178. *Red Tin*(II) *Oxide.*

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The preparation of a red modification of tin(II) oxide is described and the exact conditions under which it can be obtained are reported. The stability of the material is discussed, and the *X*-ray diffraction powder and unit-cell data are given.

A METASTABLE red modification of tin(II) oxide has been reported[1-3] by some workers; others[4,5] state that they were unable to repeat the preparations. The purpose of this work is to set down the exact conditions under which the red form of tin(II) oxide can be prepared by dehydration of a hydrous tin(II) oxide[6] or basic salt suspension. The *X*-ray diffraction powder and unit-cell data of the material are also listed.

Experimental

Preparation.—Two methods, based on the work of Roth[1] and of Fremy,[2] have been used for the preparation of red tin(II) oxide. The optimum conditions are here given along with the limits of concentration of the variable components.

Preparation based on Roth's method. Tin(II) chloride dihydrate (25 g.) of analytical reagent grade is dissolved in concentrated hydrochloric acid (20 ml.) and water (10 ml.), and the solution cleared by warming over tin metal. Hydrous tin(II) oxide is precipitated by addition of a saturated solution of sodium hydrogen carbonate until evolution of carbon dioxide ceases. A solution of sodium phosphite (0·3 g.) in N-acetic acid (125 ml.) is then added, and the pH adjusted to 5—6 by addition of a saturated solution of sodium hydrogen carbonate or of 0·1N-hydrochloric acid as necessary. The suspension is heated, with rapid stirring, under an atmosphere of oxygen-free nitrogen, on a bath at 102° (boiling $CaCl_2$ solution) until most of the precipitate has been converted into red oxide. The oxide is separated from the less dense hydrous oxide or basic chloride, firstly by decantation, and finally by passing the mixture through a cascade filter in a continuous flow of water. The cascade filter consists of 5 cloth filters of mesh size from 0·38 to 0·013 mm. The basic salt or hydrous oxide is peptised and washed away, leaving pure red tin(II) oxide on the filter. The product is dried *in vacuo* over potassium hydroxide pellets.

The effects of varying phosphite concentration, pH, and volume of acetic acid in the preparative mixture are as follows:

Red tin(II) oxide is obtained if the phosphite concentration is between 0·17 and 1·1 g. in 125 ml. of N-acetic acid. Above the upper limit no oxide formation occurs, and below the lower limit blue-black tin(II) oxide is formed. The colour of the sample ranges from purple to very red as the phosphite concentration increases, but the time for initial red oxide formation also increases from 45 min. at 0·17 g. to 4¾ hr. at 1·1 g. of phosphite. The production of a purple material indicates the presence of some blue-black oxide; this was confirmed by the presence of the strongest reflection of this oxide (2·97 Å) in the powder pattern of the purple material.

Partington and Moser[3] prepared red tin(II) oxide by a similar method but used sodium hypophosphite instead of sodium phosphite. It has been found, however, that only old samples of hypophosphite, containing phosphite impurity, give rise to red oxide in the preparation. In fact, sufficient hypophosphite must be used so that the phosphite content falls within the range 0·17—1·1 g. in the preparative mixture.

The pH of the suspension was varied by addition of varying amounts of solid sodium hydrogen carbonate, and it was found that red tin(II) oxide could only be obtained between

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[1] Roth, *Jahrb. prakt. Pharm.*, 1845, **10**, 381.

[2] Fremy, *Compt. rend.*, 1842, **15**, 1108; *Ann. Chim. Phys.*, 1844, **12**, 460.

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

[4] Bury and Partington, *J.*, 1922, **121**, 1998.

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

[6] Donaldson and Moser, preceding paper.

the pH limits 4·9—6·2. In a suspension of pH $<4{\cdot}9$ no oxide formation occurs, and only blue-black oxide is obtained from a suspension with pH $>6{\cdot}2$.

Variation of acetic acid concentration has little effect, since red tin(II) oxide can be obtained from suspensions containing from 0 to 300 ml. of N-acetic acid. The yield of red oxide, however, decreases if the acetic acid concentration is less than 80 ml. or greater than 200 ml. in the preparative mixture. The main function of the acetic acid is apparently to produce a suitable buffer solution.

Preparation based on Fremy's method. A solution of tin(II) chloride dihydrate is prepared and cleared as in Roth's method, and hydrous tin(II) oxide is precipitated by addition of an aqueous solution of ammonia (*d* 0·880; 1 : 1) until the pH is about 10. The precipitate is allowed to settle, the excess of liquid decanted off, and the suspension transferred to a 4″ evaporating dish which is heated on a boiling-water bath without stirring until red oxide begins to be formed near the sides of the dish. A little of the suspension from the centre of the evaporating dish is transferred to a larger preheated dish, and this is rotated slowly at a slight angle until a uniform film is obtained. The dish is replaced on the water-bath and heated until the film becomes red. The product, a fine powder, is removed by a jet of water, washed by decantation, and dried as before.

This preparation does not depend on the concentration of any of the components in the mixture, but is sensitive to experimental conditions. Care must be taken in transferring the suspension from one evaporating dish to another since any oxide crystals transferred will act as nuclei for the formation of blue-black oxide. This stable oxide is also obtained if the film in the second evaporating dish is not uniform or too thick, because continued moistening and heating of freshly prepared red oxide converts it into the blue-black form.

X-*Ray powder data for red tin*(II) *oxide.*

d (Å)	R.I.*	Index of refl.	$d_{\text{calc.}}$	d (Å)	R.I.*	Index of refl.	$d_{\text{calc.}}$	d (Å)	R.I.*	Index of refl.	$d_{\text{calc.}}$
5·56	vvw	002	5·56	1·888	vw	220	1·883	1·342	vvw	043	1·339
3·71	vvw	102	3·72	1·857	s	204	1·855	1·251	vw	400	1·250
3·58	w	111	3·57	1·773	mw	130	1·781	1·239	vw		
3·12	vvs	112	3·12	1·681	w	223	1·681	1·213	vw		
2·86	vw	020	2·86	1·662	vw	116	1·663	1·183	vw		
2·78	mw	004	2·78	1·610	vw	133	1·608	1·141	vw		
2·50	w	200	2·50	1·540	w	312	1·539	1·095	w		
2·25	vw	023	2·26	1·429	mw	040	1·430	1·028	vvw		
1·994	vvw	024	1·994	1·393	vw	008 042	1·390 1·385				

* R.I. = relative intensity.

Purity and Stability of Red Tin(II) *Oxide.*—Analysis for stannous tin and total tin by Donaldson and Moser's method [7] for three samples of red oxide prepared by Roth's method gave 87·5, 88·0; 87·6, 88·1; 87·4, 88·0%; and for three samples from Fremy's method gave, 86·1, 86·6; 86·0, 86·9; 86·1, 86·7%. [Calc. for SnO: Sn(II), 88·1%]. Products produced by Fremy's method are obviously contaminated by basic salts. No band attributable to either water or hydroxyl appears in the infrared spectrum of red tin(II) oxide.

Red tin(II) oxide is stable in air up to about 270°, possibly owing to the presence of a thin protective coating of tin(IV) oxide. The change from the red modification of tin(II) oxide to the blue-black form has been studied in a non-oxidising atmosphere by using high-temperature X-ray diffraction techniques; it was found that the change occurred at temperatures varying with the age of the sample.

Red tin(II) oxide can also be converted into the blue-black modification by mechanical pressure at room temperature, by treatment with strong alkali, or by contact with the stable modification, and must thus be considered metastable.

Crystallography.—Careful control of Roth's preparation by allowing a little red oxide to be formed as usual, decanting from this, and stirring the decanted suspension slowly for 2 hr. at 60° yields crystals suitable for study by X-ray diffraction.

Crystal data: red SnO, $M = 134{\cdot}7$, orthorhombic, $a = 5{\cdot}00 \pm 0{\cdot}01$, $b = 5{\cdot}72 \pm 0{\cdot}01$,

$c = 11{\cdot}12 \pm 0{\cdot}02$ Å, $U = 318{\cdot}0$ Å^3, $D_m = 5{\cdot}56$ g./c.c. (by displacement of water), $Z = 8$, $D_c = 5{\cdot}63$ g./c.c., space-group *Pbcn* D_{2h}^{14} (No. 60), filtered Cu-K_α radiation, single-crystal rotation and Weissenberg photographs about *a* and *b*.

The Table contains the *X*-ray diffraction powder data for red tin(II) oxide obtained by using 11·64 cm. cameras and a Philips *X*-ray diffractometer with filtered Cu-K_α radiation. The spacings longer than 1·25 Å have been indexed by comparison of single-crystal and powder photographs and by calculation from the unit-cell dimensions.

DISCUSSION

It is apparent from the preparation by Fremy's method that the material which is dehydrated to red tin(II) oxide is either hydrous tin(II) oxide or a basic tin(II) chloride. Any ammonia present is driven off during the preparation, thus lowering the pH of the suspension. It was found that the pH of the suspension from which red oxide could be obtained was between 5·5 and 6.

Presumably, the same material is responsible for the production of red oxide in Roth's preparation. In this case the pH is kept at about 6 by a sodium acetate–acetic acid buffer. The effect of phosphite on Roth's method indicates that both dehydration and oxide transformation can be retarded by a negative catalyst. Work is in progress to determine the exact composition of the precursor of the red oxide and to study the effect of the phosphite in the dehydration. All attempts to prepare red tin(II) oxide from pure tin(II) sulphate [8] or from hydrous oxide precipitated from a nitrate solution have failed, and although small quantities of red tin(II) oxide can be obtained from tin(II) bromide, it seems that the presence of chloride ion is essential for the production of good yields of red tin(II) oxide.

The red modification of tin(II) oxide is certainly metastable at ordinary temperatures and it is possible that the true stability range of the material lies above the disproportionation [6,9] temperature of tin(II) oxide, *viz.*, 385°.

Comparison of the *X*-ray and unit-cell data of red tin(II) oxide with those reported for yellow lead(II) oxide [10] indicates that the two materials cannot have the same structure. Work is in progress to determine the structure of red tin(II) oxide.

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[7] Donaldson and Moser, *Analyst*, 1959, **84**, 10.
[8] Donaldson and Moser, *J.*, 1960, 4000.
[9] Straumanis and Strenk, *Z. anorg. Chem.*, 1933, **213**, 301.
[10] Byström, *Arkiv Kemi, Min., Geol.*, 1943, **17**, *B*1; *Chem. Zentr.*, 1944, I, 343.