[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Chemistry of Thorium. IV. Some Observations on Thorium Hypophosphate[1]

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RECEIVED JANUARY 5, 1953

Reaction of thorium ion with dihydrogen hypophosphate ion in aqueous solution has been shown by direct analysis of the product and by both conductance and *p*H titration data to yield the normal hypophosphate, ThP_2O_6. A method is described for obtaining the normally highly gelatinous material as a dry, free-flowing powder, which is still amorphous to X-rays. Freshly precipitated thorium hypophosphate has been found to adsorb both hypophosphate and thorium ions. The extent of adsorption of the former has been followed by a radiometric technique. Adsorption of the latter in hydrochloric acid solution has been found to peptize thorium hypophosphate to clear sols which can be dialyzed and can be sedimented in the ultracentrifuge. Thorium ion in 0.5 *N* acid has been shown to sediment also in high force fields.

Introduction

Current interest in thorium chemistry has prompted reinvestigations of many thorium compounds, which although described in the early literature, have apparently been neglected for a number of years. Among the most interesting of these substances is the hypophosphate, a compound first described by Kauffman[2] and subsequently recommended as a means of removing thorium efficiently from its admixtures with the rare earth elements.[3-8] Its use in this separation is dependent upon its extremely low acid solubility, a solubility which amounts only to some 2.1×10^{-4} mole/liter even in 6 *N* hydrochloric acid solution at 25°.[9] The compound is described as a difficult to handle, white, gelatinous solid of formula $ThP_2O_6 \cdot 11H_2O$.[2-4] It is resistant to oxidation, although it is said to dissolve in mixed sulfuric and fuming nitric acids on long boiling[3] and to be converted in part to the pyrophosphate on ignition in contact with oxygen.[5,7]

The chemical inertness of thorium hypophosphate suggests further study upon some of its characteristics. The present report is concerned with investigations on the preparation of the compound in an easy to handle form, the analysis of the solid, the stoichiometry of the reaction between thorium and hypophosphate ions in aqueous solution, and some of the rather remarkable colloidal characteristics of the precipitated material.

Experimental

Materials Used.—The source of thorium ion was a sample of thorium nitrate 4-hydrate, obtained from the Lindsay Light and Chemical Company and shown to be free from rare earth metal compounds. Thorium solutions were standardized by the gravimetric oxide procedure.[8] Disodium dihydrogen hypophosphate was prepared and purified by the procedure of Leininger and Chulski,[10] suitable modification[11] being made for those samples which contained phosphorus-32. Hypophosphate solutions were standardized by the method of Wolf and Jung.[12] Other chemicals were of analytical reagent quality.

Preparation and Analysis of Thorium Hypophosphate.—The following procedure gave thorium hypophosphate as a dry, free-flowing powder. To 25 ml. of a hot 0.3507 *N* thorium nitrate solution was added, with stirring, slightly less than the equivalent quantity (1:1 reaction assumed) of a 0.1705 *N* disodium dihydrogen hypophosphate solution. The mixture was digested on a steam-bath for several hours and the precipitate separated by centrifuging. The precipitate was washed three times by suspending in water and centrifuging and then two times by treating similarly with 35-ml. portions of 95% ethanol. It was then allowed to stand overnight under absolute diethyl ether, removed by filtration, and air-dried. The resulting powder was shown to be non-crystalline by X-ray diffraction.

Because of the inertness of thorium hypophosphate, chemical determination of its composition is difficult. The following procedure gave excellent and reproducible results. A 0.1-g. sample was dissolved by heating with 25 ml. of a standard solution *ca.* 0.1 *N* in cerium(IV) ammonium nitrate and 1 *N* in nitric acid plus 5 ml. of nitric acid of sp. gr. 1.42. The resulting solution was diluted to 100 ml. with 4 *N* nitric acid, and hypophosphate was determined on an aliquot as previously described.[13] Thorium was determined on another aliquot by precipitating with oxalic acid, igniting, weighing and correcting the weight of the mixed oxides for its known cerium(IV) content. Separate analyses gave Th^{+4} to $P_2O_6^{-4}$ mole ratios of 1.03, 1.00, 1.09 and 1.05 for the compound. Evaluation of the water content showed the composition of the material prepared under the conditions described above to be given by the formula $ThP_2O_6 \cdot 2H_2O$.

Titration Studies.—Conductometric and *p*H titrations were used to establish the stoichiometry of the reaction between thorium and hypophosphate ions in solution. The former were carried out at 25 ± 1°, using 5-ml. portions of *ca.* 0.15 *N* thorium nitrate and disodium dihydrogen hypophosphate solutions, each diluted to 60 ml. Conductance was measured with a Leeds and Northrup a.c. bridge. The *p*H titrations were carried out similarly, using a Beckman *p*H meter.

Adsorption Studies.—The degree of hypophosphate adsorption by freshly precipitated thorium hypophosphate was determined radiometrically. Thorium nitrate solutions, containing the equivalent of 4.5 to 72.8 mg. of the dioxide, were treated with measured excess quantities of 0.1 *M* disodium dihydrogen hypophosphate solution containing a known activity of radiophosphorus.[11] Each of these mixtures was diluted to constant electrolyte concentration with sodium nitrate solution[14] and then to 50 ml. total volume with 6 *N* hydrochloric acid solution. The suspensions were thermostated at 25 ± 0.1° for 3 hr. The precipitates were then removed, and the filtrates were counted in annular volume tubes,[14] using a thin-walled beta counting tube and a Type A Cyclotron-Specialties Co. scalar. The quantity of adsorbed hypophosphate was determined from the activity of the solution, correction being made for that precipitated by the thorium ion.

Preparation of Thorium Hypophosphate Sols.—Freshly precipitated thorium hypophosphate, when treated with thorium ion in acidic solutions, is readily peptized to water-white, positively charged sols. Such sols result over rather wide concentration ranges, *e.g.*, mixtures both 2 *N* in hydrochloric acid and containing 0.1115 g. of disodium dihydrogen hypophosphate 6-hydrate and 1.40 g. of thorium nitrate and

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(1) For the preceding communication in this series, see T. Moeller and E. H. Kobisk, THIS JOURNAL, **72**, 2777 (1950).

(2) O. Kauffman, Dissertation, Rostock, 1899.

(3) F. Wirth, *Z. angew. Chem.*, **25**, 1678 (1912).

(4) M. Koss, *Chem. Z.*, **36**, 686 (1912).

(5) A. Rosenheim, *ibid.*, **36**, 821 (1912).

(6) F. Wirth, *ibid.*, **37**, 773 (1913).

(7) F. Hecht, *Z. anal. Chem.*, **75**, 28 (1928).

(8) T. Moeller, G. K. Schweitzer and D. D. Starr, *Chem. Revs.*, **42**, 63 (1948).

(9) T. Moeller and G. H. Quinty, THIS JOURNAL, **74**, 6123 (1952).

(10) E. Leininger and T. Chulski, *ibid.*, **71**, 2385 (1949).

(11) T. Moeller and G. H. Quinty, *ibid.*, **74**, 6122 (1952).

(12) L. Wolf and W. Jung, *Z. anorg. allgem. Chem.*, **201**, 347 (1931).

(13) T. Moeller and G. H. Quinty, *Anal. Chem.*, **24**, 1354 (1952).

(14) T. Moeller and G. K. Schweitzer, *ibid.*, **20**, 1201 (1948).

0.45 *N* in hydrochloric acid and containing 0.1068 g. of the hypophosphate and 0.8604 g. of thorium nitrate, each in a total volume of 50 ml., yielded transparent sols. For a given hypophosphate content, decreases in either thorium ion or acid concentration caused opalescence. Thorium hypophosphate sols flocculated when heated, but the flocs redispersed on cooling.

A sol prepared from 10 ml. of 0.9761 *N* thorium nitrate solution, 2 ml. of 12 *N* hydrochloric acid solution and 2.5 ml. of 0.4558 *N* disodium dihydrogen hypophosphate solution and diluted to 20 ml. was dialyzed for 12 hr. against distilled water, using a collodion membrane. Considerable osmosis was noted toward the end of this period. The transparent dialyzed sample had a *p*H of 4 and flocculated readily when treated with potassium nitrate solution.

Sedimentation Studies.—Sedimentation studies were carried out with both undialyzed and dialyzed thorium hypophosphate sols, using a Spinco Model E Ultracentrifuge. Qualitative measurements were made with a preparative rotor A and quantitative analytical measurements with an analytical rotor A. In the latter cases, sedimentation was recorded by a photographic technique using refractive index changes.

Results and Discussion

Reaction Between Thorium and Hypophosphate Ions.—Analytical data for precipitated thorium hypophosphate are in excellent agreement with the composition ThP_2O_6. Further evidence for reaction in this ratio is given by conductometric titration data. Given in Fig. 1(A) is a typical curve for the titration of a disodium dihydrogen hypophosphate solution with a thorium nitrate solution. The equivalence point agrees closely with a composition ThP_2O_6 for the precipitate. The initial rapid rise in conductance is in agreement with the release of highly mobile hydrogen ions according to the equation

$$Th^{+4} + H_2P_2O_6^{-2} \longrightarrow ThP_2O_6(s) + 2H^+ \quad (1)$$

and the somewhat less rapid increase after the equivalence point is due to the addition of excess thorium nitrate.

In the aqueous solution titration of thorium ion with dihydrogen hypophosphate, however, conductance rises rapidly to a maximum, corresponding to the equivalence 1 Th^{+4} to 1 $P_2O_6^{-4}$, drops very slightly, passes through an extremely flat minimum, and then rises regularly, but only after addition of a large quantity of hypophosphate. The initial increase in conductance is most certainly due again to release of hydrogen ions according to equation 1. The subsequent decrease indicates removal of highly conducting species by excess hypophosphate. It is reasonable to conclude that this amounts to hydrogen ion removal according to such equations as

$$H_2P_2O_6^{-2} + H^+ \longleftrightarrow H_3P_2O_6^- \quad (2)$$

$$H_3P_2O_6^{-3} + H^+ \longleftrightarrow H_4P_2O_6 \quad (3)$$

but since the first two hydrogen atoms in hypophosphoric acid are rather strongly acidic (pK_1 = 2.2, pK_2 = 2.8),[15] this effect can never be pronounced in aqueous solution. The markedly flat minimum in the conductance titration curve supports this contention.

In ethanol solution, however, it might be expected that these two hydrogen atoms would be less acidic and that removal of hydrogen ions from solution by excess hypophosphate would be correspondingly more pronounced. This is indeed the case, conductance dropping rapidly after completion of precipitation and passing through a better defined and sharper minimum. As shown in Fig. 1(B) where such a titration in 30% ethanol is described, a 1:1 stoichiometry is clearly indicated by the maximum in the curve. It is of interest that titration of hydrochloric acid in 30% ethanol with dihydrogen hypophosphate gives a conductance curve with a flat minimum corresponding in position to neutralization of the hydrogen ion from the acid.

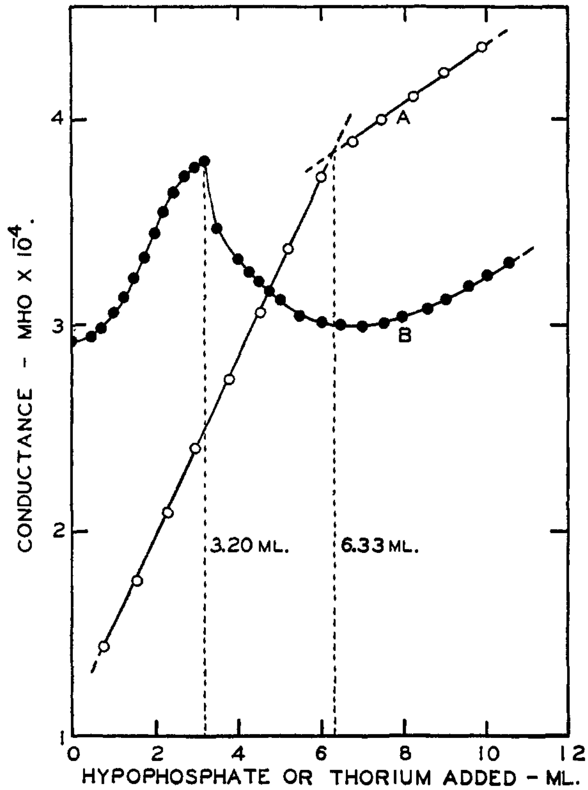

Fig. 1.—Conductance titration data: curve A, titration of 5.0 ml. of 0.1725 *N* $H_2P_2O_6^{-2}$ solution with 0.1387 *N* Th^{+4} solution; theoretical end-point at 6.32 ml.; curve B, titration of 3.0 ml. of 0.1505 *N* Th^{+4} solution with 0.1360 *N* $H_2P_2O_6^{-2}$ solution in 30% ethanol; theoretical end-point at 3.33 ml.

The reaction described by equation 1 is amenable to study by *p*H titration. Titration of thorium nitrate solution with disodium dihydrogen hypophosphate solution gives a curve with a minimum *p*H value corresponding closely to a 1:1 reaction. Reaction according to equation 1 releases hydrogen ions, but when precipitation is complete, reaction of hydrogen ions according to equations 2 and 3 and hydrolyses of the hypophosphate species combine to increase the *p*H. Titrations of dihydrogen hypophosphate with thorium ion give only rapid decreases in *p*H, followed by leveling off to constant *p*H value of *ca.* 2.5, since after release of hydrogen ions no mechanism for their removal exists. Such titrations are useless in evaluating the composition of the precipitate.

Colloidal Characteristics of Thorium Hypophosphate.—Both the highly gelatinous character of freshly precipitated thorium hypophosphate and

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(15) W. D. Treadwell and G. Schwarzenbach, *Helv. Chim. Acta*, **11**, 405 (1928).

the lack of crystallinity in the dried product are indicative of the colloidal nature of the material. The acid insolubility of the compound[9] prompted an investigation of the feasibility of developing a radiometric procedure for the determination of thorium comparable with that involving precipitation of the pyrophosphate.[14] However, studies under a variety of concentration and temperature conditions showed that the precipitate adsorbed hypophosphate so strongly that no quantitative results could be obtained.[16] As typical results, it was found that at 25° adsorption (calculated as disodium dihydrogen hypophosphate 6-hydrate) increased regularly from 0.28 to 29.85 mg. as the quantity of thorium hypophosphate (calculated as thorium dioxide) was increased from 4.55 to 72.80 mg.

Thorium hypophosphate apparently adsorbs thorium and hydrogen ions as well. This is evidenced by the ease with which the material can be peptized in solutions containing excess thorium ion and hydrochloric acid. Under these conditions, perfectly clear, mobile sols result, and in the absence of dialysis these sols resist flocculation by electrolytes. Thorium hypophosphate resembles thorium orthophosphate in the ease with which it is peptized.[17] The presence of dispersed material in a dialyzed sample of the hypophosphate sol was confirmed by complete sedimentation in 7 hr. in a force field of some 150,000 *g*, obtained by operating the ultracentrifuge at 50,470 r.p.m.

The enhanced stability of the undialyzed colloid permitted a more comprehensive study of its sedimentation. A sample prepared from 10 ml. of 0.1360 *N* hypophosphate solution, 2 ml. of 12 *N* hydrochloric acid solution and 5 ml. of 1.434 *N* thorium nitrate solution, in a total volume of 50 ml., was sedimented in the analytical rotor at 26° in a field of 20,000 *g* at a centrifuge velocity of 20,410 r.p.m. A blank consisting of 4.04 ml. of 1.434 *N* thorium nitrate solution (equivalent to the unreacted thorium ion in the hypophosphate sample) and 2 ml. of 12 *N* hydrochloric acid solution, in a total volume of 50 ml., was run simultaneously. The samples were photographed at 16 min. intervals, giving a record of the results.

It can be shown that for spherical particles at a steady state velocity of sedimentation in a centrifugal field

$$r^2 = 9\eta \ln (x_2/x_1)/2\rho\omega^2(t_2 - t_1) \qquad (4)$$

where r is the radius of the particle, x_1 and x_2 are the distances from the center of rotation of the peak in the sedimentation curve at times t_1 and t_2, η is the viscosity of the medium, ρ is the density of the suspended particle, and ω is the angular velocity of rotation. Substitution of appropriate quantities,[16] including the density of the dry solid (3.1 g.cc.$^{-1}$) as equalling that of the suspended material, gives an average particle radius of 15.1 Å. for the dispersed thorium hypophosphate. Due consideration must be given, of course, to the assumptions made in this calculation.

Sedimentation of Thorium Ion.—It is of interest that operation of the ultracentrifuge at velocities of some 29,000–50,000 r.p.m. developed concentration gradients in the thorium nitrate–hydrochloric acid blanks. Inasmuch as such solutions were too strongly acidic (*ca.* 0.5 *N*) to permit existence of hydrolyzed aggregates, it may be concluded that the heavy thorium ion was being sedimented.

It has been shown[18] that for an electrolyte consisting of a polyvalent ion combined with *n* univalent counter ions

$$S = MD(1 - \bar{v}\rho)/(n + 1)RT \qquad (5)$$

where S is the rate of sedimentation in a unit centrifugal field, M is the molecular weight of the solute, D is the rate of diffusion of the solute, $\bar{v}$ is the partial specific volume of the solute, ρ is the density, R is the gas constant, and T is the Kelvin temperature. This equation, although giving low values for sedimentation rates in the presence of additional electrolysis, can be applied to the thorium nitrate solutions used. Substitution of appropriate values[16] for a 6.89% thorium nitrate solution gave a sedimentation constant of 3.31×10^{-14} cm. sec.$^{-1}$ at 25°.

Sedimentation of a sample 0.45 *N* in hydrochloric acid and containing 0.0784 g. of thorium nitrate per milliliter was effected by centrifuging for 6.25 hr. at 50,740 r.p.m. Gravimetric analyses of solutions withdrawn from top and bottom parts of the centrifuge tube showed the passage of the equivalent of 0.033 g. of thorium dioxide through an interface into the bottom layer. Calculation of the quantity (m) passing through this interface (x_i), using the above determined sedimentation constant, from the relationship

$$S = \frac{1}{-t\omega^2} \ln \left(1 - \frac{m}{C_0 B x_i}\right) \qquad (6)$$

where C_0 is the original solution concentration and B is the cross-sectional ellipsoidal area of the centrifuge tube, gives 0.020 g. of thorium dioxide. This may be taken as satisfactory agreement with the measured quantity, since no account was taken of the presence of hydrochloric acid in the sample.

Acknowledgments.—The authors wish to express appreciation to the Office of Naval Research for partial support of this investigation and to Professor B. Roger Ray for assistance in ultracentrifugal studies and in evaluation of the results obtained from them.

URBANA, ILLINOIS

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