

1917
D 34

Dean

The Composition and the Decomposition
Products of Stannous Oxalate

THE COMPOSITION AND THE DECOMPOSITION
PRODUCTS OF STANNOUS OXALATE

BY

RALPH HIPPLE DEAN
B. A. Lake Forest College,

1916

THESIS

Submitted in Partial Fulfillment
of the Requirements for the
Degree of

MASTER OF ARTS

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1917.

1917
II 34

UNIVERSITY OF ILLINOIS
THE GRADUATE SCHOOL

~~May 31 1917~~

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
VISION BY Ralph Hipple Dean

ENTITLED The Composition and the Decomposition Products of
Stannous Oxalate

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF Master of Arts

B. S. Hopkins

In Charge of Thesis

W. A. Noyes

Head of Department

Recommendation concurred in:*

} Committee
on
Final Examination*

*Required for doctor's degree but not for master's.

7 Feb. 18 Gilley

COMPOSITION DECOMPOSITION

2



Digitized by the Internet Archive
in 2013

TABLE OF CONTENTS .

	Page.
I. Introduction - - - - -	1
II. The History of Stannous Oxalate - - - - -	1
III. Preparation of Stannous Oxalate - - - - -	2
IV. Analysis for the Tin Content of Stannous Oxalate - - - - -	3
V. The Electrolytic Determination of Tin in Stannous Oxalate - - - - -	4
VI. The Total Analysis of Stannous Oxalate	4
(a) - By Combustion - - - - -	5
(b) - Tin by Ignition - Oxalate by Titration - - - - -	5
VII. Table of Average Analyses - - - - -	9
VIII. The Solubility of Stannous Oxalate - - - - -	10
(a) - In Oxalic Acid - - - - -	10
(b) - In Oxalic Acid and Hydrochloric Acid - - - - -	10
(c) - In Water - - - - -	10
IX. The Decomposition Products of Stannous Oxalate in Vacuum - - - - -	11
X. Summary - - - - -	13

- ACKNOWLEDGEMENT -

This work was begun under Dr. H. C. P. Weber. It was continued under Dr. B. S. Hopkins, and Dr. E. W. Engle. I wish to thank these men for their interest in the work and their helpful suggestions. The supervision of Dr. Engle was especially appreciated.

THE COMPOSITION AND THE DECOMPOSITION PRODUCTS
OF STANNOUS OXALATE.

This research was undertaken with the intention of finding some suitable compound of tin, preferably one that had not been used, with which to determine the atomic weight of tin. This paper contains the results of an investigation upon stannous oxalate.

THE HISTORY OF STANNOUS OXALATE.

M. Boussingault⁽¹⁾ reported that stannous oxalate might be prepared by the action of oxalic acid on stannous acetate. He found that the salt gave water, carbon monoxide, carbon dioxide, and a tarry, oily residue, upon ignition. He judged the residue to be stannous oxide.

S. Hausmann and J. Lowenthal⁽²⁾ made stannous oxalate by the action of oxalic acid on stannous chloride. They found the salt stable in the air, very slightly soluble in cold and in hot water, insoluble in oxalic acid, and very soluble in cold, dilute acids. They stated that heating at 100° does not free the salt from water, 2 to 3 per cent remaining. This water was not driven off even on heating at 160° to 180°. When the salt was heated in a vacuum stannous oxide and some carbon remained. Samples of stannous

(1) - Annalen Chemie Physik (2) 54 (1833) 266.

(2) - Annalen 89 (1854) 104

Jahresbericht über die Fortschritte der Chemie und verwandter anderer
Wissen (1853) 408.

oxalate, prepared by the action of oxalic acid on stannous chloride, were analyzed by Hausemann and Lowenthal. Tin was determined by ignition, treatment of the residue with nitric acid and ignition to stannic oxide. The oxalic acid was determined by means of manganese peroxide and sulphuric acid in a carbon dioxide apparatus.

The following series of analyses are given:

Dried at 100°.		Dried at 160°.	
Sn O ₂	63.56%	Sn O ₂	63.61%
C ₂ O ₃	33.64%	C ₂ O ₃	33.43%
H ₂ O	<u>2.80%</u>	H ₂ O	2.91%
	100.00%		

From these results Hausemann and Lowenthal concluded that the formula of stannous oxalate was $3 \text{ Sn O}_2 - \text{C}_2 \text{ O}_3 \frac{1}{2} \text{ H}_2 \text{ O}$. This formula is not in close agreement with the results obtained.

PREPARATION OF STANNOUS OXALATE.

Metallic tin, prepared by C. A. F. Kahlbaum Co. was treated with an excess of hot, concentrated hydrochloric acid. As soon as solution was complete, the stannous chloride was placed in an atmosphere of carbon dioxide, to prevent its passing to the stannic form. The solution of stannous chloride was approximately .5 normal.

Chemically pure oxalic acid was recrystallized from the distilled water in this laboratory. A solution, approximately normal in strength, was made.

Stannous oxalate was prepared by the addition of oxalic acid to stannous chloride. This precipitation was carried on both in hot and in cold solutions. From a cold solution the salt came down as a fine powder. The salt was much more crystalline when prepared from a hot solution.

The samples were washed free from chlorides, ground in an agate mortar and portions dried in the air, in a dessicator over calcium chloride, at 110°, and at 140°.

ANALYSIS FOR TIN CONTENT OF STANNOUS OXALATE.

Weighed portions of stannous oxalate were ignited to constant weight in a covered porcelain crucible over a Bunsen burner and finally over a blast lamp. Care must be taken in heating the oxalate for it is readily reduced to metallic tin in the reducing flame. A white residue which was stannic oxide remained after ignition. In calculating the per cent of tin, the following atomic weights were used:

Tin	118.7
Carbon	12
Oxygen	16

The following series were analyzed:

(5) The sample of stannous oxalate was precipitated from a cold solution of 200 cc of normal oxalic acid and 100 cc of .5 normal stannous chloride. It was dried for sixty hours at 140°.

	gms. Stannous oxalate	gms stannic oxide	% Tin
1.	.4361	.3177	57.381
2.	.8073	.5883	57.400
3.	.6732	.4907	57.414
		Average	57.398

(6) The sample of stannous oxalate was prepared as number five, except that the solution was hot.

	gms. stannous oxalate	gms. stannic oxide	% Tin
1.	.5321	.3876	57.376
2.	.6804	.4960	57.420
3.	.4291	.3127	57.400
4.	.4811	.3505	57.384
		Average	57.395

and maintenance of these premises, the State has agreed to
 pay the cost of the same, and to provide for the same.

ARTICLE IV

Section 1. The State shall provide for the maintenance and
 improvement of the public schools, and shall provide for the
 maintenance and improvement of the public roads, and shall provide
 for the maintenance and improvement of the public buildings,
 and shall provide for the maintenance and improvement of the
 public parks and recreation grounds.

§ 1 § 2

ARTICLE V

Section 1. The State shall provide for the maintenance and
 improvement of the public schools, and shall provide for the
 maintenance and improvement of the public roads, and shall provide
 for the maintenance and improvement of the public buildings,
 and shall provide for the maintenance and improvement of the
 public parks and recreation grounds.

Year	Amount	Percentage	Total
1918	100.00	100.00	100.00
1919	100.00	100.00	100.00
1920	100.00	100.00	100.00
1921	100.00	100.00	100.00

Section 2. The State shall provide for the maintenance and
 improvement of the public schools, and shall provide for the
 maintenance and improvement of the public roads, and shall provide
 for the maintenance and improvement of the public buildings,
 and shall provide for the maintenance and improvement of the
 public parks and recreation grounds.

ARTICLE VI

Year	Amount	Percentage	Total
1922	100.00	100.00	100.00
1923	100.00	100.00	100.00
1924	100.00	100.00	100.00
1925	100.00	100.00	100.00

THE ELECTROLYTIC DETERMINATION OF TIN IN STANNOUS
OXALATE.

The sample used in this determination was precipitated from a cold solution of 100 cc of stannous chloride, and 100 cc of oxalic acid, and was dried at 140° for forty five hours.

The method employed was that of Classen⁽¹⁾. The solution of stannous oxalate in dilute hydrochloric acid was treated with a cold saturated solution of ammonium oxalate in the proportion of 20 cc to .1 gram of tin. Oxalic acid was added from time to time to keep the solution acid. The solution was then electrolysed between platinum electrodes with a rotatin anode. At the end of the electrolysis the platinum dish used for the cathode was washed with water and alcohol and dried at 90°. The method has the disadvantage of requiring from ten to twelve hours for a determination.

Results:

Gms. stannous oxalate	cc NH ₄ C ₂ O ₄	Amperage	Potential Difference	Time hrs.	Gms. Tin	% Tin
1. .3482	45	.3 amperes	3.1 volts	12	.1997	57.352
2. .2361	35	.35 "	4.0	10	.1355	57.390
Average						57.371

THE TOTAL ANALYSIS OF STANNOUS OXALATE.

The total analysis of the salt offered difficulties. The tin in the stannous form prevented titration for the oxalate since it was also affected by the reagents used. The tin may be changed to the stannic form by mercuric chloride, but the precipitate of mercurous chloride formed interferes with the end point, and is also partially oxidized in a hot solution with

(1) Quantitative Analysis by Electrolysis, Classen - Bottwood - p 212.

THE ELECTROLYTIC DETERMINATION OF TIN IN STANNOUS
OXALATE.

The sample used in this determination was precipitated from a cold solution of 100 cc of stannous chloride, and 100 cc of oxalic acid, and was dried at 140° for forty five hours.

The method employed was that of Classen⁽¹⁾. The solution of stannous oxalate in dilute hydrochloric acid was treated with a cold saturated solution of ammonium oxalate in the proportion of 20 cc to .1 gram of tin. Oxalic acid was added from time to time to keep the solution acid. The solution was then electrolysed between platinum electrodes with a rotatin anode. At the end of the electrolysis the platinum dish used for the cathode was washed with water and alcohol and dried at 90°. The method has the disadvantage of requiring from ten to twelve hours for a determination.

Results:

Gms. stannous oxalate	cc NH ₄ C ₂ O ₄	Amperage	Potential Difference	Time hrs.	Gms. Tin	% Tin
1. .3482	45	.3 amperes	3.1 volts	12	.1997	57.352
2. .2361	35	.35 "	4.0	10	.1355	57.390
Average						57.371

THE TOTAL ANALYSIS OF STANNOUS OXALATE.

The total analysis of the salt offered difficulties. The tin in the stannous form prevented titration for the oxalate since it was also affected by the reagents used. The tin may be changed to the stannic form by mercuric chloride, but the precipitate of mercurous chloride formed interferes with the end point, and is also partially oxidized in a hot solution with

(1) Quantitative Analysis by Electrolysis, Classen - Bottwood - p 212.

potassium permanganate. Analysis was undertaken by combustion.

(a) - Combustion -

Samples of stannous oxalate prepared as explained under preparation of the salt were ignited in a stream of oxygen and the decomposition products absorbed by a calcium chloride tube and potash bulbs. The white residue was weighed as stannic oxide and the percentage tin calculated from this weight. Various combustions were run but results which checked could not be obtained. The carbon dioxide value was always too low, the tin value high, and the water content varied from 0 to 5%. The samples may have been poorly dried. A better method of analysis was found and analysis by combustion was abandoned.

(b) - Tin by Ignition. Oxalate by titration -

The stannous tin in the salt was changed to the stannic form and the oxalate titrated against .1 normal potassium permanganate. The following procedure was developed.

.1 - .2 grams for stannous oxalate were gotten into solution by means of 15 cc of dilute hydrochloric acid - 15 cc of mercuric chloride solution⁽¹⁾ added with warming. The mercurous chloride formed was filtered off and the precipitate washed with cold water till the volume of the filtrate approached 200 cc. The solution was again warmed, 5 cc of manganese sulphate solution added, and the oxalate titrated against .1 normal potassium permanganate.

The following series were analyzed:

7 - The sample of stannous oxalate was prepared by adding a cold solution of 300 cc normal oxalic acid to 100 cc .5 normal stannous chloride, washed free from chlorides with cold water, ground in an agate mortar, and dried for fifty hours at 140°.

(1) 60 grams per liter water.

For Oxalate -

	gms. stannous Oxalate	cc. Potassium Permanganate	% Oxalate.
1.	.0792	6.35	42.583
2.	.1153	9.24	42.580
3.	.1125	9.01	42.533
4.	.0883	7.08	42.582
5.	.0547	4.39	<u>42.622</u>
		Average	42.580

For Tin -

	gms. stannous oxalate	gms. stannic oxide	% Tin
1.	.4862	.3541	57.367
2.	.3196	.2331	57.449
3.	.5521	.4024	<u>57.409</u>
		Average	57.408
			<hr/>
			99.988

3 - The sample was prepared by adding a cold solution of 100 cc normal oxalic acid to 100 cc .5 normal stannous chloride, washed free from chlorides with cold water, ground in an agate mortar and dried for fifty hours at 140°.

For oxalate -

	gms. stannous oxalate	cc potassium permanganate	% oxalate.
1.	.1408	11.28	42.547
2.	.1910	15.31	42.572
3.	.1576	12.63	42.560
4.	.1283	10.29	42.594
5.	.0218	7.36	<u>42.579</u>
		Average	42.570

For Tin -

	gms. Stannous oxalate	gms. stannic oxide	% Tin.
1.	.5326	.3877	57.338
2.	.4381	.3192	57.389
3.	.4692	.3420	<u>57.411</u>
		Average	<u>57.379</u>
			99.949

10 - A hot solution of 500 cc oxalic acid was added to 100 cc .5 normal stannous chloride. The stannous oxalate was washed free from chlorides with cold water, ground in an agate mortar and dried at 140° for fifty hours.

For oxalate -

	gms. stannous oxalate	cc. potassium permanganate	% oxalate	
1.	.1246	9.98	42.537	
2.	.1463	11.72	42.545	
3.	.1161	9.32	42.633	
4.	.0952	7.64	42.620	
5.	.0880	7.06	<u>42.607</u>	
		Average		42.588

For Tin -

	gms. stannous oxalate	gms. potassium permanganate	% tin	
1.	.6384	.4646	57.324	
2.	.5129	.3738	57.405	
3.	.5004	.3649	<u>57.437</u>	
		Average		57.388
				<hr/>
				99.976

9 - The stannous oxalate was prepared by adding 200 cc of normal, hot oxalic acid to 100 cc of .5 normal stannous chloride and dried six days in the air.

For Oxalate -

	gms. stannous oxalate	cc. potassium permanganate	% oxalate	
1.	.1789	13.91	41.294	
2.	.0855	6.65	41.305	
3.	.1274	9.92	41.352	
4.	.1036	8.06	<u>41.318</u>	
				41.317

For Tin -

	gms. stannous	gms. stannic oxide	% tin.	
1.	.3682	.2598	55.705	
2.	.4176	.2955	<u>55.720</u>	
				55.720
				<hr/>
				97.037

These results indicate that drying in the air does not completely free the salt from water.

8 - The sample of stannous oxalate was prepared by adding 300 cc of normal

oxalic acid to 100 cc .5 normal, hot stannous chloride, washed free from chlorides, ground in an agate mortar and dried in a dessicator over calcium chloride for thirty hours.

For oxalate -

	gms. stannous oxalate	cc. potassium permanganate	% oxalate.	
1.	.1398	10.88	41.331	
2.	.1564	12.16	41.291	
3.	.1134	8.82	41.306	
4.	.2006	15.62	<u>41.328</u>	
				41.314

For tin -

	gms. stannous oxalate	gms. stannic oxide	% tin.	
1.	.3641	.2576	55.727	
2.	.5112	.3618	<u>55.747</u>	
				55.727
				<hr/>
				97.044

Drying in a dessicator for thirty hours is not sufficient to entirely free the salt from water.

11 - The stannous oxalate was prepared by adding 250 cc. of normal oxalic acid to 100 cc. .5 normal stannous chloride, washed free from chlorides, ground in an agate mortar, and dried eight days at 110°.

For oxalate -

	gms. stannous oxalate	cc. potassium permanganate	% oxalate	
1.	.1132	9.08	42.599	
2.	.1091	8.74	42.545	
3.	.1580	12.66	42.553	
4.	.1492	11.96	42.572	
5.	.1782	14.28	<u>42.558</u>	
				42.567

For tin -

	gms. stannous oxalate	gms. stannous oxide	% tin.	
1.	.2285	.1667	57.463	
2.	.1312	.1060	<u>57.453</u>	
				<u>57.458</u>
				100.023

oxalic acid to 100 cc .5 normal, hot stannous chloride, washed free from chlorides, ground in an agate mortar and dried in a dessicator over calcium chloride for thirty hours.

For oxalate -

	gms. stannous oxalate	cc. potassium permanganate	% oxalate.
1.	.1398	10.88	41.331
2.	.1564	12.16	41.291
3.	.1134	8.82	41.306
4.	.2006	15.62	<u>41.328</u>
			41.314

For tin -

	gms. stannous oxalate	gms. stannic oxide	% tin.
1.	.3641	.2576	55.727
2.	.5112	.3618	<u>55.747</u>
			55.727
			<hr/>
			97.044

Drying in a dessicator for thirty hours is not sufficient to entirely free the salt from water.

11 - The stannous oxalate was prepared by adding 250 cc. of normal oxalic acid to 100 cc. .5 normal stannous chloride, washed free from chlorides, ground in an agate mortar, and dried eight days at 110°.

For oxalate -

	gms. stannous oxalate	cc. potassium permanganate	% oxalate
1.	.1132	9.08	42.599
2.	.1091	8.74	42.545
3.	.1580	12.66	42.553
4.	.1492	11.96	42.572
5.	.1782	14.28	<u>42.558</u>
			42.567

For tin -

	gms. stannous oxalate	gms. stannous oxide	% tin.
1.	.2285	.1667	57.463
2.	.1312	.1060	<u>57.453</u>
			<hr/>
			57.458
			100.023

TABLE OF AVERAGE ANALYSIS.

No. of Analysis	Per cent Tin	Per cent Oxalate	Total
5	57.398	- -	- -
6	57.395	- -	- -
-	57.371	- -	- -
7	57.408	42.580	99.988
3	57.379	42.570	99.949
10	57.388	42.588	99.976
9	55.720	41.317	97.037
8	55.727	41.314	97.044
11	57.458	42.567	100.023

THE SOLUBILITY OF STANNOUS OXALATE.

(a) - In Oxalic Acid.

The possibility of using stannous oxalate as a method of determining tin was considered. It was necessary to secure data as to the solubility of the salt in an excess of oxalic acid. The following procedure was used.

Weighed portions of anhydrous stannous oxalate were placed in Erlenmeyer flasks and 25 cc of normal oxalic acid added with a pipette to each sample. The flasks were placed in a thermostat for four days. The stannous oxalate was then collected in a gooch crucible, dried at 140° for thirty hours, and weighed.

The following results were obtained:

	gms. stannous oxalate	cc normal oxalic acid	stannous oxalic recovered	Solubility per cc N oxalic acid.
1.	.4067	25	.3249	.00327 g
2.	.4528	25	.3708	.00328

(b) - In oxalic acid and hydrochloric acid.

The stannous chloride used in preparation of the stannous oxalate contained a slight excess of hydrochloric acid. The solubility of stannous oxalate in a mixture of oxalic and hydrochloric acids was therefor determined.

The procedure was as that described above.

	gms. stannous oxalate	cc oxalic acid	cc conc. hydrochloric acid	gms. stan- nous oxalate recovered	Solubility per cc of solution	Solubility per cc N oxalic acid
1.	.5497	25	.5	.4662	.00328	.00334
2.	.4081	25	.5	.3250	.00326	.00332

The solubility of stannous oxalate in oxalic acid is but slightly affected by the addition of a small amount of hydrochloric acid.

(c) - In water.

In determining the solubility of stannous oxalate in water the same procedure was used.

Results:

	Gms. stannous oxalate	cc. water	gms. stannous oxalate recovered	solubility per cc. of water
1.	.4834	25	.4583	.00100
2.	.3209	25	.2952	.00103

THE DECOMPOSITION PRODUCTS OF STANNOUS OXALATE IN VACUUM.

Small portions of anhydrous stannous oxalate were heated in vacuum. The salt began to decompose slowly at approximately 240° . The decomposition point was not sharp. The heat was gradually raised and kept at 300° till the residue became black and gases were no longer carried over by the mercury of the pump. The gas, collected over mercury, was composed of carbon monoxide and carbon dioxide. The residue was composed of black stannous oxide and a small insoluble black residue. This black residue burned completely away in the air and it was concluded to be carbon. The vacuum was very good.

Small weighed portions of the oxalate were burned in ignition tubes and collected over water in a gas burette. Values for the total volume of gas involved, which checked, were obtained. The gases were also collected over potassium hydroxide in a gas burette. The carbon dioxide was absorbed by the potassium hydroxide and was determined by difference from the direct amount of carbon monoxide read on the burette. The values of carbon monoxide and carbon dioxide thus obtained were variable. The amount of insoluble matter in the residue was obtained by igniting the stannous oxide in the air to stannic oxide. The amount of stannic oxide obtained was less than that calculated from the amount of stannous oxalate. The difference between these values gave the amount of insoluble matter. This content of the residue was variable. In these analyses the apparatus contained some air. This small amount of air may have caused the variable decomposition and may have also caused the formation of some stannic oxide. The insoluble residue was not

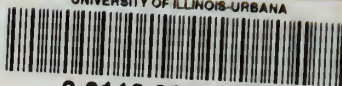
examined.

The lack of time has prevented a more complete investigation of the decomposition products.

SUMMARY.

- 1 - The composition of stannous oxalate has been shown to be constant whether prepared from a hot solution or from a cold solution.
- 2 - The water content of stannous oxalate is difficult to drive off, but may be completely removed at 110° .
- 3 - The formula for stannous oxalate has been shown to be $\text{Sn C}_2\text{O}_4$.
- 4 - The solubility of stannous oxalate in oxalic acid, in oxalic acid and a small amount of hydrochloric acid and a small amount of hydrochloric acid, and in water has been determined.
- 5 - This solubility prevents the use of stannous oxalate as a gravimetric method for the determination of tin.
- 6 - Stannous oxalate decomposes at 300° into carbon dioxide, carbon monoxide, and a residue of carbon and stannous oxide. The ratio of the decomposition products appears to be variable.

UNIVERSITY OF ILLINOIS-URBANA



3 0112 082199065