

CCXXXIX.—*Preparation and Reactions of Stannous Oxide and Stannous Hydroxides.**

By FRANK WARD BURY and JAMES RIDDICK PARTINGTON.

DITTE (*Ann. Chim. Phys.*, 1882, [v], **27**, 145) prepared stannous hydroxide by adding sodium or potassium hydroxide to a solution of stannous chloride, the precipitate being washed by decantation and dried in a vacuum at 14°. He obtained a brownish-yellow, amorphous powder to which he assigned the formula $\text{SnO}, 2\text{H}_2\text{O}$. On heating this powder at 110°, Ditte obtained small, brown scales which could be readily powdered. To this substance he assigned the formula $3\text{SnO}, 2\text{H}_2\text{O}$. Ditte does not mention the methods used in analysing the substances.

Schaffner (*Annalen*, 1844, **51**, 168) prepared a specimen of stannous hydroxide by the addition of potassium carbonate to stannous chloride solution. He dried the precipitate below 80°. The amount of water in the compound was estimated by heating it to dull redness in a bulb tube in a stream of carbon dioxide, and assuming the loss in weight to be water and the residue stannous oxide. No estimation of the percentage of tin present in the compound was made. Schaffner assigned to this compound the formula $2\text{SnO}, \text{H}_2\text{O}$. He described the precipitate produced by the addition of ammonia to stannous chloride as "a basic salt."

In view of the discrepancies between these statements, the matter was thought worthy of re-investigation. Specimens of stannous hydroxides were prepared by methods described by previous investigators and analysed.

EXPERIMENTAL.

Preparation of the Specimens of Stannous Hydroxide.

The stannous chloride solution was made by adding 22.5 grams of crystalline stannous chloride to 100 c.c. of water. This solution was clarified by addition of a minimum amount of strong hydrochloric acid and tin and heating. The calculated amount of precipitant was used, as it was noted that excess of alkali caused the stannous hydroxide to darken and become almost black.

Sample A.—To the solution of stannous chloride, sodium hydroxide solution was added until a faint permanent precipitate was produced. The calculated amount of sodium hydroxide (8 grams)

* "Stannous hydroxide" throughout this paper means a hydrated form of stannous oxide obtained by any method described, and not necessarily the definite compound $\text{Sn}(\text{OH})_2$; perhaps a more suitable name would be "hydrated stannous oxide" or "stannous oxide hydrate."

necessary for precipitation was then added. There is therefore a slight excess of stannous chloride in this solution. The precipitate was washed with cold boiled water in a Büchner funnel. No precautions were taken to prevent access of air. The precipitate was distinctly yellow, very gelatinous, and obviously colloidal. After drying in a desiccator over calcium chloride for two days, it was, when powdered, distinctly yellow and readily soluble in dilute hydrochloric acid; the solution gave a copious precipitate with mercuric chloride. The powder was placed in a vacuum desiccator over phosphoric oxide for fourteen days and then analysed.

Sample B.—To the solution of stannous chloride made as in the preparation of sample *A* a very concentrated sodium carbonate solution was added until a faint precipitate was produced. To this solution, 10.6 grams of pure anhydrous sodium carbonate were added, the liquid was filtered, and the precipitate washed with boiled water. This precipitate tended to pass through the filter. It was dried in a desiccator over calcium chloride for four days, then powdered, and placed in a vacuum desiccator during the vacation for one month, but at the end of the time the vacuum had disappeared. The sample was placed in an atmospheric desiccator over calcium chloride, phosphoric oxide, and potassium hydroxide for a further fourteen days and then analysed.

Sample C.—To the stannous chloride solution prepared as in *A*, neutralised with sodium carbonate, enough ammonia was added to give a faint smell of ammonia, and the precipitate was washed as before. The sample was left in a desiccator over phosphoric oxide.

Sample F.—According to Roscoe and Schorlemmer ("Treatise," 1913, Vol. II, p. 854) stannous hydroxide is rapidly oxidised by the air. Sample *F* was prepared in a similar way to sample *C*, but precautions were taken to exclude air and to carry out the preparation in an atmosphere of carbon dioxide.

The stannous hydroxide was precipitated in a flask filled with boiled water and filtered in a Büchner funnel arranged with a brass cover with three tubulures. Through two of these a stream of carbon dioxide was kept passing. Through the third passed a siphon tube from the flask containing the precipitate, the liquid being displaced into the funnel by a stream of carbon dioxide admitted through a second tube in the cork of the flask. This flask was afterwards filled through the second tube with boiled water, which was used for washing the precipitate.

Sample H was prepared by means of the apparatus described in the preparation of *F*, but using the calculated amount of sodium carbonate as the precipitant. The stannous hydroxide was placed

in a vacuum desiccator containing phosphoric oxide for fourteen days before analysis.

Appearance of the Specimens A, B, C, F, and H.—Samples *A, B, and H* had a yellow tinge when first precipitated, which became more marked on drying. Samples *C* and *F*, prepared by precipitating with ammonia, were white at first, but became yellow on drying. On keeping them in glass specimen tubes, they became darker on the outside, that is, the parts touching the glass. Ditte comments on this phenomenon and states that the parts of the dried specimens in contact with the glass go brown owing to their "containing less water than the original hydrate," but does not state how he drew this conclusion. It has already been mentioned that an excess of alkali darkens the stannous hydroxide, so that this change of colour may be due to traces of alkali on the glass. This explanation was confirmed by keeping the specimens in silica tubes, when no change of colour was observed. Specimens *A, B, C, F, and H* were all amorphous and colloidal towards the end of the washing and had a tendency to pass through the filter-paper. They were readily soluble in cold dilute hydrochloric acid, indicating the absence of stannic oxide. On boiling portions of the specimens with dilute nitric acid and adding silver nitrate, a slight opalescence was obtained, showing that the chloride had not been entirely removed.

Preparation of Samples D, E, and G.—In the preparation of these samples, *D* by precipitation with sodium hydroxide, *E* and *G* by precipitation with sodium carbonate, the stannous hydroxide began to pass through the Büchner filter before the precipitates were free from chloride. They were therefore mixed together and the washing continued by decantation. The flasks were arranged as wash-bottles. The solutions containing the suspended stannous hydroxide entirely filled the flasks. When the stannous hydroxide had settled down, the liquid was decanted by attaching a Kipp's apparatus, generating carbon dioxide, to the tube not acting as the syphon. The precipitate slowly became dark grey. It was left under water for several weeks in a corked flask filled with water. The walls of the flask became covered with small clusters of needle-shaped crystals in about five weeks' time, dark in appearance, with a silvery lustre. On addition of water, many similar although smaller crystals were in suspension, and gave a creamy, yellow liquid which glistened on shaking. The black solid, on treatment with water, gave a similar solution. It filtered very slowly. A little ammonium chloride solution was added, and on warming, a yellow, flocculent precipitate, which readily filtered, was obtained. We may regard the yellow solution as a

colloidal solution of crystalline stannous oxide. The precipitate was filtered off, washed, and dried in a steam-oven.

The black residue remaining in the flask was the same product as that obtained above, as on the addition of water it gave the same olive-green paste, which on further addition of water became a creamy, yellow liquid, which glistened on shaking.

A weighed portion of the mixed samples *D*, *E*, *G*, was dried in an air-oven at 110° and cooled in a desiccator.

Analyses of All Samples.

The percentage of tin was estimated by igniting the sample in a porcelain crucible and assuming the residue to be SnO_2 .

The percentage of water was estimated by finding the loss in weight on heating in an atmosphere of carbon dioxide in a bulb tube (Schaffner, *Annalen*, 1844, 51, 168). In each case there was a little sublimate produced, which dissolved readily in water and gave a black coloration with silver nitrate and a slight precipitate with mercuric chloride, indicating that the sublimate was stannous chloride. This sublimate was driven off and the tube again weighed. The loss was never more than 0.2 per cent., and in most cases was negligible.

The chloride present was also estimated by fusing a weighed portion of the sample with sodium carbonate. The residue was boiled with water and filtered. To the filtrate 10 c.c. of *N*/10-silver nitrate solution were added and the excess was estimated by titration with *N*/10-potassium thiocyanate with iron alum as indicator.

In samples *A*, *B*, *C*, *F*, and *H*, the chloride present was negligible. In sample (*D*, *E*, *G*) the chlorine found corresponded with 0.979 per cent. of stannous chloride.

The results are tabulated below :

	% Sn.	% H_2O .	% O by calculation as SnO .
<i>A</i>	80.9	7.11	10.86
<i>B</i>	79.82	8.54	10.72
<i>C</i>	79.41	8.32	10.67
<i>F</i>	80.5	8.82	10.8
<i>H</i>	80.91	7.4	10.86

Results with (*D*, *E*, *G*) after heating in an air-oven at 110°: Percentage of SnO found was 95.76; H_2O , 2.5; SnCl_2 , 0.979.

The percentage of SnO found in this sample after heating in an air-oven at 160° for two and three-quarter hours was 94.62. Thus the oxidation had become marked.

Conclusions.

- (1) The six samples were essentially the same.
- (2) Little or no reaction occurs between moist stannous hydroxide and the atmosphere at the ordinary temperature.
- (3) The precipitate with ammonia is probably the same as the others, although Schaffner states this to be a basic salt.
- Fremy (*Ann. Chim. Phys.*, 1844, [iii], **12**, 460) describes a reddish-brown stannous oxide obtained on precipitating stannous chloride with a slight excess of ammonia and boiling for some time. Attempts to obtain this variety were unsuccessful. In one case only, a slight red tinge appeared on the glass where part of the liquid had dried, but the solid in suspension did not become red.
- (4) No sample was entirely free from chlorine, although in most cases the amount was negligible.
- (5) Probable formula:

		% Sn.	% H ₂ O.	% O.
Schaffner	2SnO, H ₂ O requires	82.64	6.25	11.11
"	obtained		6.46	
Ditte	3SnO, 2H ₂ O requires	80.97	8.16	10.87
"	obtained (?)	79.13	8.87	11.11

Ditte does not in any single case give his experimental methods, but states that the specimen was obtained in "brownish scales" by drying the precipitated hydroxide at 110°. He assigns the formula SnO, 2H₂O to a brownish-yellow, amorphous powder obtained by leaving the hydrate in a vacuum at 14°.

The analyses of samples *A*, *B*, *C*, *F*, and *H* support the formula 3SnO, 2H₂O.

(6) The result with (*D*, *E*, *G*) indicates that stannous hydroxide is stable at 110°; the percentage of water then fell to 2.5. The 0.8 per cent. unaccounted for may be due to some oxidation.

(7) Stannous hydroxide, on standing under water, slowly loses water to become stannous oxide.

(8) Stannous hydroxide does not lose the whole of its water at 160°. In all probability some of the water is constitutional.

Supposed Modification: of Stannous Oxide.

Ditte describes a number of experiments with stannous hydroxide in which several varieties of stannous oxide, differing in appearance, colour, and density, were produced.

For an account of these, reference must be made to the original paper, but it may be stated that the experimental conditions are not clearly described by Ditte. In many cases it was found impossible to confirm the statements of the latter. It will be sufficient to give a brief account of the results obtained, which may be compared with those described by Ditte.

(1) *Reaction with Stannous Chloride.*—The dried specimens of the hydroxide were boiled with water and one or two crystals of stannous chloride: a faint salmon-pink suspension was obtained, which did not darken further on boiling. On the addition of excess of stannous chloride, the stannous hydroxide became white again. There was no red, green, or black colour produced, as stated by Ditte.

A sample of stannous hydroxide was prepared as in sample B, but *not dried*. It was kept under water and slowly became black on the outside when exposed to light. This stannous hydroxide is referred to as “wet stannous hydroxide.” To about 1 gram of the wet stannous hydroxide suspended in cold water, two or three crystals of stannous chloride were added. The hydroxide slowly became grey on heating, but no red colour was seen; an olive-green oxide slowly precipitated after five minutes, but a good deal of white stannous hydroxide was left.

(2) *Reaction with Hydrochloric Acid.*—No change was observed on boiling the dry or wet stannous hydroxide with very dilute hydrochloric acid.

(3) *Reaction with Ammonium Chloride Solution of Various Strengths.*—On boiling the stannous hydroxide with solutions of ammonium chloride of various strengths, Ditte obtained several modifications of stannous oxide.

These experiments were repeated with the dried specimens. No change was observed on boiling them with the ammonium chloride solutions. There was a slight change observed when the wet stannous hydroxide was used, but the amount of ammonium chloride present appeared to have no effect on the result. On boiling with the ammonium chloride solution, the stannous hydroxide slowly became grey, and a dark grey, sandy, crystalline precipitate of stannous oxide was formed in all cases. The precipitate, on washing with water, gave a milky liquid.

The product in all experiments always appears to be the same, namely, the dark grey stannous oxide which is formed slowly when the white hydroxide is kept under water. The white hydroxide appears to be an unstable substance which slowly decomposes into stannous oxide, and the various reagents described by Ditte appear to act catalytically in accelerating this change.

(4) *Reactions with Acetic Acid.*—The wet stannous hydroxide was dissolved in acetic acid solution (10 c.c. of glacial acetic acid diluted to 85 c.c.). The excess of stannous hydroxide was filtered off and the filtrate transferred to a desiccator containing concentrated sulphuric acid and potassium hydroxide. In two months, a yellow, crystalline solid was obtained. This solid, on ignition,

blackened, and then became yellow; the residue, on cooling, was nearly white. Assuming the residue to be stannic oxide, the percentage of tin found in the substance was 49.55. The percentage of tin required by the formula $\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_2$ is 50.1. This substance is probably stannous acetate containing a little water. It is rather hazardous to assign the percentage of tin to Ditte's formula, $2(\text{C}_4\text{H}_3\text{O}_3)\text{SnO}\cdot\text{HO}\cdot 2\text{HO}$, for this substance, as he does not state what atomic weights he used, and appears to use HO and H_2O indiscriminately for the formula of water.

To the wet stannous hydroxide in boiling water a few drops of glacial acetic acid were added. There was a darkening of colour, and a black precipitate was produced, but the liquid retained its yellow tint. With excess of glacial acetic acid, the precipitate became yellowish-white.

It was not found possible to prepare the red form obtained by Roth (Abegg, III, 2, 573) by heating the hydroxide with a solution of stannous oxide in acetic acid.

(5) *Reaction with Nitric Acid*.—On treating wet stannous hydroxide with dilute nitric acid, a solution was obtained. This was left in the desiccator for two months; a solid residue of a white, porcelain-like appearance remained. On ignition, white and then brown fumes were evolved, and assuming the residue to be stannic oxide, the percentage of tin contained in this substance was found to be 55.4. The substance did not detonate on heating. The compound was insoluble in cold water and not completely soluble in hot water, gave no precipitate with mercuric chloride, and is probably a basic stannic nitrate.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

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