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The Chemistry of Protactinium. IV. On the Absorption Spectra of Tetravalent Protactinium in Aqueous Solutions

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The liquid zinc amalgam method was developed as a rapid procedure for the reduction of pentavalent protactinium. Several minutes were sufficient for the complete reduction of 4.2×10^{-4} M pentavalent protactinium in both hydrochloric and sulfuric acid solutions. The stability of tetravalent protactinium in these media was investigated by spectrophotometry. Re-oxidation occurred gradually, even in the absence of atmospheric oxygen, and amounted to 8% in 15 hr. These results may be understood in terms of the slow rate of the ($2Pa^{4+}+2H^+ \rightleftarrows 2Pa^{5+}+H_2$) reaction. The formation of sulfato complexes of tetravalent protactinium was inferred by spectrophotometry with relation to the similarity of the electronic structure between $Pa^{4+}(5f^1)$ and $Ce^{3+}(4f^1)$.

In 1948, Haïssinsky and Bouissiéres first obtained a reduced form of protactinium in acid solutions by treating pentavalent protactinium with zinc amalgam, and suggested, on the bais of coprecipitation experiments, that it was tetravalent.[1,2] Since then, few papers have been

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[1] G. Bouissiéres and M. Haïssinsky, *Compt. rend.*, **226**, 573 (1948).

[2] G. Bouissiéres and M. Haïssinsky, *J. Chem. Soc.,* **1949**, S256.

reported on the tetravalent protactinium except for its absorption spectra, because of its instability in aqueous solutions.[3-8]

The purpose of this series of investigations is to establish a convenient procedure for the reduction of pentavalent protactinium and to elucidate the behavior of tetravalent protactinium in aqueous solutions by using the various methods available.

The absorption spectrum of tetravalent protactinium in a hydrochloric acid solution was first observed by Fried and Hindman, who obtained the solution by dissolving protactinium tetrachloride in 1 M hydrochloric acid.[3] Essentially the same spectra were observed by Brown and Wilkins, who obtained tetravalent protactinium by the complete reduction of pentavalent protactinium by the Jones reductor.[4,5] However, their procedures took six hours for a complete reduction and thus were inconvenient for investigating the behavior of tetravalent protactinium. Therefore, it is necessary to develop a rapid procedure for the reduction of pentavalent protactinium.

In this paper, the liquid zinc amalgam method was developed as a rapid procedure for the reduction of pentavalent protactinium, and the stability of tetravalent protactinium in aqueous solutions was investigated by spectrophotometry. The effects of the sulfate and chloride ion concentrations on the spectra of tetravalent protactinium were also investigated, and the possibility of the existence of sulfato and chloro complexes of tetravalent protactinium in aqueous solutions was discussed in relation to the similarity of the extranuclear structure between $Pa^{4+}(5f^1)$ and Ce^{3+} $(4f^1)$.

Experimental

Reagents. The long-lived ^{231}Pa which had been obtained from the Radiochemical Center, Amersham, England, was purified by the method reported by Suzuki and Inoue.[9] The chemical purity of the purified ^{231}Pa was confirmed by emission spectrophotography to be $>99.9\%$. The purified protactinium was dissolved into 1 M hydrofluoric acid and stored in a polyethylene vessel. The concentration of protactinium was determined by gravimetry as Pa_2O_5. Liquid zinc amalgam was prepared by heating 2 g of zinc and 100 g of mercury with dilute sulfuric acid (1 : 10) on a water bath for several hours.[10] All the other chemicals were of an analytical grade.

Apparatus. The reduction apparatus consists of three cells, A, B, and C, as is shown in Fig. 1. In the A cell, the protactinium solution is thoroughly deoxygenated by bubbling in argon gas. The B cell is for the reduction of pentavalent protactinium, The C cell is a 1 cm quartz spectrophotometer cell. A Hitachi EPS-3 recording spectrophotometer was used for the measurement of the absorption spectrum.

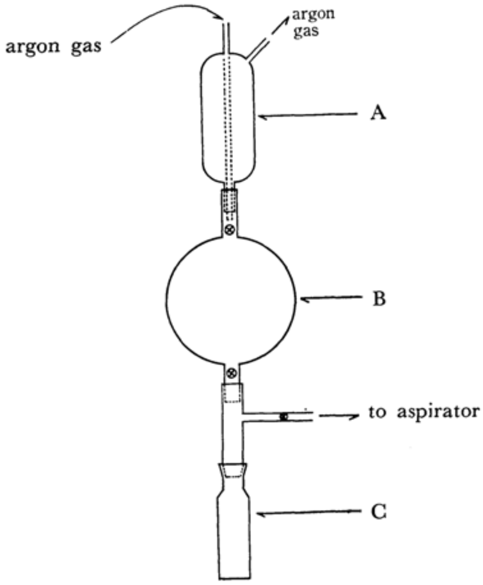

Fig. 1. Reduction apparatus.

Procedure. Protactinium hydroxide which had been precipitated from an aliquot of a stock solution was dissolved in an acid solution of the required concentration. This solution was then introduced into the A cell and thoroughly deoxygenated by bubbling in argon gas which had been passed through a dilute sulfuric acid solution of ammonium metavanadate. The deoxygenated solution was led to the B cell containing freshly-prepared liquid zic amalgam. The B cell was shaken for several minutes. The concentration of protactinium was 4.2×10^{-4} M throughout the experiment. After the reduction, the protactinium solution was put into the C cell, which had been preevacuated by an aspirator. This cell was disassembled from the reduction apparatus and was stoppered in an inert gas atmosphere. The absorption spectrum was immediately measured with reference to the acid solution of the same concentration as the sample.

Results and discussion

1) The Absorption Spectra of Tetravalent Protactinium in Hydrochloric Acid Solutions.

The absorption spectra obtained in 3.0 M and 11 M hydrochloric acid solutions are shown in

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3) S. Fried and J. C. Hindman, *J. Am. Chem. Soc.*, **76**, 4863 (1954).

4) D. Brown, A. J. Smith and R. G. Wilkins, *J. Chem. Soc.*, **1959**, 1463.

5) D. Brown and R. G. Wilkins, *ibid.*, **1961**, 3804.

6) R. Guillaumont, R. Muxart, G. Bouissiéres and M. Haïssinsky, *Compt. rend.*, **248**, 3298 (1959).

7) R. Guillaumont, R. Muxart, G. Bouissiéres and M. Haïssinsky, *J. chim. phys.*, **57**, 1019 (1960).

8) C. F. Miranda and R. Muxart, *Bull. soc. chim. France*, **1964**, 2174.

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

10) M. Ishibashi, Teiryōbunseki-jikkenhō (Practical Method of Gravimetric Analysis, ordinary volume), Fuzanbō Co., Tokyo (1953), p. 382.

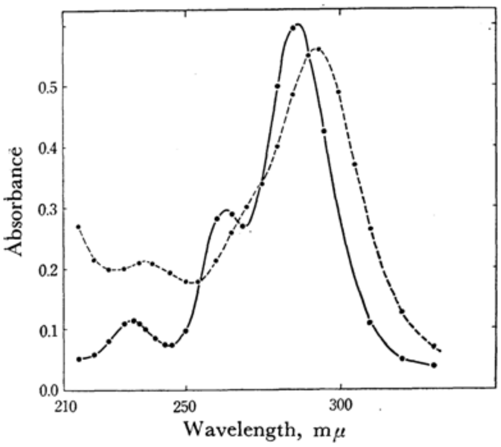

Fig. 2. Absorption spectra of Pa^{4+} in hydrochloric acid.
—— 3.0 M HCl, ---- 11 M HCl

Table 1. Absorption maxima of Pa(IV) in HCl

HCl (M)	λ_1	λ_2	λ_3 (mμ)
1.2	233	263	287
3.0	233	263	287
6.0	233	263	287
11	—	disapp.	293
*1.0	225	256	277
1.2 M H^+-3.6 M Cl^-	233	263	287
*1.5 M $HClO_4$	225	256	277

* Obtained by Brown and Wilkins.[5]

Fig. 2. These spectra are in general agreement with the results of Brown and Wilkins,[5] but the absorption maxima are somewhat different, as is shown in Table 1. The absorption spectra obtained in the hydrochloric acid solution from 1.2 M to 6.0 M are nearly identical, whereas a marked change is observed in the concentrated hydrochloric acid; the peak at 287 mμ is shifted to 293 mμ, and the peak at 263 mμ disappears and is replaced by a shoulder. The spectrum of Ce^{3+} is also remarkably changed in the concentrated hydrochloric acid, as Fig. 3 shows. The absorption maxima of Ce^{3+} in hydrochloric acid solutions and in perchloric acid solutions are listed in Tables 2 and 3 respectively. From these data it is considered that chloro complexes exist in the concentrated hydrochloric acid solution. As the solubility of protactinium is very small in perchloric acid ($<10^{-4}$ M), the spectrum of tetravalent protactinium in this medium can not be observed. In order to verify the formation of chloro complexes, the effect of chloride ion concentrations from 1.2 M to 3.6 M, at 1.2 M acidity, on the absorption spectra was investigated; we found that the spectra was little affected. Nor were the effects of the chloride ion concentration on the spectra of Ce^{3+} affected, as is shown in Table 2. These results may well be understood in terms of the general behavior of rare earths, which are reluctant to form chloro complexes in dilute hydrochloric acid solutions. Thus, it is natural to consider, from these results, that tetravalent protactinium is also reluctant to form chloro complexes in hydrochloric acid solutions more dilute than 3 M.

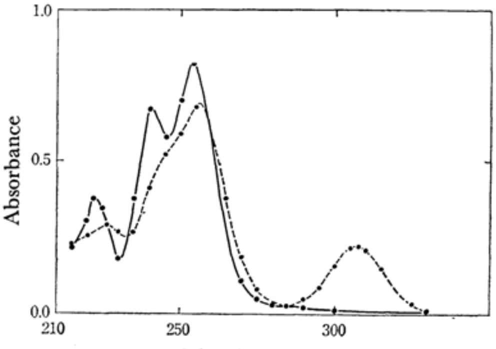

Fig. 3. Absorption spectra of Ce^{3+} in hydrochloric acid.
—— 1.2 M HCl, ---- 11 M HCl

Table 2. Absorption maxima of Ce^{3+} in HCl

HCl (M)	λ_1	λ_2	λ_3 (mμ)
0.12	223	240	254
1.2	223	240	254
3.0	223.5	240.5	254
6.0	223.5	240.5	254.5
8.0	224	242	255
11	226	disapp.	256
0.24 M H^+— 2.6 M Cl	223	240	254

Table 3. Absorption maxima of Ce^{3+} in $HClO_4$

HCl_4 (M)	λ_1	λ_2	λ_3 (mμ)
2.6	223	240	254
5.3	223	240	254
10.6	223	240	254

When the reduction is carried out in hydrochloric acid, it is necessary to note that the peak of the chloro complex of mercury, which appears at 222 mμ, overlaps the peak of tetravalent protactinium at 233 mμ. The intensity of this interfering spectrum increases both with the time and with an increase in the concentration of hydrochloric acid, as is shown in Fig. 4. Therefore, to obtain a well-defined spectrum of tetravalent protactinium, it is necessary to carry out reduction and absorption measurements as quickely as possible.

It has been reported by some investigators that

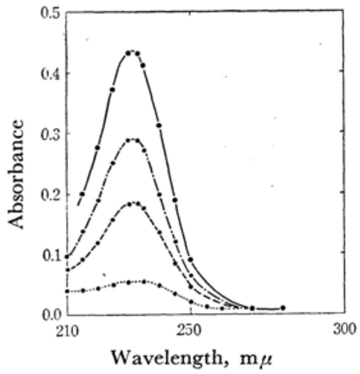

Fig. 4. Effect of time of standing on the absorption spectra of mercury in 1 M HCl.

Table 4. Absorption maxima of Pa^{4+} in H_2SO_4

H_2SO_4 (M)	λ_1	λ_2	λ_3 (mμ)
0.05	234	266	289
0.5	234	266	289
1.8	234	267	289
3.6	235	268	290
6.0	236	270	294
9.0	237	273	297

Table 5. Effects of SO_4^{2-} on the absorption maxima of Pa^{4+} at 1.2 M H^+

SO_4^{2-} (M)	λ_1	λ_2	λ_3 (mμ)
0.6	233	266	289
1.8	237	272	295
3.0	240	disapp.	300

Table 6. Absorption maxima of Ce^{3+} in H_2SO_4

H_2SO_4 (M)	λ_1	λ_2	λ_3 (mμ)
0.05	224	242	255
0.5	224	242	255
4.5	224	242	255
6.0	225	242.5	255.5
9.0	225.5	243	258

Table 7a. Effect of H^+ concentration on the absorption maxima of Ce^{3+} (SO_4^{2-} 0.6 M)

H^+ (M)	λ_1	λ_2	λ_3 (mμ)
1.2	224	242	255
5.4	224	242	255
9.7	224	242	255

Table 7b. Effect of SO_4^{2-} concentration on the absorption maxima of Ce^{3+} (H^+ 1.2 M)

SO_4^{2-} (M)	λ_1	λ_2	λ_3 (mμ)
0.6	224	242	255
1.8	225	243	256
3.0	226	245	258

the reduction was incomplete in the concentrated hydrochloric acid.[6,7] However, pentavalent protactinium in concentrated hydrochloric acid was completely reduced by this procedure; the peak of pentavalent protactinium was not observed in the freshly-reduced solution. This discrepancy may be due to the fact that the observation of the Pa(IV) spectrum by the previous investigator was not reliable enough to check the reduction because the interference by mercury was too remarkable for the absorption band of tetravalent protactinium to be measured precisely. However, the reduction in hydrochloric acid less than 6 M was complete without any doubt. The molar extinction coefficients, ε_m, at 233 mμ, 263 mμ, and 287 mμ were 310, 730, and 1470 respectively.

2) The Absorption Spectra of Tetravalent Protactinium in Sulfuric Acid Solutions. As in hydrochloric acid, the reduction was carried out for several minutes and was nearly complete in the sulfuric acid less than 6 M, since the spectra of pentavalent protactinium were not observed. The absorption band of mercury was not observed even in 9 M sulfuric acid. The absorption maxima obtained in sulfuric acid of various concentrations are listed in Table 4. These data are in good agreement with the results of Brown and Wilkins.[5] The absorption maxima are affected by the sulfuric acid concentration. In order to verify the existence of sulfato complexes of tetravalent protactinium in dilute sulfuric acid, the effect of the sulfate ion concentration on the spectrum of tetravalent protactinium was investigated at a 1.2 M hydrogen ion concentration. As Table 5 shows, the absorption maxima are remarkably affected by the sulfate ion concentration from 0.6 M to 3.0 M. In the same experiments, the spectra of Ce^{3+} were also affected by the sulfate ion concentration, as is shown in Tables 6 and 7, but the hydrogen ion concentration affected the spectra only a little as is shown in Table 7a. Thus, the effect of the sulfuric acid concentration on the spectrum is attributable to the change in the sulfate ion concentration. As it has been reported by Fronaeus that the mono, di, and tri-sulfate complexes of Ce^{3+} exist,[11] it is apparent that tetravalent protactinium also forms sulfate complexes.

3) The Stability of Tetravalent Protactinium in an Aqueous Solution. Complete re-oxidation occurred within 4 hr if the solution in a spectrophotometer cell was exposed to air. When tetravalent protactinium was stored in a stoppered cell, it was more stable both in hydrochloric and sulfuric acid; that is, in hydrochloric acid solution 8% of tetravalent protactinium was re-oxidized in 15 hr after the preparation, while in a sulfuric acid solution it was even more stable.

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[11] S. Fronaeus, *Svensk Kem. Tidskr.*, **64**, 317 (1952).

Haïssinsky and Pluchet reported the oxidation-reduction potential of the Pa(IV)-Pa(V) pair in 6 M hydrochloric acid to be -0.29 ± 0.03 V.[12] When H_2O reacts as a oxidant $(2H^+ + 2e^- \rightleftarrows H_2)$, the oxidation-reduction potential is equal to -0.06pH at 1 atm of hydrogen gas.[13] Therefore, H_2O probably reacts with Pa^{4+} and oxidizes to Pa^{5+} by the $(2Pa^{4+} + 2H^+ \rightleftarrows 2Pa^{5+} + H_2{}^-)$ reaction. The slow rate of oxidation is attributable to the slow rate of attaining the oxidation-reduction equilibrium of the H^+-H_2 couple. Thus, it is obvious that tetravalent protactinium in both hydrochloric acid and sulfuric acid is stable enough for experiments to be done without suffering from the effect of re-oxidation, if the experiments are carried out within a few hours in an atmosphere of argon.

Summary

1) Several minutes were sufficient to reduce 4.2×10^{-4} M pentavalent protactinium completely by the liquid zinc amalgam method in either hydrochloric or sulfuric acid.

2) In hydrochloric acid, λ_{max} appeared at 233 mμ, 263 mμ, and 287 mμ, and the molar extinction coefficients, ε_m, were 310, 730, and 1470 respectively. Since the chloride ion concentration had little effect on the spectra of tetravalent protactinium, it was inferred that tetravalent protactinium, much like Ce^{3+}, was reluctant to form chloro complexes.

3) At sulfuric acid concentrations of less than 3.6 M, three absorption maxima were observed, at 234 mμ, 267 mμ, and 289 mμ. In sulfuric acid concentrations of more than 3.6 M, the absorption maxima were shifted to a longer wavelength with an increase in the concentration of sulfuric acid. Since the sulfate ion concentration remarkably affected the spectra of tetravalent protactinium, it was inferred that sulfato complexes of tetravalent protactinium existed.

4) The re-oxidation percentage of tetravalent protactinium in a stoppered spectrophotometer cell was 8% in 15 hr; therefore, it was thought that the $(2Pa^{4+} + 2H^+ \rightleftarrows 2Pa^{5+} + H_2)$ reaction proceeded very slowly. Teteravalent protactinium was stable enough for experiments to be done without suffering from the effect of re-oxidation if the experiments are carried out within a few hours in an atmosphere of argon.

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.

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

[13] G. Charlot, "L'analyse qualitative et les reactions en solution," Masson et Cie, Paris (1957), p. 21.