are reported. The reduction of other types of unsaturated hydrocarbons will be described in forthcoming publications.

### Experimental

Dioxane-water mixtures containing 75% dioxane were used as a solvent, with 0.175 *M* tetrabutylammonium iodide as a supporting electrolyte. Since the half-wave potentials were unaffected by the pH of the solution (v. i.) unbuffered solutions were suitable for the measurements. Dioxane was found to be superior to acetone, isopropanol or methanol as a solvent in permitting the attainment of very negative potentials. In 50 to 85% dioxane solutions, using tetrabutylammonium iodide as the supporting electrolyte, the decomposition potential of the solvent was essentially constant at about -2.9 volts (*vs.* saturated calomel electrode), showing that the negative potential limit is determined by the discharge of the cation. Tetrabutylammonium salts were found to be superior to tetramethylanmonium salts in having a more negative discharge potential.

The dropping mercury electrode had the following characteristics. At a pressure of 46.5 cm. of mercury, the drop time in the solvent used was 3.34 seconds (open circuit).

The value of *m* was 2.05 mg. sec.<sup>-1</sup>, with a calculated value of  $m^{2/3}t^{1/3}$  of 1.973 mg.<sup>2/3</sup> sec.<sup>-1/3</sup> (open circuit). Values of  $m^{2/3}t^{1/3}$  at various potentials are given in Table II.

The electrolysis cell had a simple cylindrical shape with a mercury pool anode, and was provided with side arms for anode connection and for admission of nitrogen for the removal of dissolved oxygen. The anode potential was measured against a saturated calomel electrode (S. C. E.) by using a sintered glass salt bridge of the type described by Laitinen.<sup>2</sup> Its value was found to be reproducible at -0.452 volt in solutions of constant electrolyte concentration.

The current-voltage curves were determined with a Model XI Heyrovsky Polarograph having a current scale calibrated in microamperes. Data for the logarithmic analyses of the curves were obtained with a Fisher Electrode having specially calibrated current and voltage scales. The average resistance of the electrolytic cell was determined by the conventional Wheatstone bridge method, and found to be 2000 ohms. The half-wave potentials given in Table I are corrected for *iR* drop. All experiments were carried out at 25° in a water thermostat regulated to ±0.1°.

**Materials.**—The tetrabutylammonium iodide was prepared by a slight modification of the method used by Cox, Kraus and Fuoss.<sup>3</sup> Tri-*n*-butylamine (200 ml.) and *n*-butyl iodide (100 ml.) were heated together on a steam-bath for sixty-five hours. The resulting solid was filtered, washed with a small amount of ethyl acetate and then dissolved in the least amount of cold ethanol. The resulting solution was mixed with an equal volume of 10% potassium hydroxide in ethanol and poured into water. Removal of part of the alcohol under reduced pressure gave a crystalline precipitate of tetrabutylammonium iodide

(2) H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **13**, 398 (1941).

(1) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York, N. Y., 1941.

(3) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).