

PREPARATION OF TANTALUM PHOSPHATE, ITS STRUCTURE AND SOME PROPERTIES

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The composition and some properties were studied for tantalum phosphate precipitate forming on heating a solution containing tantalum in the fluoro complex, hydrofluoric acid, sodium phosphate, and nitric or hydrochloric acid. Annealing of the precipitate leads to the defined compound $TaOPO_4$. The tantalum-to-phosphate group ratio is 1 : 1 also in the precipitate freely dried at room temperature; in this form, tantalum undergoes hydrolysis in alkaline or weakly acidic solutions, whereas in strongly acidic solutions the hydrolysis is substantially suppressed. Annealed precipitate is stable in usual conditions. The dried precipitate exhibits sorption properties, whereas the annealed precipitate does not.

Tantalum phosphate was first synthesized by Hahn¹ by heating potassium tantalate(V) with excess mixture of phosphoric and nitric acids. The precipitate annealed at 1000°C contained 75.5% Ta_2O_5 and 24.4% P_2O_5 and could be represented by the formula $Ta_2O_5 \cdot P_2O_5$. Alternatively, tantalum phosphate was prepared by heating a solution containing tantalum sulphate complexes and ammonium phosphate². Action of excess molten crystalline phosphoric acid on $TaCl_5$ in the formation of $Ta_3(PO_4)_5$ (ref.³), action of sulphuric acid on tantalum dissolved in phosphoric acid leads to $TaOPO_4 \cdot 4.5 H_2O$ (ref.⁴). The $TaOPO_4$ compound has been identified by using the infrared spectroscopy⁵ and X-ray diffraction⁶ techniques.

In all the above works, tantalum phosphate was prepared in media free from fluoride ions. However, as found by us⁷, heating of urine acidified with nitric acid and containing tantalum fluoro complex results in the separation of a precipitate, whose composition after annealing is identical with that of the precipitate obtained by Hahn¹. A method of separation of ^{182}Ta from urine has been devised⁷ based on precipitation of tantalum in the form of tantalum phosphate after prior addition of a tantalum carrier.

The aim of the present work was to establish the conditions of formation of tantalum phosphate in solution containing tantalum in the form of its fluoro complex, sodium dihydrogen phosphate, and nitric or hydrochloric acid, and to determine the composition of the precipitate formed, its solubility and sorption properties.

EXPERIMENTAL

Reagents and Apparatus

^{182}Ta -labelled tantalum in the fluoro complex form was prepared by dissolving tantalum metal and ^{182}Ta , obtained on irradiation of tantalum metal by thermal neutrons in a reactor, in hydrofluoric acid. The resulting solution contained Ta and HF in concentrations $0\cdot03316$ and $1\cdot5\text{ mol l}^{-1}$, respectively. Unlabelled tantalum fluoro complex was prepared likewise. Solution of ^{32}P -labelled NaH_2PO_4 was obtained by dissolving $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and an NaH_2PO_4 preparation (Amersham, England) in distilled water.

The activity of the samples beta (or gamma) was measured on an NRB-213 low-background anti-coincidence kit (Tesla). The thermogravimetric analysis was carried out using a Thermoanalyser 1 apparatus (Mettler).

Working Procedure

25 ml of solution containing $3\cdot316 \cdot 10^{-3}\text{ mol l}^{-1}$ Ta (^{182}Ta -labelled), $0\cdot15\text{ mol l}^{-1}$ HF, $0\cdot1\text{ mol l}^{-1}$ NaH_2PO_4 , and HNO_3 or HCl (in various concentrations) was heated on water bath, and the precipitate separated was centrifuged and washed successively with 30 ml of 2M- HNO_3 , 30 ml of 10M- HNO_3 , and 30 ml of 2M- HNO_3 . Tantalum in the precipitate was determined radiometrically. The precipitate was then dissolved in 5 ml of 5M-HF + 5M-HCl, and tantalum was extracted from the solution with 2×5 ml of methyl isobutyl ketone⁸. The aqueous phase after the extraction was evaporated, the residue was dissolved in nitric acid, and phosphorus in the solution was determined gravimetrically as ammonium molybdatophosphate.

Thermogravimetric analysis. A sample, 16.50 mg, was heated on air in static conditions using the rate of 6°C min^{-1} . Tantalum phosphate precipitate was prepared by heating 25 ml of solution containing $3\cdot316 \cdot 10^{-2}\text{ mol l}^{-1}$ Ta, $0\cdot15\text{ mol l}^{-1}$ HF, $0\cdot5\text{ mol l}^{-1}$ NaH_2PO_4 , and 8 mol l^{-1} HNO_3 ; the precipitate was separated by centrifugation, washed successively with 30 ml of 2M- HNO_3 , 30 ml of 10M- HNO_3 , and 30 ml of 2M- HNO_3 , and dried freely at room temperature.

Solubility study. The solubility of tantalum phosphate in acids, alkali, and water was also investigated for the precipitate dried on air at ambient temperature and that heated at 1050°C for 3 h. ^{32}P - and ^{182}Ta -labelled precipitates were prepared in the same conditions, using the procedure applied to the preparation of samples for thermogravimetric analysis. Portions of 10 mg of the precipitate and 5 ml of the solution under study were placed in 10 ml polyethylene vessels, shaken for 20 min, and centrifuged, and the solutions were sampled for radioactivity measurements. The precipitates were allowed to stand in contact with the solutions for 5 days with occasional stirring; samples for radioactivity measurements were taken the 3rd and 5th days.

Sorption properties. Sorption of uni- and divalent cations was examined on both the dried and the annealed precipitates, using the procedure applied to the study of zirconium phosphate⁹. 40 mg portions of the precipitate were placed in 10 ml polyethylene vessels, and 4 ml of $0\cdot1\text{ mol l}^{-1}$ HNO_3 containing the element under study was added. The latter was present either as the radioisotope solely in trace concentration, or as the radioisotope together with the isotopic carrier in the total concentration $1 \cdot 10^{-3}\text{ mol l}^{-1}$. The samples were shaken for three days at room temperature. The mass distribution coefficients D_g were calculated by using the relation

$$D_g = (A_p/A_s) (V/m) \quad (1)$$

(in ml g^{-1}), where A_p and A_s is the radioactivity of the radioisotope after the sorption in the precipitate and in the solution, respectively, V is the total volume of the solution, and m is the weight of the sorbent.

RESULTS

A voluminous white precipitate is formed on heating solution containing tantalum as the fluoro complex, hydrofluoric acid, sodium dihydrogen phosphate, and nitric or hydrochloric acid. For a given fluoride concentration, the formation of the precipitate is the faster, the higher is the concentration of the nitric or hydrochloric acid: for instance, in solution of $0.15\text{M-HF} + 15\text{M-HNO}_3$ or 11M-HCl the precipitate separates within 5 min, whereas in $0.15\text{M-HF} + 3\text{M-HNO}_3$ or 2.5M-HCl the process takes approximately 40 min. The tantalum-to-phosphate weight ratio in the precipitate approaches the theoretical value of 1.906, independent of the nitric or hydrochloric acid concentration (Table I).

Thermogravimetric analysis of the sample revealed that water is liberated from the sample rapidly at the very beginning of the sample heating, which is accompanied by a pronounced endothermic effect. The most rapid is the weight loss at 80°C . At 125°C , the liberation of water slows down; an additional slow liberation of water sets in at temperatures above 190°C and ceases above 900°C . In the fast dehydration step, thirteen molecules of water are released; the remaining two molecules are released during the slow dehydration resulting in the formation of anhydrous tantalum phosphate.

The weight change for the precipitate annealed for a longer period at 1050°C corresponds exactly to the transformation to TaOPO_4 . Analogous results have been obtained with niobium phosphate prepared by heating a solution containing niobium

TABLE I

Ta/PO_4 Weight Ratio in the Precipitate for Various Concentrations of Nitric or Hydrochloric Acid in the Solution

$c(\text{HNO}_3)_{\text{init}}$ mol l^{-1}	Ta/PO_4 weight ratio	$c(\text{HCl})_{\text{init}}$ mol l^{-1}	Ta/PO_4 weight ratio
3	2.04	2.5	1.95
9	1.91	7.5	2.06
15	1.83	11.0	1.88

in the fluoro complex and phosphoric and nitric acids¹⁰. The composition of the tantalum phosphate precipitate dried on air at room temperature could not be determined from our results; it can only be concluded that in the substance, a tantalum atom combines with one phosphate group.

The concentration of tantalum in the solutions and the proportions of tantalum and phosphate passed from the precipitate into the solution after 3 days' shaking

TABLE II

Concentration of Tantalum in the Solutions and Fractions of Ta and PO_4 Passed from the Precipitate into the Solution after 3 Days' Shaking

Solution	Precipitate labelled with ^{182}Ta		Precipitate labelled with ^{32}P	
	concentration of Ta in the solution mol l^{-1}	fraction of Ta passed into the solution %	fraction of PO_4 passed into the solution %	
Dried precipitate				
pH 12 ^a	$1.5 \cdot 10^{-4}$	3.3	100	
pH 7	$<1.3 \cdot 10^{-6}$	<0.028	15.2	
0.1M-HNO ₃	$<1.3 \cdot 10^{-6}$	<0.028	10.0	
5M-HCl	$<1.3 \cdot 10^{-6}$	<0.028	6.7	
12M-HCl	$1.8 \cdot 10^{-6}$	0.041	0.8	
5M-HNO ₃	$<1.3 \cdot 10^{-6}$	<0.028	4.0	
15M-HNO ₃	$2.5 \cdot 10^{-6}$	0.055	1.9	
5M-H ₂ SO ₄	$1.0 \cdot 10^{-5}$	0.22	4.5	
18M-H ₂ SO ₄	$1.6 \cdot 10^{-4}$	3.5	10.3	
Annealed precipitate				
pH 12 ^a	$6.6 \cdot 10^{-6}$	0.10	2.10	
pH 7	$<1.1 \cdot 10^{-6}$	<0.016	<0.05	
0.1M-HNO ₃	$<1.1 \cdot 10^{-6}$	<0.016	<0.05	
5M-HCl	$<1.1 \cdot 10^{-6}$	<0.016	<0.05	
12M-HCl	$<1.1 \cdot 10^{-6}$	<0.016	<0.05	
5M-HNO ₃	$<1.1 \cdot 10^{-6}$	<0.016	<0.05	
15M-HNO ₃	$<1.1 \cdot 10^{-6}$	<0.016	<0.05	
5M-H ₂ SO ₄	$<1.1 \cdot 10^{-6}$	<0.016	<0.05	
18M-H ₂ SO ₄	$6.6 \cdot 10^{-6}$	0.10	0.36	

^a Adjusted with NaOH.

are given in Table II. In the case of the precipitate annealed at 1050°C for 3 h, the fractions of tantalum and phosphate that passed into the solution (except for the solutions of pH 12 and of 18M-H₂SO₄) were below their limit of determination attained in our conditions. In the case of the dried precipitate, all the phosphate was transferred into the solution in alkaline medium (pH 12); at pH 7 and in 0.1M-HNO₃, the transferred fractions were 15 and 10%, respectively. Tantalum remained completely in the solid. This can be ascribed to the formation of a low-soluble tantalum com-

TABLE III

Values of the Mass Distribution Coefficients (D_g) for Radioisotopes on the Precipitate Annealed at 1050°C

Conditions: 0.1M-HNO₃, $V = 4.0$ ml, $m = 30$ mg.

Radioisotope	D_g , ml g ⁻¹	
	Carrier-free concentration	in the presence of carrier $c = 1 \cdot 10^{-3}$ mol l ⁻¹
²² Na	1	0.2
⁸⁶ Rb	11	0.7
¹³⁷ Cs	30	0.3
⁴⁵ Ca	3	0.1
¹³³ Ba	31	0.1

TABLE IV

Values of the Mass Distribution Coefficients (D_g) for the Radioisotopes on the Precipitate Dried on Air at Room Temperature

Conditions: 0.1M-HNO₃, $V = 4.0$ ml, $m = 30$ mg.

Radioisotope	D_g , ml g ⁻¹	
	carrier-free concentration	In the presence of carrier $c = 1 \cdot 10^{-3}$ mol l ⁻¹
²² Na	41	30
⁸⁶ Rb	3 700	650
¹³⁷ Cs	5.700	920
⁴⁵ Ca	52	50
¹³³ Ba	240	65

pound as a result of hydrolysis. The hydrolysis takes place even in hydrochloric and nitric acids, but its extent diminishes with increasing concentration of the acid — the fraction of phosphate in the solution was lower in 15M-HNO₃ or 12M-HCl than in 5M-HNO₃ or 5M-HCl. In sulphuric acid, on the other hand, the precipitate partly dissolves on account of formation of tantalum sulphate complexes.

Tantalum in the dried tantalum phosphate precipitate is hydrolyzed rather rapidly particularly in alkaline solutions. After 20 min shaking of the precipitate, 10·4 or 2% of the phosphate passed into the solutions of pH 7 and of 0·1M-HNO₃, respectively. After five days' shaking, an amount of phosphate exceeding that given in Table II was found only in solutions of pH 7, 0·1M-HNO₃, and 18M-H₂SO₄ (in the last case, this applied also to tantalum).

On the precipitate annealed at 1050°C, the radioisotopes used practically do not sorb from 0·1M-HNO₃ (Table III). In the case of the dried precipitate, the radioisotopes do sorb, but the sorption is significantly lowered if the isotopic carrier is present even in a concentration as low as 10⁻³ mol l⁻¹ (Table IV). It is rather difficult to elucidate the mechanism of the sorption, because owing to hydrolysis of tantalum, the composition of the solid is variable. The sorption can be explained in terms of ion exchange for H⁺ at the hydrogenphosphate groups (as is the case with inorganic ion exchangers of the type of Zr, Ti hydrogenphosphates), the sorption may occur on hydrated tantalum(V) oxide, whose sorption properties have been reported.

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