

Tin(IV) Hypophosphite

By W. B. SIMPSON

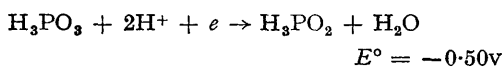
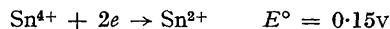
(Department of Chemistry, Trinity College, Dublin 2, Eire)

No information appears to be available on simple compounds of quadrivalent tin with strongly reducing anions. Here is reported the preparation of the first such compound, tin(IV) hypophosphite.

Everest¹ dissolved tin(IV) hydroxide in hypophosphorous acid but failed to isolate tin(IV) hypophosphite. He did, however, obtain a mixed chloride-hypophosphite, $\text{Sn}(\text{H}_2\text{PO}_2)_4 \cdot \text{SnCl}_4$, by reacting tin(IV) chloride with hypophosphorous acid. During a study of the u.v. spectra of metal ions in simple phosphorous acids,² the spectrum of divalent tin in hypophosphorous acid was found to be time dependent, the rate being increased if oxygen was bubbled through the solution. It is obvious, therefore, that the bivalent tin in solution is oxidised giving, presumably, quadrivalent tin.

A saturated solution of tin(II) oxide in hypophosphorous acid (50 ml., 1 : 1 30% H_3PO_2 : water) was prepared. Oxygen gas was bubbled through the solution for 24 hr., to give colourless crystals. Tin was determined by precipitation of tin(IV) sulphide and subsequent ignition to tin(IV) oxide: hypophosphite was determined by Bernhart's method³ (this also showed the absence of phosphite, a possible contaminant). [Found: Sn, 31.2; H_2PO_2^- , 68.6%. $\text{Sn}(\text{H}_2\text{PO}_2)_4$ requires: Sn, 31.3; H_2PO_2^- , 68.7%.] The infrared spectrum of the compound is consistent with the formulation as an anhydrous hypophosphite.

This compound is of interest since it represents the first simple solid compound containing quadrivalent tin and a strongly reducing anion. It might have been expected that any oxidation of tin(II) by oxygen would be counteracted by reduction of tin(IV) by the hypophosphite ion in solution [hypophosphite reduces germanium(IV) to germanium(II)⁴]. Consideration of the reduction potentials:



makes it even more surprising that the product should have the tin oxidised and the hypophosphite unchanged although this may be governed by the kinetics of hypophosphite reductions which are often slow at room temperature. Also, it may be that it is only possible to isolate the solid anhydrous material because of its extreme insolubility.

The reaction may be a general one for the preparation of tin(IV) compounds since time-dependent u.v. spectra are obtained for bivalent tin dissolved in phosphorous, sulphuric, perchloric, and sulphurous acid.

(Received, September 11th, 1967; Com. 972.)

¹ D. A. Everest, *J. Chem. Soc.*, 1951, 2903.

² G. A. Lonergan and W. B. Simpson, to be published.

³ D. B. Bernhart, *Analyt. Chem.*, 1954, **26**, 1798.

⁴ L. M. Dennis and R. E. Hulse, *J. Amer. Chem. Soc.*, 1930, **52**, 3553.