737. *Further Observations on the Absorption Spectra of Protactinium-*(IV) *and* -(V) *in Certain Solutions.**

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The absorption spectra of protactinium(IV) in various mineral acids are described and their significance is discussed. The solubility and spectra of protactinium pentachloride in certain organic solvents are investigated.

SEVERAL publications have appeared since the earlier work of Elson [1] on the absorption spectra of protactinium(V) and protactinium(IV) in acid media. The spectra of protactinium(V) in hydrochloric acid have been thoroughly examined and interpreted.[2,3,4] The spectrum of protactinium(IV) in hydrochloric acid was first obtained by Fried and Hindman [5] who dissolved protactinium tetrachloride in M-hydrochloric acid. Essentially the same spectrum was obtained by complete reduction of protactinium(V) by zinc amalgam in hydrochloric acid.[3] More recently the spectra of protactinium(V) and of protactinium(IV), containing small amounts of protactinium(V), in hydrochloric and other acids have been described.[4]

We report now the spectra of protactinium(IV) in hydrobromic, sulphuric, and perchloric acid and some isolated observations on solutions of solid protactinium pentachloride in certain organic solvents.

EXPERIMENTAL

Materials.—The long-lived α-active ^{231}Pa was used. The concentration of protactinium was determined by radioassay in an argon gas-flow proportional counter. Protactinium was purified by a method, simpler and more quantitative than that previously described,[3] and based on results obtained by Goble *et al.*[6] The addition of anhydrous aluminium chloride to a hydrochloric-hydrofluoric acid solution containing protactinium(V) allowed extraction by isobutyl methyl ketone from which protactinium was removed again by a similar mixed acid. After several cycles, silica was removed by evaporation with hydrogen fluoride in a platinum crucible, and protactinium was precipitated from 20M-hydrofluoric acid as potassium fluoroprotactinate. This solid was dissolved, with a small amount of aluminium trichloride, in 6M-nitric acid, extracted into isobutyl methyl ketone, and removed therefrom into dilute hydrofluoric acid. Finally protactinium(V) hydroxide was precipitated and either dissolved in the required acid or used as the starting material for the preparation of protactinium pentachloride.[7] Reduction of this with hydrogen produced tetrachloride.[5,7] For more details see ref. 3*b*.

Benzene, methanol, and acids were of "AnalaR" grade. Benzene and tetrahydrofuran were dried by sodium, and anhydrous methanol was obtained by Lund and Bjerrum's method.[8] Thenoyltrifluoroacetone was distilled twice *in vacuo* before use, and isobutyl methyl ketone was distilled once.

Reduction and Spectral Experiments.—Stock solutions of protactinium(V) in sulphuric acid (2 mg./c.c.) were diluted as required and reduced with zinc amalgam as described previously.[3] Protactinium(V) hydroxide was only sparingly soluble in 8M-hydrobromic acid ($\sim$8·0 × 10^{-5}M), and solutions were reduced immediately after preparation to prevent hydrolysis. The solubility of protactinium hydroxide in 6M-perchloric acid was very small [4] (about 2 × 10^{-3} mg./c.c.)

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[1] Elson, "The Chemistry of Protactinium," in "The Actinide Elements," ed. Seaborg and Katz (National Nuclear Energy Series), McGraw-Hill, New York, 1954, p. 125.

[2] Casey and Maddock, *J. Inorg. Nuclear Chem.*, 1959, **10**, 58.

[3] (*a*) Brown, Smith, and Wilkins, *J.*, 1959, 1463; (*b*) Brown, Ph.D. Thesis, Sheffield, 1960.

[4] Guillaumont, Muxart, Bouissières, and Haissinsky, *Compt. rend.*, 1959, **248**, 3298; *J. Chim. phys.*, 1960, **57**, 1019.

[5] Fried and Hindman, *J. Amer. Chem. Soc.*, 1954, **76**, 4863.

[6] Goble, Golden, Maddock, and Toms, "Progress in Nuclear Energy," Series III, Vol. II, "Process Chemistry," Pergamon, London, 1958, p. 86.

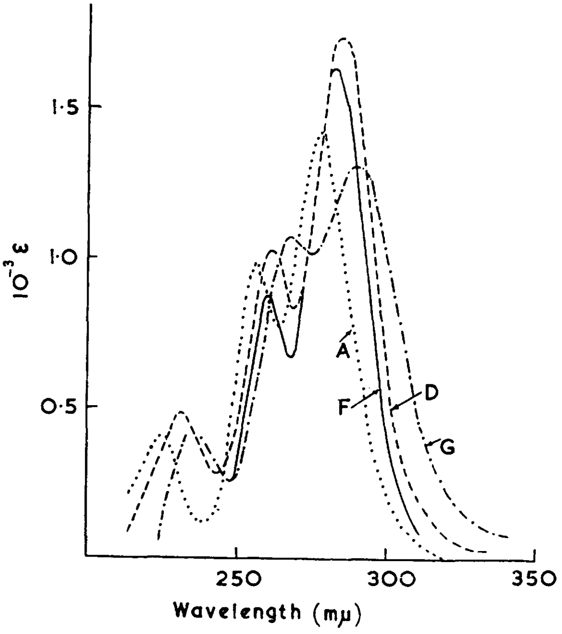
[7] Sellers, Fried, Elson, and Zachariasen, *J. Amer. Chem. Soc.*, 1954, **76**, 5935.

[8] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

and such solutions would not give sufficient absorption after reduction. Attempts to reduce a suspension of the hydroxide in 6M-perchloric acid were unsuccessful. Consequently the tetrachloride was dissolved in oxygen-free perchloric acid. Oxygen was removed from perchloric acid by a stream of nitrogen which had been passed through a solution of chromous chloride and dried with phosphorus pentoxide. Samples of the tetrachloride (in small capillary tubes) were dissolved in 1·0M- and 11·0M-hydrochloric acid. Cells were filled in an atmosphere of argon or nitrogen.[3] All controls for spectral work were treated in an identical manner to those containing protactinium, and the spectra were measured with 2 cm. matched stoppered quartz cells in a Unicam S.P. 500 spectrophotometer.

RESULTS AND DISCUSSION

The spectra of protactinium(IV) in solutions of various acids are reproduced in the Figure. In the Table are listed the peak positions for protactinium(IV) in different media.



Ultraviolet absorption spectra of protactinium(IV) *solutions.*

A, D, F, G: *see Table.*

Solvent	$\lambda_{max.}$ (mμ)	Solvent	$\lambda_{max.}$ (mμ)
A, 1·5M-$HClO_4$	225, 256, 277	E, 11·0M-HCl	— —[b] 293
B, 1·0M-HCl	225, 256, 277	F, 8·0M-Br^- (5·6M-H^+)	—[c] 260, 282
C, 1·0M-HCl[a]	224, 255, 276	G, 3·0M-SO_4^{2-} (4·4M-H^+)	235, 267, 289
D, 7·0M-Cl^- (1·7M-H^+)	229, 260, 282		

[a] Ref. 5. [b] Obscured by protactinium(V) produced by traces of oxygen. [c] This peak was not observable because of high absorption of bromide ion below 250 mμ.

As with hydrochloric acid,[3] complete reduction to the lower valency state occurs in hydrobromic and sulphuric acid, provided freshly prepared solutions of protactinium(V) in relatively high acidity are in contact with zinc amalgam for about 6 hours. It is difficult then to understand the incomplete reduction observed in high concentrations of sulphuric and hydrochloric acid;[4] only two maxima for protactinium(IV) were reported, the third, at lowest wavelengths, being obscured by absorption due to protactinium(V).

Re-oxidation is observed when protactinium(IV) in sulphuric acid is stored in sealed cells. This can be estimated as ~10% in three days, from the increased optical density below 220 mμ. Complete oxidation occurs within two hours if the solutions are exposed to the atmosphere. In contrast to the behaviour in hydrochloric acid solutions,[3] the spectra of the re-oxidised solutions from different experiments are similar and resemble that of protactinium(V) in sulphuric acid with a peak at 215 mμ and a slight inflection around 290 mμ.[9]

A sufficient concentration of protactinium(IV) in perchloric acid could only be obtained by dissolving protactinium tetrachloride in 1·5M-perchloric acid, in which it is readily soluble. Re-oxidation takes place when the solutions are stored overnight in sealed cells, and more quickly when exposed to the atmosphere. The protactinium(V) perchlorate produced is rapidly hydrolysed and settles as a white solid.

The close similarity between the spectra of protactinium tetrachloride in dilute perchloric and hydrochloric acid solutions, and in the values for the molar extinction coefficients at the maxima, suggests that the same species may exist in both solutions. This may be $PaCl_4$ or *lower* chloride complexes or even the non-complexed $\text{Pa}^{\text{IV}}_{\text{aq.}}$, since the chloride concentration in the perchloric acid cannot much exceed 10^{-3}M. However, this criterion of identical spectra must not be forced, since although the spectra of uranium(IV) [10] and plutonium(IV) [11] in dilute hydrochloric acid do not differ noticeably from those in perchloric acid, there is clear evidence for complexing of uranium(IV) [12] and plutonium(IV) [13] by chloride ions. The displacement of spectral maxima at higher chloride concentrations, in bromide and especially in sulphate media (see Table), does, however, constitute definite evidence for complex-formation between protactinium(IV) and these anions. An attempt was made to examine the ion-exchange behaviour of protactinium(IV) in sulphuric acid.[3b] Because of the scarcity of material, we had to use 3×10^{-5}M-protactinium(IV) solutions, and in this dilution we found that re-oxidation occurred on contact with the resin, even if the latter was especially treated to remove traces of oxygen.

Protactinium pentachloride dissolves readily in anhydrous and aqueous methanol, to give a stable colourless solution. No spectral changes * or loss of protactinium from a 9×10^{-5}M-solution were detected during three weeks. The solubility in methanol has been used by Flegenheimer [14] in his analysis of protactinium pentachloride. The solutions probably contain a stable methoxide. The solutions of protactinium pentachloride in tetrahydrofuran (6×10^{-5}M) are colourless (ε at max. 232 mμ $= 1{\cdot}16 \times 10^4$) and the spectrum shows little change during three days provided the solutions are stored in a sealed cell. A stable complex must be formed in these solutions, since addition of thenoyltrifluoroacetone produces no yellow colour (see below). If the solutions are left in open vessels, however, hydrolysis and deposition of protactinium(V) occur rapidly.

The intense yellow colour of the complex formed between protactinium(V) and thenoyltrifluoroacetone has been repeatedly observed during the extraction of protactinium(V) from hydrochloric acid solutions.[3b] The spectrum of a solution of protactinium pentachloride ($\sim 10^{-5}$M) in 0·1M-solutions of thenoyltrifluoroacetone in benzene has a peak at 414 mμ (ε $1{\cdot}55 \times 10^4$). Such solutions obey Beer's law at this wavelength, but the absorption is unlikely to be analytically valuable for the estimation of protactinium(V) since many metal–thenoyltrifluoroacetone complexes absorb strongly around 400 mμ.[15] Observations at wavelengths lower than this are prevented by the absorption of thenoyltrifluoroacetone in benzene.

* A solution of protactinium pentachloride in anhydrous methanol absorbs significantly only below 305 mμ. There is no peak to our limit of observation (225 mμ), values of ε here being $\sim 10^4$.

[9] Brown, Sato, Smith, and Wilkins, *J. Inorg. Nuclear Chem.*, in the press.

[10] Hoekstra and Katz, "The Chemistry of Uranium," in "The Actinide Elements," ed. Seaborg and Katz, McGraw-Hill, New York, 1954, p. 163.

[11] Hindman, as ref. 10, p. 337.

[12] Kraus and Nelson, *J. Amer. Chem. Soc.*, 1950, **72**, 3901.

[13] Rabideau, *J. Amer. Chem. Soc.*, 1956, **78**, 2705.

[14] Flegenheimer, Ph.D. Thesis, Cambridge, 1959.

[15] Khopkar and De, *Chem. and Ind.*, 1959, 291, 854.

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