177. *Hydrous Tin*(II) *Oxide.*

By J. D. DONALDSON and W. MOSER.

The preparation of pure hydrous tin(II) oxide [tin(II) hydroxide] has been investigated. The impossibility of preparing the compound free from both tin(IV) and anionic impurity by precipitation is demonstrated. Analysis indicates that the material cannot have any of the compositions previously suggested, and evidence given shows that the most probable composition is $5SnO,2H_2O$ [$Sn_5O_3(OH)_4$]. Hydrous tin(II) oxide is dehydrated in one stage at temperatures above 120° to give an orange amorphous material, not previously reported; this rapidly changes to blue-black tin(II) oxide on continued heating. The non-existence of the oxide Sn_3O_4 in the disproportionation product of tin(II) oxide is proved.

THE precipitate [1,2] obtained by raising the pH of a solution of a stannous salt to about 10, by addition of any alkaline solution, is normally called tin(II) hydroxide. The chemical formula of the material is, however, not $Sn(OH)_2$ and throughout this work it is referred to more suitably as hydrous tin(II) oxide.

There are two conflicting reports of the chemical composition of the material, neither composition being founded on complete chemical analysis. Bury and Partington's [1] formula, $3SnO,2H_2O$, is based on analysis of total tin and water, and Weiser and Milligan's [2] formula, $2SnO,H_2O$, on the results of dehydration. Hydrous tin(II) oxide is dehydrated to blue-black tin(II) oxide when heated *in vacuo* or in a non-oxidising atmosphere, all the water being lost between 120° and 160°. At ~100° the material gradually becomes yellow and this colour darkens to orange; it is reported [2] that these colour changes are due only to changes in particle size. The disproportionation of the blue-black tin(II) oxide at higher temperatures has also been studied. Straumanis and Strenk [3] report that the disproportionation product is not a β-modification [2] of tin(II) oxide but a mixture of tin and tin(IV) oxide. Other authors [4,5] state that the products are tin and the oxide Sn_3O_4.

We have studied the composition of the hydrous tin(II) oxide precipitate, obtained the most likely formula for the material, and extended the data on its dehydration and on the disproportionation of tin(II) oxide.

EXPERIMENTAL

Preparation and Analysis.—Hydrous tin(II) oxide was prepared by addition of oxygen-free solutions of alkali or alkali carbonate to oxygen-free solutions of tin(II) sulphate,[6] under oxygen-free nitrogen, until the pH of the solution was between 10 and 12. The product was filtered off, washed either with deaerated distilled water or with alcohol followed by ether, and dried overnight *in vacuo* over various desiccants. Stannous and total tin were determined by Donaldson and Moser's method,[7] and water by heating the sample in a stream of oxygen and weighing the water in an anhydrone absorption tube. All water assays were checked by dehydration studies, under oxygen-free nitrogen, on a Stanton thermobalance.

Table 1 contains typical analyses of samples prepared with different precipitants. Average analytical data for 2 samples are reported in each case. Care must be taken when sodium hydroxide or sodium carbonate solutions are used as precipitants, because partial dehydration of the hydrous oxide to tin(II) oxide occurs if the pH rises above 12. Table 2 shows the effect of prolonged storage of hydrous tin(II) oxide *in vacuo* over various desiccants.

---

[1] (*a*) Bury and Partington, *J.*, 1922, **121**, 1998; (*b*) Proust, *J. Phys.*, 1800, **51**, 173; 1804, **61**, 338; Schaffner, *Annalen*, 1884, **51**, 168; Ditte, *Ann. Chim. Phys.*, 1882, **27**, 145; Britton, *J.*, 1925, **127**, 2120.

[2] Weiser and Milligan, *J. Phys. Chem.*, 1932, **36**, 3039.

[3] Straumanis and Strenk, *Z. anorg. Chem.*, 1933, **213**, 301.

[4] Spandau and Kohlmeyer, *Z. anorg. Chem.*, 1947, **254**, 65.

[5] Spandau and Ullrich, *Z. anorg. Chem.*, 1953, **274**, 271.

[6] Donaldson and Moser, *J.*, 1960, 4000.

[7] Donaldson and Moser, *Analyst*, 1959, **84**, 10.

Samples prepared from solutions of tin(II) chloride dihydrate contained more tin(IV) as impurity than did those from tin(II) sulphate.

The change in composition of the precipitate—hydrous oxide or basic sulphate—with pH was studied by a series of preparations carried out under oxygen-free nitrogen in an air-tight compartment and with completely deaerated solutions. The preparations were as follows: N-Sodium hydroxide (varied amounts) was added to a solution of tin(II) sulphate[6] (5 g.) in 2N-sulphuric acid (20 ml.); the precipitate was washed with distilled water and dried overnight *in vacuo* over potassium hydroxide pellets. Tin and water were determined as above and sulphate by collecting any sulphur dioxide liberated in the water determination in a weighed soda–asbestos absorption tube. It is assumed that any sulphate present will decompose, giving tin(IV) oxide and sulphur dioxide by an internal oxidation–reduction, as does tin(II) sulphate.[6] Even if the reaction is not quantitative in the case of basic sulphates, it does give an indication of the amount of sulphate present in the precipitate and this is sufficient for the present work. Table 3 contains the analytical data for the precipitates obtained at different pH values.

TABLE 1. *Analytical data for hydrous tin*(II) *oxide.*

	Average results from analysis				Average results from analysis		
Precipitant	Stannous tin (%)	Total tin (%)	Water (%)	Precipitant	Stannous tin (%)	Total tin (%)	Water (%)
N-NaOH	79·5	81·0	4·63	Saturated aq. $NaHCO_3$	78·0	80·2	4·20
	78·4	81·4	4·42		78·3	80·4	4·23
Saturated aq. Na_2CO_3	79·1	81·0	4·20	2N-NH_3	79·3	82·1	4·41
	77·9	80·0	4·22		80·0	82·7	4·18

TABLE 2. *Effect of storage of hydrous tin*(II) *oxide* in vacuo *over various desiccants.*

	7 Days' storage		14 Days' storage	
Desiccant	Stannous tin (%)	Total tin (%)	Stannous tin (%)	Total tin (%)
P_2O_5	78·6	80·2	75·8	81·2
Conc. H_2SO_4	78·0	80·0	76·1	82·1
$Mg(ClO_4)_2$	78·2	80·1	77·8	81·4
KOH	78·1	80·2	76·1	82·2

TABLE 3. *Composition of the basic sulphate or hydrous tin*(II) *oxide with* pH.

	Average results from analysis				
pH of mother-liquor	Stannous tin (%)	Total tin (%)	Sulphate (%)	Water (%)	*X*-Ray diffraction powder pattern of ppt.
2·4	75·9	75·8	12·3	3·72	Basic sulphate
2·9	77·2	77·0	11·0	3·75	
4·1	79·0	79·2	5·37	4·25	Some lines of basic sulphate and of hydrous oxide
4·2	80·9	80·9	3·99	4·63	
5·2	80·9	80·8	3·05	4·68	
6·3	80·1	82·5	1·77	4·83	Hydrous oxide
6·9	80·8	82·5	1·10	4·84	
9·6	80·0	82·1	0·63	4·94	
10·1	80·1	82·2	0·63	4·92	
10·6	80·8	82·6	0·61	4·98	
11·7	79·5	82·2	traces	4·97	

Hydrous tin(II) oxide can be prepared in a crystalline form by the hydrolysis of some basic tin(II) salts. When basic tin(II) nitrate[8] is stored for a few days under deaerated distilled water, yellow nuggets of hydrous tin(II) oxide are deposited. These nuggets contain some tin(IV) and nitrate as impurity and although they are suitable for study by *X*-ray diffraction[9] they are less pure than samples prepared by precipitation.

Thermal Dehydration of Hydrous Tin(II) *Oxide.*—The dehydration was followed on a Stanton thermobalance in an atmosphere of oxygen-free nitrogen. The water is lost in one stage at

---

[8] Donaldson and Moser, in the press.

[9] Donaldson, *Acta Cryst.*, in the press; Donaldson, Moser, and Simpson, following paper.

temperatures above 120°, but the initial dehydration product is an orange material and not blue-black tin(II) oxide as previously reported.[2] We thus show that Weiser and Milligan wrongly reported that the yellow and the orange colour were connected with the particle size of the hydrous oxide. The material contains no more tin(IV) than was present in the hydrous oxide from which is was prepared and contains no water. The composition of the material is, therefore, SnO. Its *X*-ray diffraction powder pattern which consists of a single diffuse band (at 2·97 Å) shows that the material is amorphous. The orange material, unlike the blue-black and the red [10] modifications of the monoxide, is converted into tin(IV) oxide by a few days' contact with air, in agreement with the small particle size of an amorphous solid.

The disproportionation of tin(II) oxide was studied by *X*-ray-diffraction techniques at the decomposition temperature (385°). The powder pattern above this temperature contains only lines due to tin(IV) oxide; there is no evidence for the presence of a new phase Sn_3O_4. When the sample is cooled below 230° additional lines appear in the pattern but these are all assignable to the tin phase which solidifies at this temperature.

TABLE 4. X-*Ray diffraction powder data for hydrous tin*(II) *oxide.*

d (Å)	Rel. intensity	*d* (Å)	Rel. intensity	*d* (Å)	Rel. intensity	*d* (Å)	Rel. intensity
6·02	vw	2·42	mw	1·67	m	1·304	vw
5·68	vw	2·29	w	1·63	m	1·282	vvw
5·01	vvw	2·00	vvw	1·568	m	1·244	w
4·60	vvw	1·94	m	1·539	m	1·207	vvw
3·55	s	1·92	m	1·503	vw	1·200	vvw
3·31	m	1·83	w	1·476	m	1·188	s
3·00	s	1·78	s	1·427	vvw	1·162	vvw
2·82	vs	1·77	w	1·398	mw	1·149	vvw
2·52	mw	1·74	w	1·341	vw	1·123	m

Table 4 contains the *X*-ray diffraction powder pattern of hydrous tin(II) oxide obtained by using 11·64 cm. cameras and a Philips *X*-ray diffractometer with filtered Cu-K_α radiation. The data improve upon those in the A.S.T.M. index (No. 7-194) in content and accuracy. The powder pattern of a freshly prepared paste of hydrous tin(II) oxide is identical with that of the dried material, showing that drying does not lead to appreciable quantities of a new phase.

DISCUSSION

In the analysis of hydrous tin(II) oxide all previous workers have relied on determination of total tin and neglected the possible presence of tin(IV). However, the analytical data above show that even samples prepared in the complete absence of elemental oxygen contain about 2% of tin(IV). The buff colour of the dried material is presumably due to the presence of this impurity. The results (Table 2) strongly suggest that it is impossible to prepare, by precipitation, a sample of hydrous tin(II) oxide which is free from both tin(IV) and sulphate. Sulphate contamination of over 1% occurs up to a pH of about 7, and appreciable oxidation of tin in the sample occurs from pH 6·3. The only explanation of the formation of tin(IV) in experiments under nitrogen and in vacuum-desiccators (Table 3) seems to be reduction of water (hydroxyl) by the bivalent tin. Measurement of the potential of a platinum electrode in a solution of pure tin(II) sulphate in water with increasing pH shows a sharp change of about 0·1 v between pH 6·0 and 6·2. This is due to the initial rise in tin(IV) concentration from traces to about 2%, a result in agreement with those in Table 3.

Derivation of a formula for the material is difficult for three reasons: (1) It is not certain whether the impurities form a separate phase or whether they are in some way distributed homogeneously throughout the hydrous oxide phase. For the stannic tin impurity, homogeneous distribution seems more likely because of the darkening of colour with increase in tin(IV) content. All precipitates of hydrous tin(II) oxide are white when freshly prepared and become buff only on drying. This suggests that the stannic tin occupies sites in the hydrous oxide lattice and may in part arise from the internal reaction,

---

[10] Partington and Moser, *Nature*, 1944, **154**, 643.

$2Sn^{2+} + 2OH^- \longrightarrow Sn^{4+} + 2O^{2-} + H_2$. (2) It is not certain how much of the water is associated with impurity phases but the one-stage dehydration suggests that all of the water is associated with one phase and this must be the hydrous oxide phase. (3) It is not certain how much of the tin is associated with the traces of sulphate impurity.

It is obvious, however, from the fact that the amount of water in the sample never exceeds 5%, that the formulæ $3SnO,2H_2O$ (requiring 8·18% of water) [1a] and $2SnO,H_2O$ (requiring 6·26% of water) [2] are inadmissible. A formula containing less water is more likely. If we make the assumptions (*a*) that the tin(IV) present occupies sites in the hydrous oxide lattice and (*b*) that the traces of sulphate are essentially sorbed impurities, the tin and water percentages for the last four samples in Table 3 become: 83·7, 5·00; 83·5, 5·00; 83·4, 5·03; 83·4, 5·04. From these figures it seems that the most probable composition of hydrous tin(II) oxide is $5SnO,2H_2O$ (requiring 83·7% of tin, 5·07% of water). Further support for the suggested formula comes from unit-cell and density data; [9] the probable contents of the large triclinic cell are more nearly a multiple of $5SnO,2H_2O$ than of any other simple formula. Finally, in view of the similarity between the compounds of tin and lead, the fact that the composition of hydrous lead(II) oxide is reported [11] as $5PbO,2H_2O$ may be taken as evidence for the suggested formula.

The gradual yellowing and darkening of hydrous tin(II) oxide heated in the absence of oxygen, as reported by Weiser and Milligan,[2] was observed and may indicate the onset of dehydration. Hydrous tin(II) oxide is dehydrated completely, to give an orange amorphous material which, from its colour, is presumably related to the red modification of tin(II) oxide but is converted, if further heated, into the more stable blue-black tin(II) oxide before sizeable crystals of the red form can develop. The disproportionation products of tin(II) oxide are confirmed as tin and tin(IV) oxide, as reported by Straumanis and Strenk.[3] This disproportionation is an example of the internal oxidation–reduction common in oxygen-containing tin(II) compounds. In the case of tin(II) oxide the material is simultaneously oxidised to the very stable tin(IV) oxide and reduced to tin metal. Spandau and Kohlmeyer [4] postulated the existence of the oxide Sn_3O_4 to avoid an apparent phase-rule difficulty. The difficulty, however, only arises because of the analytical method which they used. Their method depended on the mechanical separation of tin by sieving, but failure to remove all of the tin results in its inclusion in the analytical report as SnO. Moreover, in some cases they found it impossible to remove the metallic tin, and analyses were obtained by weighing the residue, which would not dissolve in concentrated hydrochloric acid, and assuming it to be the total original tin(IV) oxide. The tin and tin(II) oxide percentages were then obtained by difference, with allowance for the oxygen originally present in the SnO sample. This procedure is meaningless, because any original tin(IV) oxide small enough to be dissolved or reactive enough to be reduced (by dissolution of metal) during the hydrochloric acid extraction necessarily appears as tin(II) oxide. The fact that *X*-ray-diffraction studies indicate the absence of lines due to tin(II) oxide or to a possible new phase, Sn_3O_4, proves that this oxide does not exist in the decomposition products of tin(II) oxide, either as a mixed oxide or as a separate phase.

One of us (J. D. D.) is grateful to D.S.I.R. for a Research Grant.

CHEMISTRY DEPARTMENT, UNIVERSITY OF ABERDEEN,
OLD ABERDEEN, SCOTLAND.

[*Received, September* 16*th*, 1960.]

---

[11] Clark and Tyler, *J. Amer. Chem. Soc.*, 1939, **61**, 58.