55. *Tin*(II) *Phosphite.*

By J. D. DONALDSON, W. MOSER, and W. B. SIMPSON.

The preparation and analysis of pure tin(II) phosphite are described. The material is anhydrous and one of the most stable tin(II) compounds yet prepared. Its solubility in various solvents is reported. Its thermal decomposition has been studied in detail; the decomposition temperature is 325° and the products are phosphine, hydrogen, tin(II) pyrophosphate, and tritin(II) bisorthophosphate. It was not possible to prepare a basic tin(II) phosphite by precipitation. The unit-cell dimensions, cell contents, and *X*-ray diffraction powder data of tin(II) phosphite are also reported.

THERE has been only one report of the preparation of tin(II) phosphite and it is doubtful whether the method described could lead to a pure product. Rose [1] prepared this material by treating phosphorus trichloride with an excess of aqueous ammonia and refluxing the product with a saturated aqueous solution of tin(II) chloride. Although the amount of water in the samples varied widely, Rose stated that the material was tin(II) phosphite monohydrate, $SnHPO_3,H_2O$.

We have found that tin(II) phosphite is anhydrous and readily accessible, and can be prepared in a very pure state.

EXPERIMENTAL

Preparation and Analysis.—Four methods for preparing tin(II) phosphite were studied and the yield, purity, and crystal size of the products were compared.

(1) *Action of phosphorous acid on tin*(II) *oxide.* Phosphorous acid (10 g.) was heated until molten (74°) and the temperature was then raised slowly but kept well below the decomposition temperature (*ca.* 200°). Tin(II) oxide (10 g.) was slowly added to the melt, dissolving readily to yield a clear, viscous liquid, which, on cooling, failed to give any solid material. Addition of water, however, converted the mass into small transparent crystals (15 g., 90%) which were collected, washed with water, alcohol and ether, and dried *in vacuo*. This material was used in subsequent work.

(2) *Action of phosphorous acid on hydrous tin*(II) *oxide.* An excess of hydrous tin(II) oxide was added to boiling 50% w/w aqueous phosphorous acid. The suspension was filtered hot and allowed to cool slowly. Large crystals, of irregular form and containing appreciable amounts of tin(IV), were obtained by this method.

(3) *Action of phosphorous acid on metallic tin.* Finely divided tin (10 g.) was refluxed with phosphorous acid (15 g.) and water (60 ml.) for 50 hr. The solution was filtered rapidly and then cooled slowly. The product consisted of large, perfectly formed crystals but the yield (1·2 g.) was poor and the method time-consuming.

(4) *Preparation from copper phosphite.* Copper oxide (10 g.) was dissolved in 20% aqueous phosphorous acid (100 ml.). This copper phosphite solution was heated with tin (30 g.) at 70° for 80 hr. under oxygen-free nitrogen. Reduction of cupric ions to copper was completed

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[1] Rose, *Ann. Phys. Chim.*, 1827, **9**, 23.

at ~100°. The clear solution, when filtered and concentrated in a vacuum rotary evaporator, gave a very small yield of crystalline *tin*(II) *phosphite.*

In assessing the purity of tin(II) materials most previous workers have relied on a determination of total tin, generally by ignition to tin(IV), thus neglecting the possible presence of stannic tin as impurity. We have found that phosphite does not interfere with determinations of stannous tin and total tin by Donaldson and Moser's method,[2] which was used in the present work. A sample of tin(II) oxide was analysed for stannous and total tin in the presence of varying amounts (0·2—1·6 g.) of sodium phosphite and the results were shown to be identical within the limits of experimental error.[2]

For phosphite assay, we determined total reductants by dissolving tin(II) phosphite (~0·1 g.) in 25% v/v sulphuric acid, adding an excess of standard ceric sulphate, warming the mixture for 30 min., cooling it, and determining the excess of cerium(IV) by titration with standard iron(II) ammonium sulphate with ferroin as indicator. It was then possible to obtain the amount of phosphite from the difference between total reductant and tin analyses. Three typical samples, prepared by Method (1), gave: Sn(II), 59·6, 59·5, 59·6; total Sn, 59·7, 59·6, 59·7; and PHO_3^{2-}, 40·2, 40·2, 40·3% [tin(II) phosphite, $SnHPO_3$, requires Sn(II) 59·7; PHO_3^{2-}, 40·3%].

Solubility of Tin(II) *Phosphite.*—The solubility of tin(II) phosphite in five common solvents (see Table 1) under a non-oxidising atmosphere at various temperatures was measured by titrating [2] the tin(II) in solution.

TABLE 1.

Solubility (g. per 100 ml. of solution) of tin(II) phosphite.

Solvent/Temp.	20°	40°	50°	70°	100°
Water	0·0133	0·0157	0·0164	0·0173	0·0180
Acetone	0·0252	0·0221	0·0188	—	—
Ethanol	0·0152	0·0136	0·0131	n.d.	—
2N-Acetic acid	0·0232	0·0257	0·0269	0·0288	0·0316
N-Phosphorous acid	0·0329	0·0406	0·0470	0·0651	0·1004

n.d. = not determined.

Stability of Tin(II) *Phosphite.*—Tin(II) phosphite is very stable; it can be stored for several months in a glass vessel in daylight with no alteration in appearance, analytical composition, or *X*-ray diffraction powder pattern. It can also be kept unchanged under water for at least 20 weeks, and even after this time no products of hydrolysis can be detected by analysis or by *X*-ray diffraction.

The thermal stability of tin(II) phosphite was studied by using a m. p. apparatus. The material melted at 316° and decomposed at 325°. After being heated to different temperatures (below the m. p.) under oxygen-free nitrogen in a liquid-paraffin bath, it showed no alteration in composition or *X*-ray powder pattern.

The decomposition was accompanied by deflagration and evolution of a gas (smell of phosphine) that was collected and shown by its spectrum to contain phosphine.[3] A fraction of the gas was not condensed in a liquid-nitrogen trap but was adsorbed on metallic palladium; the *X*-ray diffraction powder pattern of the metal then showed the presence of palladium hydride [4] and thus proved that the evolved gases contained hydrogen. The solid residue was grey and consisted of two phases, a white microcrystalline phase and traces of a black glass-like phase. The solid residue, which was fairly pure tin(II) material containing about 61% of tin, was shown by *X*-ray diffraction to be a mixture of tin(II) phosphates. For comparison, monotin(II) bisorthophosphate, $Sn(H_2PO_4)_2$, tritin(II) bisorthophosphate, $Sn_3(PO_4)_2$, and tin(II) bismetaphosphate, $Sn(PO_3)_2$, were prepared by Jablczynski and Wieckowski's method,[5] but with tin(II) sulphate instead of tin(II) chloride. The orthophosphate, $SnHPO_4$, was obtained by adding tin(II) sulphate (10 g.) in water (50 ml.) to a solution of phosphoric acid (*d* 1·75; 20 ml.) in water (40 ml.). The crystalline product was washed with water and acetone, and dried *in vacuo*. It had m. p. 327—330°, losing water at 395° and giving tin(II) pyrophosphate.

It was found that all of the reflections in the powder pattern of the solid decomposition

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

[3] Robertson and Fox, *Proc. Roy. Soc.*, 1928, *A*, **120**, 128.

[4] McKeechan, *Phys. Rev.*, 1923, **20**, 82.

[5] Jablczynski and Wieckowski, *Z. anorg. Chem.*, 1926, **152**, 207.

product could be assigned to either tin(II) pyrophosphate or to tritin(II) bisorthophosphate. Therefore, tin(II) phosphite decomposes thermally to give phosphine, hydrogen, and a mixture of tin(II) phosphates.

Attempted Preparation of Basic Tin(II) *Phosphite.*—When a concentrated solution of ammonia (*d* 0·880) or alkali was added to a solution of tin(II) phosphite in 50% phosphorous acid, precipitation occurred, initially at pH 0·83, and continued until the pH was 2·98. At pH ~3, the precipitate started to re-dissolve and the tin remained in solution until pH 8·84, when further precipitation occurred. Analysis of the products showed that the precipitate formed from pH 0·8 to pH 3 was tin(II) phosphite and that the precipitate obtained at pH > 8·8 was hydrous tin(II) oxide.

Crystallography.—Tin(II) phosphite consists of long, thin, transparent crystals which show parallel extinction and have $n > 1{\cdot}74$, negative elongation, and high birefringence. *X*-Ray data show that the crystals are orthorhombic with a long *b*-axis and (001) cleavage.

Crystal data. $SnHPO_3$, $M = 198{\cdot}7$. Orthorhombic, $a = 4{\cdot}60 \pm 0{\cdot}01$, $b = 6{\cdot}18 \pm 0{\cdot}01$, $c = 12{\cdot}34 \pm 0{\cdot}02$ Å, $U = 351$ Å^3, $D_m = 3{\cdot}77$ g./c.c. (by suspension in a solution of thallous formate and thallous malonate in water). $Z = 4$. $D_c = 3{\cdot}76$ g./c.c. Filtered Cu–K_α radiation, single-crystal and Weissenberg photographs about all three axes.

There were the following systematic absences of reflection: $h00$ absent for h odd, $0k0$ absent for k odd, $00l$ absent for l odd, $0kl$ absent for $k + l$ odd, and $h0l$ absent for $h + l$ odd. The space group is, therefore, *Pnnm* (D_{2h}^{12}, No. 58) or *Pnn*2 (C_{2v}^{10}, No. 34).

TABLE 2.

X-Ray powder data for tin(II) phosphite.

d (Å)		Index of refln.	d_{hkl}	*d* (Å)		Index of refln.	d_{hkl}	*d* (Å)		Index of refln.	d_{hkl}	*d* (Å)		*d* (Å)		*d* (Å)	
6·16	w	002	6·17	2·40	w	114	2·38	1·756	mw	214	1·766	1·429	w	1·223	vw	1·120	vvw
5·51	vs	011	5·52	2·31	mw	200	2·30	1·710	w	026	1·711	1·399	m	1·211	vw	1·114	vw
4·33	s	101	4·31	2·29	w	015	2·29	1·682	mw	223	1·683	1·370	vw	1·201	vw	1·096	vw
3·72	vvw	110	3·69	2·17	mw	202	2·16	1·651	w	107	1·647	1·329	mw	1·178	w	1·084	vw
3·39	vvs	013	3·42			123	2·18	1·524	w	008	1·524	1·311	vw	1·164	vvw	1·065	vvw
3·09	ms	020	3·09	2·05	vw	006	2·06			040	1·525	1·297	vvw	1·154	vw	1·046	vw
		004	3·09			115	2·05	1·500	w	135	1·497	1·282	vw	1·141	w	1·024	vw
3·07	mw	103	3·07	2·00	m	212	2·02	1·491	w			1·269	vw			1·003	w
2·75	mw	022	2·76			124	1·99	1·468	vw			1·239	vw			0·9927	vw
2·51	vw	121	2·51	1·827	mw	221	1·824	1·437	vw								

Table 2 contains the *X*-ray diffraction powder data for tin(II) phosphite obtained by using 11·64-cm. cameras and a Philips *X*-ray diffractometer with filtered Cu–K_α radiation. The spacings longer than 1·50 Å have been indexed by comparison of single-crystal and powder photographs and by calculation from the unit-cell dimensions.

DISCUSSION

Thermal decomposition of phosphites normally leads to the formation of phosphine and a mixture of phosphates (mainly pyrophosphate), although red phosphorus and more complicated oxy-acids of phosphorus are also found. Decomposition of tin(II) phosphite follows the general pattern, although the formation of hydrogen and, to a small extent, tritin(II) bisorthophosphate is unexpected. It is interesting that at the decomposition temperature, 325°, it is the phosphite which is attacked, the tin(II) remaining essentially unaffected [the decomposition residue contains less than 2% of tin(IV)]. At this temperature, complete decomposition of the material might have been expected with the formation of tin(IV) oxide, the usual product of thermal decomposition of oxygen-containing tin(II) compounds.[6,7]

The failure of tin(II) phosphite to form a basic salt is also interesting, especially in the context of the formation of red tin(II) oxide.[8] Redissolution of the phosphite in mother-liquor at pH >3 is presumably due to the formation of complex ions. Further work on these is in progress.

Tin(II) phosphite is probably one of the most stable tin(II) compounds known. It can

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[6] Donaldson and Moser, *J.*, 1961, 1996; Straumanis and Strenk, *Z. anorg. Chem.*, **1933**, **213**, 301.

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

[8] Donaldson, Moser, and Simpson, *J.*, 1961, 839.

certainly be stored for longer periods than tin(II) sulphate.[7] However, use of the material as a general reagent is limited by its poor solubility in common solvents.

Since both phosphites and tin(II) are good reducing agents, the use of the compound in various reductions merits investigation.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY, OLD ABERDEEN.
[Present addresses: (J. D. D.) CHELSEA COLLEGE OF SCIENCE and TECHNOLOGY,
LONDON S.W.3.
(W. B. S.) THE UNIVERSITY, NOTTINGHAM.]

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