BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2822—2825 (1967)

The Chemistry of Protactinium. V. The Separation of Pa(IV) and Pa(V) by Co-precipitation with Thorium Fluoride

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(Received June 13, 1967)

The separation of Pa(IV) and Pa(V) was investigated using various co-precipitants which were insoluble in acidic solutions. Among them, thorium fluoride was found to be the most useful co-precipitant. The conditions for the separation of both valency states of protactinium were also investigated in detail. This method was applicable to protactinium solutions in the concentration range down to tracer level. It was difficult to reduce Pa(V) completely on a tracer scale by means of a liquid zinc amalgam. When Cr(III) was added to the system, however, the complete reduction of ^{233}Pa(V) was readily attained. The role of Cr(III) was considered to be that Cr(II) formed by liquid-zinc-amalgam reduction mediates the reduction of Pa(V) and protects Pa(IV) from re-oxidation. By this method tetravalent protactinium in a perchloric acid medium was also confirmed to be very stable.

In a previous paper, the liquid-zinc-amalgam method as a rapid procedure for the reduction of Pa(V) and the stability of tetravalent protactinium in an aqueous solution were investigated, and it was observed that Pa(IV) was quite stable in an atmosphere of argon.1) The valency states of protactinium were identified by absorption spectroscopy based on the fact that Pa(V) had an absorption band at 210 mμ,2,3) while Pa(IV) had characteristic peaks at 233 mμ, 262 mμ and 289 mμ.1) However, this method requires a concentration of protactinium higher than 10^{-4} M, since the molar absorptivity is 1470 even at the highest peak.1) It is very difficult to obtain protactinium in a large amount because of its natural scarcity, and so experiments in lower concentrations are desirable. Besides, the study of the behavior of the element at a tracer concentration is a very interesting problem in itself. Therefore, it would be very convenient to have a method by which the valency states of protactinium could be identified in the concentration range down to tracer level.

The purpose of the present investigation is to

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1) T. Mitsuji, This Bulletin, **40**, 2091 (1967).

2) R. Guillaumont, R. Muxart, G. Bouissières and M. Haïssinsky, *Compt. rend.*, **1959**, 3298.

3) A. T. Casey and A. G. Maddock, *J. Inorg. Nucl. Chem.*, **10**, 58 (1959).

establish a co-precipitation method which is both simple in procedure and applicable to carrier-free ^{233}Pa for the separation of Pa(IV) from Pa(V); for this purpose thorium fluoride was found to be an excellent co-precipitant.

Experimental

Reagents. All the reagents used were of the highest grade in purity. The ^{233}Pa tracer and the ^{231}Pa carrier were prepared by the method reported by Suzuki and Inoue.4) The water was carefully purified by distillation in a quartz apparatus after demineralization by ion exchange.

Apparatus. Both reduction and co-precipitation were carried out in the reduction apparatus described in a previous report.1) A Marusan-Superior centrifuge, Model 30-1, was used for the separation of the precipitate from the solution. The γ-ray spectra were measured with a Kobe Kogyo, Model PS-400, well-type NaI(Tl) scintillation probe (1¾ in. × 2 in. NaI-(Tl) crystal), coupled with a Kobe Kogyo 100-channel pulse-height analyzer, Model AN-100. A Toa Dempa Kogyo pH-meter, Model HM-5A, was used for the pH measurements. A Hitachi recording spectrophotometer, EPS-3, was used for the measurement of the absorption spectra and for the determination of chromium.

Procedure. *Measurement of Radioactivity.* Since natural Th and U as well as ^{233}Pa have γ-activity, it is necessary to distinguish the γ-activity of ^{233}Pa from those of Th and U in the calculation of the co-precipitation rate of protactinium. The γ-spectrum of ^{233}Pa has two peaks, at 100 keV and 310 keV, while that of natural thorium has two peaks, at 90 keV and 260 keV, and that of natural uranium has three peaks, at 60 keV, 90 keV and 190 keV. It is clear that the measurement of the γ-activity of ^{233}Pa at 100 keV is interferred with, while that at 310 keV is not at all interfered with by either natural thorium or natural uranium. Therefore, the photo-peak at 310 keV was used for assaying the radioactivity of ^{233}Pa.

Co-precipitation. After 5 m*l* of a hydrochloric acid solution containing $^{233}Pa^{5+}$, Th^{4+}, and Cr^{3+} had been thoroughly deoxygenated by bubbling in argon gas which had previously been passed through an acidified ammonium metavanadate solution, protactinium was reduced by means of a liquid zinc amalgam.1) The performance of the reduction of Pa(V) was checked by the color change of the solution from green to light blue. The role of Cr(III) will be described below.

After reduction, thorium fluoride was precipitated by the rapid addition of a potassium fluoride solution which had been thoroughly deoxygenated. Then, the precipitate was separated by centrifuging the mixture for 3 min at 3000 R. P. M. The γ-activity of both the solution and the precipitate was measured, and the co-precipitation ratio was calculated.

The pH of the supernatant liquid was measured with a pH-meter. Co-precipitation with other co-precipitants was also carried out in a similar way. U^{4+} was prepared by the reduction of uranyl acetate by using a liquid zinc amalgam, after which it was exposed to air for an hour. The valency state of uranium was confirmed by absorption spectroscopy. The behavior of Pa(V) upon co-precipitation was investigated in the same way except for the reduction.

Results and Discussion

Preliminary Experiments. To find out good co-precipitants for the separation of Pa(IV) and Pa(V), the co-precipitation of each valency state was examined by using various co-precipitants which were insoluble in an acidic solution and which were considered to be suitable for the present purpose.

Twenty milligrams of each cation and a large excess of the corresponding anion were used for precipitation. As is clearly shown in Table 1, all the precipitates studied carried down Pa(IV) quantitatively, while Pa(V) was not carried down at all with thorium fluoride and uranium tetrafluoride. These findings can be understood by considering the chemical properties of protactinium. Stein synthesized PaF_4 from 20—230 mg of Pa-231 and it was reported to be isomorphous with both ThF_4 and UF_4 (monoclinic crystal structure).5) The ionic radius of Pa^{4+} is almost equal to that of Th^{4+} or U^{4+}. Therefore, it is probable that Pa(IV) forms the isomorphous mixed crystal with both ThF_4 and UF_4. On the other hand, Pa(V) is well known to form stable fluoro-complexes which can not be co-precipitated with such fluorides.6)

TABLE 1.

Co-precipitant	% co-precipitation	
	Pa(IV)	Pa(V)
Thorium fluoride	>95	<5
Uranium tetrafluoride	>95	<5
Cerous fluoride	>98	>98
Lanthanum fluoride	>98	>98
Thorium oxalate	>95	>50
Thorium iodate	100	100
Thorium arsenate	100	100
Thorium phosphate	100	100
Zirconium phosphate	100	100

From these findings, it seems that thorium and uranium fluorides are promising co-precipitants for the quantitative separation of Pa(IV) and Pa(V). The use of uranium, however, is inconvenient because of the cumbersome procedure needed for its precipitation. Therefore, thorium fluoride may be considered to be most suitable; the conditions for the separation of two valency states of protactinium were investigated in detail.

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4) S. Suzuki and Y. Inoue, This Bulletin, **39**, 490 (1966).

5) L. Stein, *Inorg. Chem.*, **3**, 995 (1964).

6) M. N. Bukhsh, J. Flegeheimer, F. M. Hall, A. G. Maddock and C. Ferreira de Miranda, *J. Inorg. Nucl. Chem.*, **28**, 421 (1966).

Co-precipitation with Thorium Fluoride.

The Relation between % Co-precipitated and the Amount of Thorium. The relation between the % co-precipitated of Pa(IV) and the amount of thorium was investigated at a hydrochloric acid concentration of 1 M. In this case, 15 times as much fluoride as thorium (based on the molar ratio) was added. It is apparent from Fig. 1 that the co-precipitation of Pa(IV) is almost complete when more than 15 mg of thorium is added. However, Pa(V) was not carried down with the thorium fluoride precipitate, regardless of the quantity of thorium added.

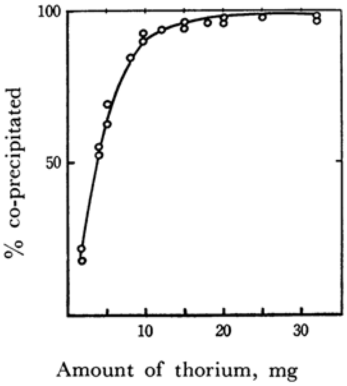

Fig. 1. Relation between % co-precipitated and amount of thorium.

The Relation between % Co-precipitated of Pa(IV) and the Amount of Fluoride Ion. The co-precipitation of Pa(IV) was examined as a function of the quantity of fluoride ions when the solution contained 20 mg of thorium. As is clearly shown in Fig. 2, the addition of 5 m*l* or more of a 0.2 M potassium fluoride solution is needed for the quantitative recovery of Pa(IV). This corresponds to the fluoride-to-thorium molar ratio of 12.5. Pa(V) was not carried down regardless of the quantity of fluoride added.

The Effect of the pH. The effect of the pH upon the % co-precipitated was also examined, as is shown in Fig. 2. The percentage co-precipitated of Pa(IV) is independent of the pH value studied. On the contrary, the co-precipitation of Pa(V) increased somewhat with an increase in the pH value. This observation can be well understood in light of the facts that Pa(V) is one of the ions apt to hydrolyse and that thorium fluoride probably carries a part of the protactinium species which are produced as a result of hydrolysis.

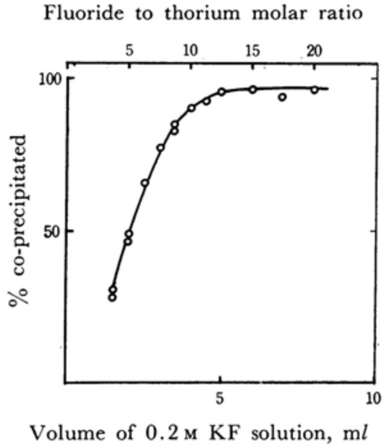

Fig. 2. Relation between % co-precipitated and amount of fluoride.

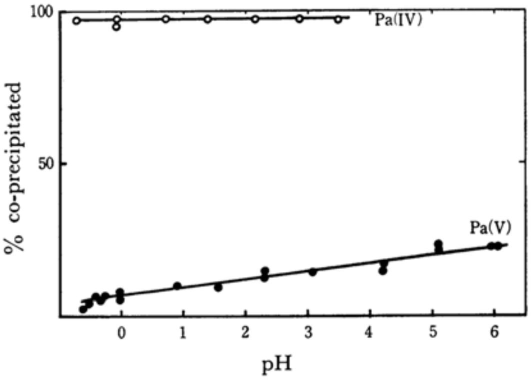

Fig. 3. Effect of pH upon % co-precipitated.
○: Pa(IV), ●: Pa(V)

Cr(II) as a Holding Reductant. The reduction of protactinium in high concentrations was reported to be quantitative in the previous paper, but it was incomplete when carrier-free ^{233}Pa was used, as only 10—30 percent was co-precipitated with thorium fluoride. Furthermore, the reproducibility of co-precipitation was not good. The reason for this phenomenon may be considered to be as follows.

At extremely low concentrations of protactinium, the contact between protactinium and amalgam is unsatisfactory and the protactinium reduced is affected by any traces of oxygen which might remain in the solution. If this explanation is true, the addition of the oxidized form of some redox reagent, which is effectively reduced by the amalgam and the reduced form of which can reduce Pa(V), will improve the reduction of protactinium (carrier for reduction) and avoid the effect of oxygen. Cr(III) is expected to be adequate for this purpose because the oxidation-reduction potential of the Cr(II)-Cr(III) pair (−0.40 V)⁽⁷⁾ is lower than that of the Pa(IV)-Pa(V) pair (−0.29±0.03 V).⁽⁸⁾ In view of this, Cr(III) was used as the carrier for reduction. The relationship between the concentration of

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7) G. S. Forbes and H. W. Richter, *J. Am. Chem. Soc.*, **39**, 1140 (1917).

8) M. Haïssinsky and E. Pluchet, *J. chim. phys.*, **59**, 608 (1962).

Cr(III) and the % co-precipitated was investigated; it was found that at least 10^{-4} M of chromium was necessary for the quantitative reduction of a tracer amount of Pa(V), as is shown in Fig. 4. The quantity of chromium remaining in the solution was determined spectrophotometrically as chromic ions, after the chromous ions had been re-oxidized to chromic ions by exposure to air. In all cases it was confirmed that more than 98% of chromium remained in the solution phase after the precipitation of thorium fluoride.

When divalent chromium which had beforehand been prepared by the liquid zinc amalgam reduction of chromic ions was added to a solution containing ^{233}Pa(V), and when then thorium fluoride was precipitated, protactinium was also recovered quantitatively. This result shows that Cr(II) acts as a reductant for Pa(V). Furthermore, so long as the color of the solution remained light blue, the protactinium was completely carried down with thorium fluoride. This means that divalent chromium is useful in protecting Pa(IV) from re-oxidation by H_2O (holding reductant) in addition to acting as a carrier for reduction. From the above results, it can be said that co-precipitation with thorium fluoride is a useful method for identifying Pa(IV) in microquantities.

The Effect of Protactinium Concentration. To examine the applicability of this method to protactinium solutions with higher concentrations than tracer level, the experiment was performed by using a 10^{-7} M protactinium solution and ^{231}Pa as a carrier. As Fig. 4 shows, the curve for 10^{-7} M protactinium coincides with that for carrier-free ^{233}Pa. Therefore, this method is applicable to protactinium solutions over a wide concentration range.

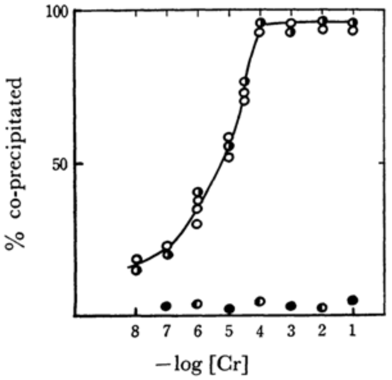

Fig. 4. Relation between concentration of chromium and % co-precipitated.

Pa(IV), ○ tracer concentration, ◑ 10^{-7} M
Pa(V), ● tracer concentration, ◐ 10^{-7} M

Recommended Procedure. From the above results, the following procedure is recommended for the separation of Pa(IV) and Pa(V). Five milliliters of a 0.02 M thorium chloride solution is added to 5 m*l* of a sample solution which has been made more acidic than 1 N. Thorium fluoride is then precipitated by the addition of 5 m*l* of a 0.2 M KF solution and separated from the supernatant liquid by centrifuging. The radioactivity of both phases is measured, and the percentages of Pa(IV) and Pa(V) is calculated.

The Stability of Pa(IV) in Dilute Perchloric Acid. The absorption spectrum and the stability of Pa(IV) in a perchloric acid solution was not examined in the previous paper, because the solubility of protactinium was too low ($<10^{-4}$ M) to make spectrophotometric measurements.

As one of the applications of the proposed method, the stability of Pa(IV) in a 1 M $HClO_4$ solution in an atmosphere of argon was, therefore, investigated. Protactinium was reduced by a liquid zinc amalgam in the presence of chromic ions and was stored in a stoppered cell for one day. The co-precipitation of protactinium with thorium fluoride was nearly complete. Therefore, it may be concluded that Pa(IV) is very stable in dilute perchloric acid in an atmosphere of argon.

Summary

1) The separation of Pa(IV) and Pa(V) was investigated using various co-precipitants which were insoluble in an acidic solution.

2) Among these co-precipitants, thorium fluoride was found to be the most useful co-precipitant, and the conditions for the separation of both valency states of protactinium were investigated in detail.

3) It was difficult to reduce Pa(V) completely on a tracer scale by means of a liquid zinc amalgam. When Cr(III) was added, however, the complete reduction of ^{233}Pa(V) was readily attained.

4) Cr(II) can not only reduce protactinium, but also hold it in the tetravalent state.

5) The stability of Pa(IV) in 1 M $HClO_4$ was investigated by the proposed method; it was found that Pa(IV) in the presence of Cr(II) was very stable.

The author wishes to thank Professor Hidehiro Goto, Professor Shin Suzuki and Dr. Yasushi Inoue for their kind and valuable advices throughout this study. A part of the expense has been defrayed by a grant-in-aid by the Ministry of Education.