The Solubility of Tin(II) Orthophosphate and the Phosphate Complexes of Tin(II)

By William A. Cilley

Tin(II) orthophosphate, first described by Jablczynski and Wieckowski,[1] and having the empirical formula $SnHPO_4 \cdot 0.5H_2O$, is a highly insoluble compound. It is probably by reason of this insolubility that no measure has previously been taken of the interaction, in aqueous solution, between tin(II) and orthophosphate. Other oxyanions are known to complex tin(II) to varying degrees. For example, evidence has been found by Donaldson for complexes in the formate[2] and acetate[3] systems. The decomposition of tin(II) phosphite to form, among other products, tin(II) oxide is interpreted[4] by Donaldson to indicate strong donor bonds between tin(II) and the phosphite ion. Pyrophosphate ion, an anion closely related to orthophosphate, was found by Davis[5] and later by Vaid[6] to form rather strong complexes with tin(II): $\log K_1(Sn^{2+} \cdot H_2P_2O_7{}^{2-})$, 4.98^5; $\log K_1(Sn^{2+} \cdot P_2O_7{}^{4-})$, 13.6.[6] A pure sample of tin(II) orthophosphate was prepared according to the direction of Jablczynski.[1] This compound has been used to determine the solubility product, $K_s = [Sn^{2+}][HPO_4{}^{2-}]$, and to study the association in solution between tin(II) and orthophosphate ions in a medium of $0.20\ M$ sodium perchlorate at pH 2.5.

Reagents.—Freshly boiled, distilled, deionized water was used throughout. All handling of solutions containing tin(II) was carried out in a nitrogen atmosphere. Unless stated otherwise, chemicals used were commercial reagent grade (J. T. Baker). Standard solutions of tin(II) were prepared by dissolution of weighed amounts of tin metal shot in hydrochloric acid. Standard solutions of potassium dichromate were prepared by dissolution of weighed amounts of the solid in $0.1\ M$ sulfuric acid. An orthophosphate stock solution was prepared from sodium dihydrogen phosphate monohydrate. Perchloric acid was used, without further purification, to prepare sodium perchlorate by reaction with sodium carbonate. The reagent used for the indirect colorimetric analysis for tin(II) was prepared by dissolving 0.25 g of 1,5-diphenylcarbohydrazide (Matheson Coleman and Bell) in 10 ml of glacial acetic acid and making this up to 100 ml with ethanol.

Preparation of Tin(II) Orthophosphate.—Tin metal (118.7 g) was dissolved in 85% orthophosphoric acid

(500 ml) by heating to about 170°.[1] When dissolution was complete, the solution was cooled to about 130° and boiling water (175 ml) was cautiously added. A white solid precipitated, was removed by filtration, and was recrystallized from concentrated phosphoric acid. The resulting solid was deposited as white, lustrous platelets which were removed by filtration and washed with dilute phosphoric acid and then with alcohol. The crystals were dried in a nitrogen atmosphere over phosphorus pentoxide. The X-ray diffraction pattern of this solid corresponds to that of Collins'[7] β-phase tin(II) orthophosphate. *Anal.* Calcd for $SnHPO_4 \cdot 0.5H_2O$: Sn, 53.1; PO_4, 42.5. Found: Sn, 52.4; PO_4, 41.0.

Solubility of $SnHPO_4 \cdot 0.5H_2O$ in Phosphate Solution.—Solid tin(II) orthophosphate was equilibrated with aqueous orthophosphate solutions of varying concentration. Perchloric acid was used to adjust the pH to 2.5, as measured with a glass electrode system. The ionic strength of each solution was adjusted by the addition of sodium perchlorate so that the concentration of sodium ion was made $0.20\ M$. Equilibrations were carried out at 25° for 3 weeks during which time the reaction vessels were agitated vigorously once each day. Portions of the supernatant were removed by filtration and aliquots were taken for tin(II) analysis. Each solution was analyzed at least in duplicate. Selected points were repeated in duplicate after 75 days without noticeable change in the concentration of dissolved tin(II). The pH of each solution was reread at the time of the sampling, but no measurable change in pH was observed. Several of the solids, taken from solutions at the extremes of the phosphate concentration range, were examined by electron diffraction for changes in their surface structure following the equilibration, but none could be found.

Tin(II) Analysis.—The analysis for tin(II) was indirect and made use of the reaction between tin(II) and dichromate in acid solution. Excess dichromate was determined by the diphenylcarbizide method. To the sample, with excess dichromate, in a 50-ml volumetric flask was added 2 ml of the diphenylcarbizide reagent. The solution was brought up to volume with $0.1\ M$ sulfuric acid and the absorbance was read after 2 min at 550 mμ in a Beckman Model B spectrophotometer. It was found that Beer's law was obeyed for dichromate solutions 0.2×10^{-6} to $8.0 \times 10^{-6}\ M$ when read in a 5-cm cell against an acid blank of the color reagent. It was shown that orthophosphate, sodium perchlorate, and chromium(III) at the levels used in the dissolution and analysis did not cause interference with the color development or analysis for tin(II).

Results and Discussion

The dissolution of the solid may be interpreted in terms of the formation of complex ions and, if it is assumed there are no species formed containing more

(1) K. Jablczynski and W. Wieckowski, *Z. Anorg. Allgem. Chem.*, **152**, 207 (1926).

(2) J. D. Donaldson and J. F. Knifton, *J. Chem. Soc.*, 4801 (1964).

(3) J. D. Donaldson, W. Moser, and W. B. Simpson, *ibid.*, 5942 (1964).
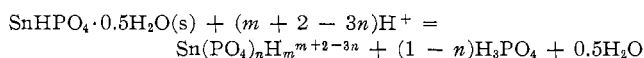
(4) J. D. Donaldson, W. Moser, and W. B. Simpson, *ibid.*, 323 (1964).

(5) J. A. Davis, Ph.D. Thesis, Indiana University, 1955.

(6) J. Vaid and T. L. Rama Char, *Bull. India Sect. Electrochem. Soc.*, **7**, 5 (1958).

(7) R. W. Collins, Ph.D. Thesis, Indiana University, 1962.

than one metal atom, the equation representing the dissolution is

$$SnHPO_4 \cdot 0.5H_2O(s) + (m + 2 - 3n)H^+ =$$
$$Sn(PO_4)_nH_m{}^{m+2-3n} + (1 - n)H_3PO_4 + 0.5H_2O$$

where $n = 0, 1, 2, \ldots$ and $m = 0, 1, 2, \ldots, 3n$. Because the acidity of the solutions was kept essentially constant,[8] a set of hydrogen ion dependent equilibrium quotients may be defined for this set of equilibria

$$Q_n = [Sn(PO_4)_nH_m][H_3PO_4]^{1-n}$$

From this equation it may be seen that the slope of a plot of the logarithm of solubility *vs.* the logarithm of the total concentration of phosphoric acid in the solution is related to the number of phosphate groups bound to each tin.[9] Thus, the slope equals $\Sigma_n f_n \cdot (n - 1)$, where f_n is the fraction of dissolved tin present as $Sn(PO_4)_nH_m$. Such a plot was made. Its slope of -0.53 for phosphate concentration from 0 to 0.03 M indicates that in that region the uncomplexed tin(II) and the monophosphate complex ion are of chief importance. At the higher concentrations of phosphate the slope has a value of 1.3 indicating that species involving at least three phosphate ions are present in solution.

The solubility product for the solid can be determined from these data. The total concentration of tin(II) in solution, C_{Sn}, can be most generally represented as

$$C_{Sn} = [Sn]\left\{1 + \sum_{n=1}^{N} \sum_{m=0}^{3n} \beta_{nm}[PO_4]^n[H]^m\right\}$$

where

$$\beta_{nm} = \frac{[Sn(PO_4)_n(H)_m]}{[Sn][PO_4]^n[H]^m}$$

It can be seen that at a constant pH this reduces to

$$C_{Sn} = [Sn]\{1 + q_1 C_{PO_4} + q_2 C_{PO_4}{}^2 + \ldots\}$$

where $q_n = \Sigma_n \Sigma_m \beta_{nm}[H]^m f_{PO_4}{}^n$ and f_{PO_4} = the fraction of the total phosphate in the form $PO_4{}^{3-}$. That is, the q_n are quotients involving the formation constants of all tin–phosphate complexes formed in a $1:n$ ratio. If it is chosen to represent K_s as the product $[Sn^{2+}][HPO_4{}^{2-}]$, the total solubility may be expressed as a function of the total phosphate concentration, the fraction of phosphate in the $HPO_4{}^{2-}$ form, f_{HPO_4}, and such a series of acid-dependent formation quotients

$$C_{Sn} = \frac{K_s}{C_{PO_4} f_{HPO_4}}\{1 + q_1 C_{PO_4} + q_2 C_{PO_4}{}^2 + \ldots\}$$

Thus, a plot of $C_{Sn} C_{PO_4}$, sometimes called the apparent solubility product, *vs.* C_{PO_4} will have as an intercept K_s/f_{HPO_4} and will be linear as long as only the first two terms in the braces of the above equation are important. The slope of such a plot will be a function of pH, and will be related to the summation of all

associations between tin(II), one phosphate ion, and all possible hydrogen ions. Such a plot was made for data collected at a measured pH of 2.48 and was in fact found to be linear up to total phosphate concentrations of about 0.02 M. The lowest values of the phosphate concentration were determined by correcting the nominal values for that amount added through dissolution of the solid. From the intercept of this plot K_s was found to be $(1.54 \pm 0.33) \times 10^{-13}$ M^2 using the acid dissociation constants[10-13] of phosphoric acid at 25° and 0.2 M ionic strength. The slope of the linear plot was found to be $(1.034 \pm 0.024) \times 10^{-5}$, which when divided by the intercept gave a value of $(9.27 \pm 2.05) \times 10^2$ M^{-1} for q_1.

Given in Table I are values of the solubility itself

TABLE I
THE SOLUBILITY OF TIN(II) ORTHOPHOSPHATE AT VARIOUS PHOSPHATE CONCENTRATIONS

Total phosphate, $M \times 10^5$	Solubility, $M \times 10^5$ Found[a]	Solubility, $M \times 10^5$ Calcd[b]	Total phosphate, $M \times 10^3$	Solubility, $M \times 10^5$ Found[a]	Solubility, $M \times 10^5$ Calcd[b]
0.298	4.81	4.74	15.0	1.07	1.14
0.530	3.30	3.10	17.5	1.11	1.16
0.780	2.66	2.43	20.0	1.11	1.18
1.02	2.42	2.09	22.5	1.07	1.21
1.27	2.02	1.88	25.0	1.12	1.24
1.52	1.78	1.73	30.0	1.11	1.32
1.76	1.45	1.63	40.0	1.48	1.53
2.01	1.27	1.55	50.0	1.69	1.81
2.27	1.69	1.49	60.0	2.19	2.16
2.51	1.43	1.44	70.0	2.55	2.57
10.0	1.14	1.14	80.0	3.10	3.04
12.5	1.15	1.14	90.0	3.64	3.58

[a] pH 2.48, $[Na^+] = 0.20$ M, temperature 25°. [b] Calculated assuming: $K_s = 1.54 \times 10^{-13}$ M^2, $q_1 = 8.96 \times 10^2$, $q_2 = 0$, and $q_3 = 2.85 \times 10^5$.

along with values of the total phosphate concentration. The total solubility may be represented by the equation

$$C_{Sn} = \frac{K_s}{f_{HPO_4}}\left\{\frac{1}{C_{PO_4}} + q_1 + q_2 C_{PO_4} + q_3 C_{PO_4}{}^2\right\}$$

Having previously determined K_s, the coefficients q_1, q_2, and q_3 were determined as giving the best least-squares fit to the data. For this fit the values found for q_1 and q_3 were $(8.96 \pm 2.02) \times 10^2$ and $(2.85 \pm 0.68) \times 10^5$, respectively. Error limits reflect the extent of the 95% confidence band for these values. A regression analysis of the data revealed that the coefficient q_2, that is, the term which could be related to the formation of diphosphatotin(II) complexes, was nonsignificant. The fit was, to a small extent, better $(R^2 = 0.97056$ *vs.* $R^2 = 0.95895)$ when q_2 was included, but in this case q_2 became negative. The third column of the table, *i.e.*, solubilities calculated from the derived constants, was therefore obtained by using the above values for q_1 and q_3 and assuming q_2 to be zero. In view of the electron configuration of the tin(II) ion, which

(8) The pH of the solutions was kept constant, and, to the extent that activity coefficients in the solution are constant at constant ionic strength while the medium changes from 0.2 M sodium perchlorate to 0.155 M perchlorate plus 0.045 M sodium dihydrogen phosphate, the concentration of hydrogen ion is constant.

(9) R. G. Denotkina, A. I. Moskvin, and V. B. Shevchenko, *Russ. J. Inorg. Chem.*, **5**, 731 (1960).

(10) For this calculation $pK_1 = 2.10$,[11] $pK_2 = 7.19$,[12] $pK_3 = 12.38$,[13] and $f_{HPO_4} = 1.38_5 \times 10^{-5}$.

(11) R. G. Bates, *J. Res. Natl. Bur. Std.*, **47**, 127 (1951).

(12) R. G. Bates and S. F. Acree, *ibid.*, **30**, 129 (1943).

(13) C. E. Vanderzee and A. S. Quist, *J. Phys. Chem.*, **65**, 118 (1961).

allows sp³ hybridization of the metal orbitals with one of the orbitals occupied by a lone pair of electrons, it is not too surprising to find that a triphosphate complex is apparently formed without appreciable formation of a diphosphate species. Other systems of tin(II) complexes have previously been shown to exhibit this behavior.[14]

At the pH of these experiments the predominant phosphate species, in the absence of tin, are H_3PO_4 and $H_2PO_4^-$. Even though it is impossible to specify, without a measure of the acid dependence of the quotients q_1 and q_3, the acid dissociation constants of the tin phosphate complexes, it is fair to say that these complexes must be stronger acids than $H_2PO_4^-$. If we then assign the formulas $SnHPO_4$ and $Sn(HPO_4)_3^{4-}$ to the respective complexes, we calculate formation constants for them of $\beta_{11} = (6.7 \pm 1.5) \times 10^7$ and $\beta_{33} = (1.1 \pm 0.3) \times 10^{10}$. These values do not seem unreasonable and provide an estimate of the interaction between tin(II) and orthophosphate.

(14) J. D. Donaldson, "A Review of the Chemistry of Tin(II) Compounds," Tin Research Institute, Columbus, Ohio, 1964.


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## Preparation of Tungsten Bronzes from Metal Halides[1]

By Lawrence E. Conroy and George Podolsky

Tungsten bronzes, M_xWO_3 (M is a metal and $0 < x < 1$), containing alkaline earth metals (Ba and Sr) were first prepared by Conroy and Yokokawa,[2] utilizing the reaction of the corresponding alkaline earth chloride with mixtures of tungsten trioxide and tungsten dioxide at 900–1000°

$$xMCl_2 + xWO_2 + WO_3 \longrightarrow M_xWO_3 + xWO_2Cl_2 \quad (1)$$
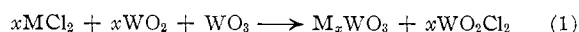
Tungsten metal may also serve as the reducing agent at such temperatures

$$xMCl_2 + (x/3)W + [1 + (2x/3)]WO_3 \longrightarrow M_xWO_3 + xWO_2Cl_2(g) \quad (2)$$
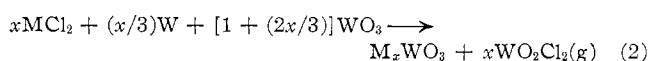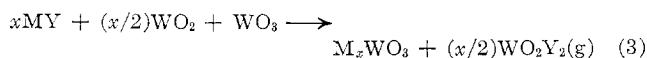
Further experiments have shown that this type of reaction, utilizing the volatilities of the tungsten oxyhalides, will function with the corresponding bromides or iodides in place of the chlorides. The method is of general utility for the preparation of tungsten bronzes from either monohalides or dihalides. The
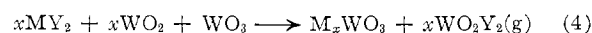
assumed stoichiometry for monohalides with WO_2 and WO_3 is then

$$xMY + (x/2)WO_2 + WO_3 \longrightarrow M_xWO_3 + (x/2)WO_2Y_2(g) \quad (3)$$

and for dihalides

$$xMY_2 + xWO_2 + WO_3 \longrightarrow M_xWO_3 + xWO_2Y_2(g) \quad (4)$$

where Y is Cl, Br, or I.

Experimental Section

Materials.—LiCl, NaCl, NaBr, NaI, KCl, KBr, KI, $MgCl_2$, $MgBr_2$, $CaCl_2$, $CaBr_2$, CaI_2, $SrCl_2$, $BaCl_2$, and $PbCl_2$ were reagent grade. LiBr, LiI, MgI_2, $SrBr_2$, $BaBr_2$, BaI_2, $PbBr_2$, and TlCl were obtained from City Chemical Corp. in Purified or USP grades. CsCl and CsI were BDH 99%. BrCl was Alfa Inorganics, Inc., 96+%. Nd_2O_3 was Lindsay Rare Earth Chemicals Code 217. WO_3 was Sylvania Chemical and Metallurgical Division Grade TO-2, and tungsten was A. D. Mackay, Inc., 99.99%. WO_2 was prepared by the reaction of W and WO_3 at 950° under purified argon. Commercial grade argon was purified in a reduction column described previously.[2] Solid chemicals were dried 3 hr at 400° and 10^{-2} torr.

Nd_2O_3 was converted to $NdCl_3$ by heating with excess NH_4Cl for 3 hr at 320°.

Preparations.—Mixtures of the halide, WO_3, and WO_2 were prepared employing an excess of the halide and using the WO_2-limiting reactant to limit x. The reactants were ground together, packed into recrystallized alumina combustion boats, and heated in Vycor tubes under vacuum (10^{-5} torr) or under purified argon. The reaction tube was situated in the tube furnace with at least one-fourth of the length extending from the furnace, so that this cool portion served as a condenser for the volatilized tungsten oxyhalides. The temperature of the hot zone was raised slowly past the melting point of the halide to some arbitrary maximum temperature. The reactants were held at the maximum temperature for at least 3 hr, and then were allowed to cool rapidly to room temperature. The products were purified by successively heating in water, dilute HCl, and dilute NH_3, in the case of the alkali metal preparations, and by heating in 10% oxalic acid solution for 6 hr, followed by leaching with dilute NH_3, in the case of the other compounds. Silica was removed by washing with 48% aqueous HF.

Chemical Analysis.—The alkali metal and alkaline earth bronzes were analyzed by heating in a stream of dry HCl–air mixture to volatilize tungsten and oxygen as the oxychloride, leaving a residue of the metal halide in the combustion boat.[2,3] The metal content of the chloride residue was determined by flame or atomic absorption spectrophotometry for all but the magnesium chloride residues. Magnesium was determined gravimetrically as the 8-hydroxyquinolinate. All of the chloride residues were checked for purity by determining chloride using the Volhard method. For all of the alkali metal and alkaline earth metal bronzes, tungsten was determined from the weight loss following the volatilization of the oxychloride.

The lead content in that bronze was determined by precipitating the very insoluble $PbWO_4$. A similar method was employed as an independent analysis for the alkaline earth metals. The bronze was fused with a 3:1 weight mixture of Na_2CO_3–$NaNO_3$ at red heat in a porcelain crucible. The cooled fusion cake was dissolved in water and made acid with HCl. After heating to expel CO_2 the solution was made basic with NaOH to dissolve any WO_3. The precipitate of MWO_4 was then filtered off, washed, dried at 750°, and weighed. The tungsten remaining in solution was determined as the trioxide by the nitric acid–cinchonine precipitation.[4] The thallium bronze was determined by the

(2) L. E. Conroy and T. Yokokawa, *Inorg. Chem.*, **4**, 994 (1965).

(3) C. W. Lutz and L. E. Conroy, *Anal. Chem.*, **38**, 139 (1966).

(4) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1931, p 226.