S 52. *A Tracer Study of the Chemistry of Protoactinium.*

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The paper describes the results of a tracer investigation made in connection with the development of a method for the separation of natural protoactinium. The results emphasize the difficulty of interpreting the evidence of precipitation on carriers in the case of an element whose compounds are so prone to hydrolysis. The conditions for the stability of tracer concentrations of protoactinium in aqueous solutions have been investigated. The chemistry of aqueous solutions of protoactinium compounds more closely resembles that of zirconium compounds than of tantalum. Similarities with the adjacent elements thorium and uranium are not marked.

The discovery of the transuranic elements, and speculation concerning the " 5*f* " electrons, has led to renewed interest in the chemistry of element 91 (see *e.g.*, Seaborg, *Science*, 1946, **104**, 379; Zachariasen, *Physical Rev.*, 1948, **73**, 1104). Until very recently, it had been customary to discuss the chemistry of protoactinium in terms of those elements which were used as carriers in its extraction, particularly tantalum and zirconium. The little that was known was based mainly on experiments directly related to the separation of the element. Even elementary details of its chemistry have, however, yet to be established with certainty—as, for example, the valency states of the element (see Bouissières and Haissinsky, this vol., p. S 256). Most of the information which was available was of the type that is listed in the following table. For example, it had been noted that protoactinium is precipitated with zirconium phosphate from strongly acid solution, and that, unlike zirconium, it is carried on tantalic acid. The table includes results obtained in this investigation. Such qualitative data, however, although relevant to the separation of the element, tell us little about its chemistry; for that, it is necessary to know something of the mode of operation of the carrier. Greater reliance can be placed on the evidence of those properties the investigation of which is independent of the concentration, that is to say, on solvent extraction of complexes, electrolytic transport, and similar characteristics.

Comparison of some reactions of protoactinium with those of zirconium (and hafnium), tantalum, and thorium.

	Observed behaviour of protoactinium is :					
	Like Zr.	Unlike Zr.	Like Ta.	Unlike Ta.	Like Th.	Unlike Th.
Insol. in alkalis	*	—	—	*	*	—
Pptd. by H_3PO_4 in 6N-HCl	*	—	*	—	—	*
Pptd. with Ta_2O_5 in 1N-HCl	—	*	*	—	—	*
Pptd. with MnO_2 in acid	—	*	—	?	—	*
Soluble in HF pH 1—9	*	—	*	—	—	*
Pptd. by acid H_2O_2	*	—	—	*	*	—
Sol. in $(NH_4)_2CO_3$ soln.	*	—	—	*	—	*
Pptd. by HIO_3 in dil. HNO_3	*	—	—	—	*	—
Pptd. by ammonium phenylarsonate in dil. HNO_3	*	—	—	—	*	—
Cupferronate stable in 2N-HCl	*	—	—	*	—	*
Sol. in tartaric acid, pH 1—10	*	—	*	—	*	—
Sol. in citric acid, pH 1—10	*	—	*	—	*	—
Sol. in oxalic acid, pH 1—9	*	—	*	—	—	*

(1) *Hydrolysis of Protoactinium Solutions.*—Preliminary experiments suggest that, except in the presence of certain complexing agents, protoactinium would not be in true aqueous solution even at a pH as low as 1·0. It was most desirable to define the conditions under which it is in solution at tracer concentrations in ionic, or molecular form, and not as a radio-colloid. Accordingly, a series of protoactinium solutions, of different composition and acid concentrations, were centrifuged at high speed (about 20,000 **g.**) and the losses compared. The results show that true solutions were only obtained with the mineral acids at normalities greater than 3, and with the complexes produced in 1·5N-citric acid or 0·5M-ammonium fluoride solutions.

(2) *Electrolytic Transfer Experiments.*—The sign of the principal protoactinium ion in various solutions can be determined, even at tracer concentrations, by measurement of electrolytic transport using a cell with isolated electrode compartments. The results show that the principal protoactinium-containing ion is a cation in hydrochloric acid solutions. However, in citric acid and ammonium fluoride solutions the whole of the protoactinium is present as an anion.

(3) *Coprecipitation Experiments.*—Inferences about the chemical properties of an element drawn from coprecipitation experiments are more reliable if the process can be shown to be due to isomorphous incorporation of the submicroscopic component. Coprecipitation by adsorption or chemisorption processes is distinguished by the dependence of the efficiency of coprecipitation on the conditions, temperature, pH, presence of other ions, and manner of addition of reagents. In such cases macroscopic quantities of the compound of the tracer adsorbed will generally be found more or less insoluble in the medium in which coprecipitation occurs.

When uniform incorporation of the tracer takes place, it may be due to isomorphous incorporation or, in a more limited number of cases, it may result from mixed crystals due to complex ion formation. Uniform incorporation of the tracer is characterised by greater insensitivity of the efficiency of co-precipitation to the conditions and, when the precipitation of the macroscopic component is incomplete, by a linear relation between the fractions of the two components that are precipitated.

Using these criteria, the coprecipitation of protoactinium on mixtures of zirconium and hafnium phosphates, iodates, and phenylarsonates, and on thorium iodate, tantalic acid, and lanthanum fluoride was investigated. In no case was evidence of uniform incorporation obtained. In the case of tantalic acid a comparison was made of the efficiency of coprecipitation obtained in solutions at various acidities with the extent of hydrolysis of the protoactinium as shown by the centrifugation experiments. Strong reducing agents such as hydrazine, sulphur dioxide, and zinc amalgam appeared to be without effect on the behaviour of tracer concentrations of protoactinium with lanthanum fluoride.

(4) *Experiments in Alkaline Media.*—It seemed desirable to confirm the absence of soluble alkali salts of a protoactinium anion and to determine which complex protoactinium anions are stable in solutions of high pH. It was shown that protoactinium, under a variety of conditions,

is insoluble in the alkali hydroxides and ammonium hydroxide. It is also not rendered soluble by sodium peroxide. Likewise, it does not appear to produce a soluble complex cyanide which is stable in alkaline solutions. Evidence of soluble complex carbonates, citrates, and tartrates which are stable in alkaline solution was, however, obtained. The formation of a soluble complex ammonium carbonate stable up to pH 10 is in surprising contradiction with other investigators (Graue and Käding, *Angew. Chem.*, 1934, **47**, 652).

(5) *Organic Complexes.*—The formation of selective organic complexes which can be extracted from aqueous solution by organic solvents would greatly facilitate the separation of protoactinium. Complexes were obtained with cupferron, acetylacetone, and 8-hydroxyquinoline (oxine) which could be extracted from aqueous solutions by amyl acetate and other solvents. The stability of the " cupferronate " in strongly acid solutions established its value as a separation procedure (see this vol., p. S 253).

Conclusions.—No examples of isomorphous inclusion of protoactinium were discovered. In some cases, as, *e.g.*, the carrying of protoactinium on tantalic acid, the removal of the radio element closely follows its hydrolysis in solutions of the same acidity, and it is possible that the coprecipitation is entirely due to the physical affinity of the products of hydrolysis for the surface of tantalic acid precipitates. It is probable that other coprecipitation experiments previously recorded involve the hydrolysis of the protoactinium. However, in a number of the experiments described, the conditions of precipitation were such that the protoactinium, on the evidence of the centrifugation experiments, should not have hydrolysed to any appreciable extent. It seems likely, therefore, that in these instances the precipitation of the protoactinium was due to the low solubility of the compound adsorbed. For example, protoactinium probably forms a phosphate which is less soluble in mineral acids than zirconium phosphate. Thus, in comparing the tracer chemistry of protoactinium with that of other elements, less emphasis should be given to the evidence of coprecipitation reactions, whose mechanisms are not fully known, than to solubility data and the formation and stability of its complex ions. Therefore only very limited conclusions as to the chemical nature of protoactinium can be drawn from the experiments described. It would appear that the charge on the protoactinium cation is large from its ready hydrolysis and the stability of the " cupferronate " in mineral acids. No evidence of multivalency has been obtained, but states which are unstable in aqueous solution (Haissinsky and Bouissières, *Compt. rend.*, 1948, **226**, 573) are difficult to detect at tracer concentrations.

The above reservations being borne in mind, the foregoing table would suggest that protoactinium bears the most pronounced similarity to zirconium but that much of the evidence consists only of similarities in solubilities. There is little direct evidence of chemical similarity between protoactinium and tantalum under tracer conditions, although the principal macroscopic work on protoactinium (von Grosse, *Proc. Roy. Soc.*, 1935, *A*, **150**, 363) has established the existence of the analogous compounds Ta_2O_5, Pa_2O_5; K_2TaF_7, K_2PaF_7.

The nature of protoactinium is such as to render the interpretation of tracer experiments very uncertain, and an extended investigation with macroscopic concentrations of the element is being prepared.

EXPERIMENTAL.

Experiments were conducted on both the β-active ^{233}Pa and the natural α-active ^{231}Pa. The separation of these materials is described in the following paper. The activity of β-active materials was measured by particulate counting with a Geiger–Müller counter and electronic scaling unit, and the activity of α-active samples by means of an air-filled ionisation chamber and a linear amplifier. Corrections for self-absorption and coincidence losses were made where appropriate.

(1) *Centrifugation Experiments.*—The experiments were conducted in 50-ml. plastic centrifuge tubes, and measurements of the decrease in activity of the protoactinium containing solution made. Preliminary experiments showed that the activity reached a steady value after about 30 minutes. The results tabulated were obtained by spinning each solution for 2 hours. A few experiments in the more acid solutions were continued for longer periods, up to 2 days, with no appreciable change.

The first series of experiments was made with ^{233}Pa in buffered sodium acetate solutions from pH 1·6 to 9·0. The results were erratic, possibly owing to peptisation and sol formation in this pH range :

Batch no.	B	B	A	B	E	B	A	B	C	B	A	E	C	C	B	C
pH	9·0	5·35	4·5	4·2	4·2	3·6	3·5	3·1	3·1	2·9	2·3	2·1	2·1	1·8	1·6	1·6
Loss of Pa, %	92	90	51	67	72	59	55	44	65	49	45	35	59	61	47	48

Similarly, irregular results were obtained in ammonium nitrate and nitric acid solutions between pH 0·65 and 1·0 :

pH	1·0	1·0	1·0	0·75	0·65
Loss of Pa, %.........................	11	22	60	30	45

However, in more acid solutions the results were reproducible and the losses considerably smaller :

	Nitric acid.			Hydrochloric acid.			
Normality	1·0	3·0	6·0	0·5	1·0	3·0	6·0
Loss of Pa, %	24	8	2	45	36	15	0

Solutions in citric acid and ammonium fluoride were stable at all pH values.

Citric acid	0·5M.	0·5M. + aq.NH_3 to pH 4·0	NH_4F	0·5M.	0·5M. + aq.NH_3 to pH 9·0
Loss of Pa, %	0	0	Loss of Pa, %	0	2

The possibility of the reduction of protoactinium to a presumably less readily hydrolysed state was examined by heating a solution with hydrazine hydrochloride, cooling it, and determining the hydrolysis at different pH values: pH 0·55, loss 41%; pH 1·0, loss 40%. The results are not significantly different from the untreated solution.

(2) *Electrolytic Transport.*—The apparatus consisted of two sintered-glass micro-filters, about 1 cm. in diameter, fitted to a reservoir of about 15-ml. capacity. The reservoir and stems of the filters up to the sintered plates were filled with the protoactinium solution. The upper parts of the funnels, which served as the electrode compartments, each of about 2-ml. capacity, were filled with a protoactinium-free solution of the same electrolyte as that contained in the reservoir. The electrodes were strips of platinum foil. The solution level in the electrode compartments was maintained by capillary siphons dipping into a reservoir of inactive solution. About 20% of the cell current was shunted through the siphons.

Measurements of the activity of the solutions in the electrode compartments were made after electrolysis, first in one direction (*A*) and then the other (*B*), thus ensuring that the effects observed were really due to electrolytic transfer. In the case of the citric acid solution, normal diffusion effects were estimated by an experiment run without electrolysis. The possibility of the deposition of protoactinium on the electrodes masking the results was eliminated by treating the electrodes with hot ammonium fluoride solution after the electrolysis and showing the washings to contain less than 2% of the protoactinium in the electrode compartment. The current was in each case about 10 ma. and the time of electrolysis about 12 hours. The applied potential varied from 12 volts in the case of hydrochloric acid to 90 volts in the citric acid solution.

Electrolytic transport in protoactinium solutions.

		^{233}Pa (c./min./ml.).			
Solution.		Bulk of solution.	Anode solution.	Cathode solution.	Sign of Pa ion.
6N-Hydrochloric acid :	*A*	2,000	25	105	+
	B	—	45	145	+
0·5M-Ammonium fluoride :	*A*	8,400	350	No count	—
	B	—	450	No count	—
0·5M-Citric acid :	*A*	20,000	700	30	—
	B	—	850	175	—
Citric acid		20,000	25	185	" Blank "

(3) *Coprecipitation Experiments.*—The experiments were conducted in 2-ml. centrifuge tubes, the carrier concentrations being about 0·1M. unless otherwise stated.

(*a*) *Zirconium phosphate.* The variation in the coprecipitation of protoactinium with the fraction of a zirconium–hafnium mixture precipitated by phosphoric acid was investigated by the determination of the protoactinium and zirconium–hafnium mixture in the remaining solution by means of their α- and β-activity. The initial solution contained the natural α-active ^{231}Pa and a β-active mixture of ^{95}Zr and ^{181}Hf. (The larger neutron-activation cross-section for ^{181}Hf production than for ^{95}Zr production results in nearly half the disintegrations in a ten-days-old irradiated sample of commercial zirconium being due to ^{181}Hf.) The experiments were conducted in 3N-nitric acid solution, and the amount of zirconium precipitated was controlled by the addition of the phosphoric acid :

Zirconium phosphate precipitated, %	7	21	40	70
Protoactinium carried down, %	33	76	91	96

(*b*) *Zirconium iodate.* The same procedure was used, with precipitation with iodic acid from 3N-nitric acid solutions :

Zirconium iodate precipitated, %	22	54	95
Protoactinium carried down, %	75	91	99

(*c*) *Zirconium phenylarsonate.* By the same procedure, precipitation being with ammonium phenylarsonate solution from 5N-hydrochloric acid in the presence of lanthanum :

Zirconium phenylarsonate precipitated, %	25	46
Protoactinium carried down, %	75	99

(*d*) *Thorium iodate.* Similar procedure, using ^{233}Pa in 3N-nitric acid solution; precipitation by controlled addition of iodic acid :

Thorium iodate precipitated, %	5·6	19	36
Protoactinium carried down, %	51	90	98

(*e*) *Tantalic acid.* Similar procedure, using ^{231}Pa and β-active ^{182}Ta; precipitation made from tartrate complex by 6N-hydrochloric acid at 80°, and precipitate centrifuged off and examined at intervals :

Ratio of β/α activity in precipitate	4·2	2·0	3·3
Tantalum precipitated, %	47	65	81

The effect of the hydrochloric acid concentration on the coprecipitation efficiency with and without zirconium was determined by agitation of equal aliquots of a freshly prepared slurry of tantalic acid for 90 minutes at 80° with solutions of ^{233}Pa in various normalities of hydrochloric acid :

	In absence of zirconium.			In presence of zirconium.		
Acid concentration, N.	0·5	2·0	6·0	0·5	2·0	6·0
Protoactinium carried down, %	100	50	10	35	20	5

(*f*) *Lanthanum fluoride.* The variation in the proportion of ^{233}Pa coprecipitated on lanthanum fluoride with the volume of lanthanum chloride solution (20 mg. of La per ml.) added to the 4N-hydrofluoric acid solution containing the ^{233}Pa was measured :

Vol. of lanthanum solution, ml.	0·02	0·05	0·1
Protoactinium carried down, %	14	57	100

When the hydrofluoric acid was added to a mixture of the protoactinium in hydrochloric acid with 0·05 ml. of the lanthanum solution, the precentage of protoactinium carried down fell to 31%.

In the presence of zirconium salts the amount coprecipitated was reduced to about 10%. Treatment of a zirconium-containing protoactinium solution with sulphur dioxide, hydrazine hydrochloride, and zinc amalgam for periods up to 48 hours in either hot or cold solutions and in an atmosphere of hydrogen produced no detectable difference in their behaviour with lanthanum fluoride precipitates.

(4) *Experiments in Alkaline Media.*—(*a*) ^{233}Pa was added to a mixture of vanadyl and lanthanum chlorides, and the mixture precipitated with sodium hydroxide. After centrifugation the activity of the supernatant liquid showed that less than 1% of the initial protoactinium remained in solution. The separated precipitate was treated with sodium peroxide and water, wherupon the vanadium went into solution. Less than 1% of the activity passed into the solution. The experiment was repeated with the same result, aluminium being used in place of vanadium.

(*b*) A mixture of ferric and cobalt hydroxides was precipitated by the addition of the minimal amount of ammonium hydroxide to a mixture of these salts in protoactinium solution. The activity of the supernatant solution showed that it contained less than 1% of the initial activity. Dissolution of the cobalt in excess of concentrated ammonium hydroxide removed less than 1% of the activity from the precipitate.

(*c*) A mixture of zirconium and lanthanum chlorides in a ^{233}Pa solution was precipitated by the addition of dilute ammonium carbonate solution. Activity measurements on the supernatant solution showed that less than 2% of protoactinium remained in solution. Leaching the precipitate with hot ammonium carbonate solution removed 75% of the activity from the precipitate. In the absence of the zirconium 50% of the protoactinium passed into solution and a similar quantity was removed from a calcium carbonate precipitate. Hot ammonium carbonate solution also removed 20% of the activity from a protoactinium-carrying ferric hydroxide precipitate.

(*d*) About 10 mg. each of ferric and lanthanum chlorides were dissolved in a ^{233}Pa solution and precipitated by the addition of aqueous potassium cyanide. Less than 1% of ^{233}Pa remained in solution. Addition of excess of potassium cyanide dissolved the ferric cyanide but less than 1% of the activity passed into solution.

(5) *Organic Complexes.*—(*a*) *Cupferron.* Preliminary experiments showed that the addition of cupferron (ammonium nitrosophenylhydroxylamine) to a ^{233}Pa solution produced a complex that could be extracted from the aqueous solution by organic solvents such as benzene, ether, chloroform, and amyl acetate. In the last solvent the ratio of the activity of the organic to that of the aqueous phase exceeded 10 for ^{233}Pa solutions between pH 1·0 and 4N. in mineral acids.

(*b*) *Acetylacetone.* 0·5 Ml. of the reagent was dissolved in 1 ml. of benzene and shaken with 1 ml. of the ^{233}Pa solution :

Nature and concn. of solution.	$CH_3{\cdot}CO_2H$, N.	Satd. NaOAc.	Satd. $(NH_4)_2CO_3$.	NaOH, 2N.
$\frac{\text{Activity of organic phase}}{\text{Activity of aqueous phase}}$	<0·01	0·65	<0·01	<0·01

(*c*) *Oxine.* 1 Mg. of oxine in 8N-acetic acid was added to 1 ml. of the ^{233}Pa solution and the mixture shaken with 1 ml. of amyl acetate :

Nature and concn. of solution.	$CH_3{\cdot}CO_2H$, 4N.	Satd. NaOAc.	Satd. $(NH_4)_2CO_3$.
$\frac{\text{Activity of organic phase}}{\text{Activity of aqueous phase}}$	<0·01	<0·02	2·1

No extraction into amyl acetate could be obtained with 1-nitroso-2-naphthol or 2-nitroso-1-naphthol from acetic acid, sodium acetate, or ammonium carbonate solutions of protoactinium.

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