284. *Spectra of Protactinium-*(IV) *and* -(V) *in Hydrochloric Acid.*

By D. BROWN, A. J. SMITH, and R. G. WILKINS.

Spectral changes occurring when protactinium(V) is reduced by zinc amalgam are noted.

As a preliminary to proposed studies of electron transfer between protactinium-(IV) and -(V), it was necessary to investigate the reduction of the latter in acid solution. Haissinsky and Bouissières [1] first obtained a reduced form of protactinium in acid solution by treating protactinium(V) with reducing agents, particularly zinc amalgam, and from co-precipitation experiments suggested it was protactinium(IV). Later they [2] investigated the behaviour of the reduced state towards various reagents (its most striking and distinguishing feature being the insolubility of the fluoride) and from oxidations with cerium(IV) confirmed that the reduced form was protactinium(IV). The most recent investigation [3] of protactinium(IV) in solution has been concerned with its solvent-extraction behaviour and, in particular, it was shown that Pa^{IV}, unlike Pa^{V}, was not extracted into isobutyl methyl ketone from 6M-hydrochloric acid.

Several solid protactinium(IV) compounds have been prepared [4] and the spectrum of a

---

[1] Haissinsky and Bouissières, *Compt. rend.*, 1948, **226**, 573; *J.*, 1949, S256.
[2] Haissinsky and Bouissières, *Bull. Soc. chim. France*, 1951, 146.
[3] Haissinsky and Bouissières, *Compt. rend.*, 1957, **244**, 573.
[4] Sellers, Fried, Elson, and Zachariasen, *J. Amer. Chem. Soc.*, 1954, **76**, 5935.

solution from solid protactinium tetrachloride (in 1M-hydrochloric acid) has been examined.[5] We now report the conditions for complete zinc amalgam reduction of Pa^{V}, and the spectrum of the product, so as to compare it with that obtained by direct methods.[5] Preliminary experiments on the spectra of reduced protactinium in sulphuric and perchloric acids have been reported.[6]

EXPERIMENTAL

Materials.—The naturally-occurring α-active ^{231}Pa was used. The concentration of protactinium was determined by radio-assay in an argon gas-flow proportional counter, and the samples were mounted on tantalum trays. Protactinium was purified from its daughter elements before a set of experiments by extraction of Pa from 7M-hydrochloric acid by di-isopropyl ketone [7] followed by stripping into 6M-hydrochloric acid containing 0·2M-hydrofluoric acid. The radiochemical purity of the product was confirmed as $\geqslant 99\%$ by α-pulse analysis. Protactinium was further purified from other elements present such as niobium, aluminium, and iron, indicated by spectrography. The addition of anhydrous aluminium chloride to the HCl–HF solution allowed the extraction of protactinium into 0·5M-thenoyltrifluoroacetone in benzene. More than 85% of Pa was thus extracted and re-stripped into 6M-hydrochloric–0·2M-hydrofluoric acid solution. After addition of more aluminium chloride, the protactinium was re-extracted into fresh thenoyltrifluoroacetone in benzene, and after repeated washing of this extract with 6M-hydrochloric acid, was stripped into 0·2M-oxalic acid solution and precipitated by the addition of ammonia. The precipitate was quickly dissolved in cold concentrated hydrochloric acid to form the stock solution for the experiments. The second extraction with thenoyltrifluoroacetone ensures the complete elimination of iron(III) as shown by the absence of an absorption band around 360 mμ. Spectroscopic analysis of the final product showed the absence of other elements likely to interfere in the spectral study. Polythene apparatus was used in this work.

Thenoyltrifluoroacetone was distilled twice *in vacuo* before use, and di-isopropyl ketone distilled once. The other materials used were " AnalaR," where possible.

Reduction and Spectral Experiments.—The spectrum of protactinium(V) was examined in different molarities of hydrochloric acid, by dilution of the stock solution, shortly after it had been prepared as described above. All spectra were measured on a Unicam S.P. 500 spectrophotometer. Freshly prepared zinc amalgam (from " AnalaR " zinc shot) was used for reduction, which was carried out in an atmosphere of argon. At the end the protactinium solution was run into a spectrophotometer cell in an argon atmosphere and the cell was stoppered without exposure of the solution to the air. The effectiveness with which oxygen was excluded during these operations was confirmed by preparing 10^{-3}M-chromium(II) in the apparatus and noting the absence of absorption by chromium(III) from the final solution. For the measurement of spectra of protactinium(IV), a " blank " was prepared. Although there is strong absorption by mercury chloride complexes below 250 mμ, there are only small differences in absorption between two identically run blanks and from this, and the appearance of the final protactinium(IV) spectra, we conclude that the error introduced by the production of optically absorbing complexes during the reduction is small. All manipulations with protactinium were performed in a fume-cupboard and stringent precautions taken to avoid the spread of contamination.

RESULTS AND DISCUSSION

The spectra of protactinium(V) in hydrochloric acid of different molarities are reproduced in Fig. 1. The work was almost completed before we learnt from Dr. A. G. Maddock that this system had been studied in more detail at the University Chemical Laboratories, Cambridge.[8] Where our results overlap, in general good agreement is found. In hydrochloric acid above 6M, one absorption band only is obtained (213 mμ) and although there are semblances of bands at around 260 mμ and 300 mμ these only develop at lower acidities.

---

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

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

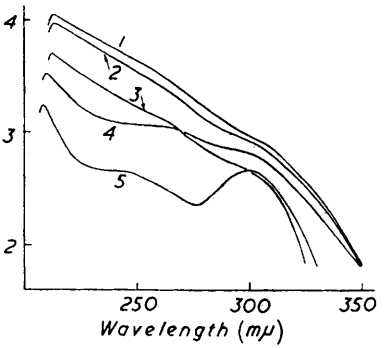
[7] Golden and Maddock, *J. Inorg. Nuclear Chem.*, 1956, **2**, 46.

[8] Casey and Maddock, *ibid.*, to be published.

In 1·7M-hydrochloric acid there is a definite peak at 300 mμ, although in some solutions (at this acidity), because of the onset of hydrolysis and the appearance of a peak at 262 mμ, it appears only as a flattening and is not as pronounced as shown in Fig. 1. Like Casey and Maddock [8] we observe considerable spectral changes with time; for example, the peak at 300 mμ in 1·7M-hydrochloric acid disappears within a few hours and a strong peak at 262 mμ develops. The latter has been noted as characteristic of protactinium(V) in all acidities and is associated with the onset of hydrolysis which is accompanied by the disappearance of solvent extractability.[8]

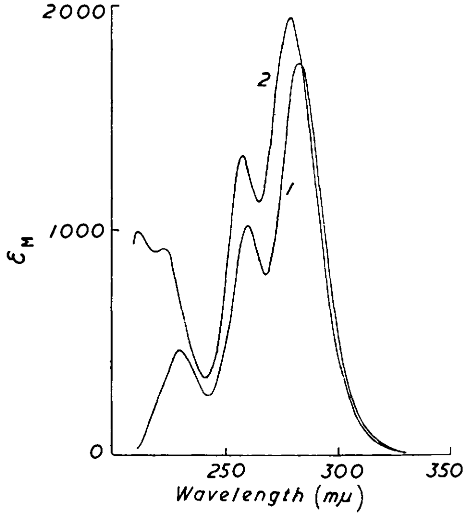
The spectra of the products from the reduction experiments are shown in Fig. 2. The intense absorption band of protactinium(V) at 213 mμ is of great assistance in determining the conditions for complete reduction. We have always obtained incomplete reduction (curve 2) even with six hours' reduction if we commence with 4M-hydrochloric acid solutions. Provided, however, that the solution is at least 6M in hydrochloric acid at the commencement of reduction (it will finish at about 2M) then 5—6 hours is sufficient to complete the reduction of 10^{-4}M-protactinium(V) solutions (curve 1). We ascribe the incomplete reduction of protactinium at lower starting acidities to the presence of colloidal protactinium,[9] which defies easy reduction. The spectrum of protactinium(IV) shows lower optical absorption than protactinium(V), with the development of peaks at 229, 260, and 282 mμ with ε_M values of 470, 1010, and 1730 respectively. The general form of the absorption spectrum resembled closely that obtained by Fried and Hindman [5] by the dissolution of protactinium tetrachloride in M-hydrochloric acid, who report absorption (ε_M) and peak values of 425 (224 mμ), 980 (255 mμ), and 1520 (276 mμ). In fact the absorption curve is modified surprisingly little when it is remembered that our solutions are 1·7M in H^+ and 7M in Cl^-. In other experiments we find that the protactinium(IV) peaks are little affected in height or position by acidity changes from 1 to 3M at 6M-chloride-ion concentration.

FIG. 1. *Absorption spectra of protactinium*(V) *in hydrochloric acid.*



All solutions 0·0375mM in ^{231}Pa. HCl: 1, 11·1M; 2, 8·40M; 3, 5·83M; 4, 3·45M; 5, 1·7M.

FIG. 2. *Absorption spectra of protactinium*(IV) *in hydrochloric acid.*



1. Pa^{IV}: 0·133mM-^{231}Pa with 1·7M-H^+ and 7M-Cl^-. Initially Pa^{V} in 7M-HCl; reduction period 6 hr. 2. Pa^{V}–Pa^{IV} mixture, 0·178mM in ^{231}Pa, with 1·6M-H^+ and 4M-Cl^-. Initially Pa^{V} in 4M-HCl; reduction period 6 hr.

When the solutions stand in air for about 1 hr., the three protactinium(IV) peaks

---

[9] Maddock and Miles, *J.*, 1949, S248.

disappear. The new spectra are not very reproducible and change with time as might be expected from the behaviour of the original protactinium(v). However the dominance of the 213 mμ peak has disappeared in the reoxidised solution and peaks at 213 mμ and 230 mμ are obtained which slowly become one peak at 230 mμ. We propose to examine the spectra of protactinium(v) and the reduced product in other acids.

We thank Mr. H. A. C. McKay, Dr. L. E. J. Roberts, and others at the Atomic Energy Research Establishment, Harwell, for help, the Authority for a grant and maintenance grant (to D. B.), and Dr. A. G. Maddock for information.

SHEFFIELD UNIVERSITY. [*Received, December 2nd,* 1958.]