645. *The Hypophosphites of Tin.*

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The following hypophosphites of bivalent tin have been prepared : $Sn(H_2PO_2)_2,6H_2O$; $Sn(H_2PO_2)_2$; $3Sn(H_2PO_2)_2,SnCl_2$; $Sn(H_2PO_2)_2,SnCl_2$. The existence of the quadrivalent tin hypophosphite, $Sn(H_2PO_2)_4,SnCl_4$, has been confirmed in the anhydrous state only. Conditions for the reduction of quadrivalent tin to the bivalent state by means of hypophosphorous acid have been established.

Since hypophosphorous acid has been used for reducing quadrivalent germanium to the bivalent state (Dennis and Hulse, *J. Amer. Chem. Soc.*, 1930, **52**, 3553), a reaction which can be quantitative under the correct conditions (Ivanov-Emin, *Zavod. Lab.*, 1947, **13**, 161), it was thought to be of interest to establish the conditions for a similar reduction of quadrivalent tin and to investigate the type and nature of the tin hypophosphites.

The only report hitherto on the tin hypophosphites was by Terni and Padovani (*Atti Accad. Lincei*, 1925, [vi], **2**, 501), who prepared $Sn(H_2PO_2)_4,SnCl_4,3H_2O$ by the action of sodium hypophosphite on a concentrated solution of stannic chloride. This substance was found to lose water when heated above 140°, and to decompose above 190° with evolution of phosphine. These authors did not observe any reduction of the quadrivalent tin by the sodium hypophosphite.

Of the corresponding lead compounds, the simple hypophosphite has been prepared as an anhydrous crystalline material by the action of sodium hypophosphite on a soluble lead salt (Rammelsburg, *J.*, 1873, **26**, 1; Rose, *Pogg. Ann.*, 1827, **9**, 225). This compound was only sparingly soluble in water. Two double lead hypophosphites have also been described, $Pb(H_2PO_2)_2,Pb(NO_3)_2$ (von Hertz, *Z. ges. Schiess. u. Sprengstoffw.*, 1916, **11**, 365; *Chem. Zentr.*, 1919, i, 271) and one with equimolecular parts of lead hypophosphite and lead styphnate (McNutt and Ehrlich, U.S.P. 2,352,964). Both these compounds were highly explosive. The information given about all three substances was scanty and of little assistance in predicting the nature of the corresponding tin compounds.

Hypophosphites of Bivalent Tin.—Three distinct compounds have been isolated, *viz.*, stannous hypophosphite, $Sn(H_2PO_2)_2$ (m. p. 105°), and two double salts, $3Sn(H_2PO_2)_2,SnCl_2$ (m. p. 130°) and $Sn(H_2PO_2)_2,SnCl_2$ (m. p. 181°). In addition the hydrated stannous hypophosphite, $Sn(H_2PO_2)_2,6H_2O$ (m. p. 65—67°), was identified, and evidence for a second hydrate, $Sn(H_2PO_2)_2,2H_2O$ (m. p. 70—90°), has been obtained. These compounds were all fairly stable in air; they were soluble in dilute sulphuric and in dilute and concentrated hydrochloric and hypophosphorous acids, their solubility being decreased and their ease of oxidation heightened with increased chlorine content. They were all hydrolysed by water with formation of stannous hydroxide, the ease of hydrolysis falling off with decreasing solubility.

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Concentrated sulphuric and nitric acids readily attacked them, sulphuric acid first liberating hydrogen chloride and then causing decomposition with deposition of phosphorus and formation of phosphine; nitric acid caused oxidation even in the cold, with evolution of nitrous fumes. No conditions were found under which hypophosphorous acid could reduce stannous compounds to the metal.

Hypophosphites of Quadrivalent Tin.—The only compound actually isolated was anhydrous $Sn(H_2PO_2)_4,SnCl_4$; Terni and Padovani (*loc. cit.*) had reported a hydrate, but no evidence of any definite hydrates could be obtained. $Sn(H_2PO_2)_4,SnCl_4$ was insoluble in most solvents but was dissolved by hot hydrochloric acid, the ease of solution rising with increased acid concentration. It was also slowly dissolved by concentrated hypophosphorous acid, in which it was very soluble, giving a yellow solution which was apparently the same as that formed when stannic hydroxide was dissolved in the same solvent. Concentrated sulphuric or nitric acids readily attacked it, the reaction being similar to that with the stannous hypophosphites. With water, it was hydrolysed to stannic hydroxide. As stated by Terni and Padovani, $Sn(H_2PO_2)_4,SnCl_4$ differed from the stannous hypophosphites in having no melting point; the substance usually decomposed at about 195°, although this was subject to variation, some samples not decomposing till above 220°.

Attempts were made to prepare stannic hypophosphite by dissolving chloride-free stannic hydroxide in hypophosphorous acid. It was extremely soluble, giving a yellow solution, the colour deepening with increased tin concentration. No solid compounds could be separated, for on evaporation these solutions set to a glass. Addition of alcohol gave a precipitate consisting principally of stannic hydroxide, hydrolysis having occurred.

Reduction of Quadrivalent Tin to the Bivalent State.—This reduction, which was slow, was carried out in an inert atmosphere, as aerial oxidation was rapid especially in the presence of hydrochloric acid. It was established (see p. 2905) that in 3N-hydrochloric acid, in the presence of excess of hypophosphorous acid, stannic chloride and $Sn(H_2PO_2)_4,SnCl_4$ were completely reduced to the bivalent state. In more dilute hydrochloric acid reduction was incomplete, and in the absence of hydrochloric acid, or if sulphuric acid was substituted for it, no reduction was observed.

No reduction was found when either stannic hydroxide or $Sn(H_2PO_2)_4,SnCl_4$ was heated with hypophosphorous acid. The reason for this is not clear, but it may be due to complex formation stabilising the quadrivalent state, a postulate which is supported by the extreme solubility of stannic hydroxide and $Sn(H_2PO_2)_4,SnCl_4$ in hypophosphorous acid. In other solvents the chief factor limiting the extent and rate of reduction is the sparse solubility of $Sn(H_2PO_2)_4,SnCl_4$, which is always precipitated when hypophosphorous acid is added to a solution of stannic chloride. The amount of reduction and the solubility both increased with increased hydrochloric acid concentration, and in 3N-sulphuric acid, in which it is insoluble, no reduction occurred.

EXPERIMENTAL.

(All m. p.s are uncorrected.)

Analytical Procedures.—*Tin.* Method 1. After reduction to the bivalent state by being boiled with nickel foil and hydrochloric acid (1 : 1) for 45 minutes, the cooled solution was titrated in an inert atmosphere with 0·1N-iodine (standardised with metallic tin).

Method 2. Bivalent tin was directly determined by addition of the sample dissolved in 10N-hydrochloric acid to excess of 0·1N-iodine (standardised against potassium iodate through sodium thiosulphate) and immediate back-titration with 0·1N-sodium thiosulphate. The procedure could only be applied when the sample dissolved readily in hydrochloric acid.

Hypophosphorous acid. The sample was dissolved as far as possible in 3N-sulphuric acid and this solution, together with any undissolved material, was added to excess of 0·3N-potassium permanganate. Reaction then took place according to the equation $Sn(H_2PO_2)_2 + 2KMnO_4 + 3H_2SO_4 = Sn(OH)_4 + 2H_3PO_4 + K_2SO_4 + 2MnSO_4$. In the absence of chloride the solution was warmed to 40° for 2 hours, or in presence of chloride left for 24—48 hours at room temperature, to allow completion of the reaction. Excess of 0·3N-oxalic acid was then added, and afterwards back-titrated with 0·3N-potassium permanganate. This procedure gave the total reduction equivalent of the compound rather than its hypophosphite content.

Chlorine. The sample was boiled with sodium carbonate solution, and after separation of the crystalline stannous oxide formed, the hypophosphite was oxidised with alkaline hydrogen peroxide (15-vol.). The solution was then acidified with 3N-nitric acid, any tin remaining being precipitated as hydroxide. After removal of the latter, the chloride was precipitated as silver chloride. The chief difficulty encountered was the complete oxidation of the hypophosphite, and as a result the silver chloride was usually contaminated with a little metallic silver formed by reduction of the silver nitrate. This was removed as far as possible by washing the precipitate with warm diluted nitric acid (1 : 1), but it was usually found that the chloride values obtained were slightly higher than the theoretical.

Stannous hypophosphite. Stannous hydroxide (Bury and Partington, *J.*, 1922, **121**, 1998) was dissolved in hot 25% hypophosphorous acid. On cooling, stannous hypophosphite hexahydrate (m. p. 65—67°) crystallised, the solutions showing supercooling. The crystals were washed with a little water and rapidly dried between sheets of filter-paper [Found : Sn, by method 2, 33·6. $Sn(H_2PO_2)_2,6H_2O$ requires Sn, 33·3%]. This *hydrate* lost water on being kept in air or washed with alcohol; when heated to 45—50° in a vacuum, the salt was completely dehydrated, giving the *hypophosphate* as a powder, m. p. 105°, and decomposing a few degrees above this temperature [Found : Sn, by method 2, 47·8; by method 1, 47·6%; reduction equiv., 25·0. $Sn(H_2PO_2)_2$ requires Sn, 47·7%; reduction equiv., 24·9].

When left for 12 hours in a vacuum at room temperature, the hexahydrate gave a *dihydrate* as a powder of indefinite m. p. (70—90°) [Found : Sn, by method 2, 41·6. $Sn(H_2PO_2)_2,2H_2O$ requires Sn, 41·7%].

Double Salt, $3Sn(H_2PO_2)_2,SnCl_2$.—This *salt* (m. p. 130°) [Found : Sn, by method 1, 50·6; by method 2, 50·2; Cl, 7·8%; reduction equiv., 29·3. $3Sn(H_2PO_2)_2,SnCl_2$ requires Sn, 50·7; Cl, 7·6%; reduction equiv., 29·2] was formed when a small quantity of hydrochloric acid was added to a warm solution of stannous hypophosphite in 25% hypophosphorous acid. A deficiency of hydrochloric acid was used in order to avoid precipitation of the less soluble $Sn(H_2PO_2)_2,SnCl_2$.

Double Salt, $Sn(H_2PO_2)_2,SnCl_2$.—This *salt* was prepared by dissolving the colourless crystalline precipitate (10 g.), obtained by the action of hypophosphorous acid on a solution of stannous chloride in 3N-hydrochloric acid, in 50% hypophosphorous acid (10 ml.) containing 10N-hydrochloric acid (15 ml.), and warming the solution for 30 minutes with metallic tin. When the solution was cooled in an inert atmosphere, crystals separated (m. p. 181°). These were rapidly filtered off, washed with a little water and absolute alcohol, and dried in a vacuum at 50—60° [Found : Sn, by method 1, 53·8; Cl, 16·7%; reduction equiv., 37·5. $Sn(H_2PO_2)_2,SnCl_2$ requires Sn, 54·2; Cl, 16·2%; reduction equiv., 36·5]. The analytical discrepancies are probably due to oxidation.

Double Salt, $Sn(H_2PO_2)_4,SnCl_4$.—Stannic chloride pentahydrate (5 g.) was dissolved in warm water (20 ml.), and 50% hypophosphorous acid (5 ml.) added; a thick white precipitate was rapidly formed. This was filtered off, washed with water and absolute alcohol, and dried in a vacuum at 50—60° to give the anhydrous *compound* [Found : Sn, by method 1, 37·5; Cl, 22·4%; reduction equiv., 41·3. $Sn(H_2PO_2)_4,SnCl_4$ requires Sn, 37·1; Cl, 22·2%; reduction equiv., 40·0]. The conditions for the isolation of the trihydrate prepared by Terni and Padovani (*loc. cit.*) were not established. Some samples of $Sn(H_2PO_2)_4,SnCl_4$ slowly liquefied whilst being dried. This was due to incomplete washing out of hypophosphorous acid and, when heated, this small amount of free acid was sufficient to dissolve the whole sample. This demonstrated the high solubility of $Sn(H_2PO_2)_4,SnCl_4$ in hypophosphorous acid.

Reduction Experiments.—The table shows the results of a series of reduction experiments. An inert atmosphere was maintained throughout.

Reduction soln. (vols., in ml.)		Reduction, %, after 45 mins.' boiling.	Reduction soln. (vols., in ml.)		Reduction, %, after 45 mins.' boiling.
H_3PO_2 (50%).	Other reagents.		H_3PO_2 (50%).	Other reagents.	
		Reduction of $SnCl_4,5H_2O$ (1 g.).			
5	H_2O, 25	<1 *	5	1·5N-HCl, 25	45 *
5	3N-H_2SO_4, 25	<1 *	5	3N-HCl, 25	~100
5	0·1N-HCl, 25	4 *	5	6N-HCl, 25	~100
5	0·7N-HCl, 25	7 *			
		Reduction of $Sn(H_2PO_2)_4,SnCl_4$ (1 g.).			
5	H_2O, 25	<1 *	—	3N-HCl, 30	40
20	H_2O, 10	<1	5	3N-HCl, 25	~100

* Solutions where complete dissolution was not attained.

Percentage reduction was estimated by titrating the stannous tin with iodine (standardised against potassium iodate through sodium thiosulphate).

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