

Conversion of Protactinium Monocarbide to the Penta- and Tetra-halides

By David Brown,* Giovanni De Paoli, and Brian Whittaker, Chemistry Division, A.E.R.E., Harwell, Oxon OX11 0RA

Protactinium monocarbide has been prepared by carbothermic reduction of the pentaoxide. It reacts with iodine (400 °C), bromine (350 °C), and thionyl chloride (200 °C) in evacuated sealed vessels to yield the appropriate pentahalide. The tetraiodide, PaI_4 , is obtained by interaction of the monocarbide with either protactinium penta-iodide (600 °C) or mercury(II) iodide (500 °C) *in vacuo*. X-Ray powder-diffraction results and vibrational spectral data are reported for the halides.

ALTHOUGH protactinium penta-iodide has been prepared by a variety of reactions,¹ the only satisfactory ones, in the absence of protactinium metal, involve halogen exchange between the pentachloride or pentabromide and silicon tetraiodide. Similarly, the easiest route to the pentabromide is to treat the pentachloride with refluxing boron tribromide,² alternative reactions involving the pentaoxide³ being much less satisfactory. The obvious choice of starting material for the preparation of protactinium halides is the metal, but until recently only

milligram amounts have been prepared. Current work at both Harwell⁴ and Karlsruhe⁵ has indicated that this situation should shortly be remedied. Thus, using a modified Van Arkel technique with protactinium monocarbide and iodine individual batches of up to 0.2 g have been prepared.

The monocarbide is relatively easy to prepare and, since it is an intermediate for the currently most satisfactory route to the metal and the preparation of the latter involves further special apparatus and techniques, we have investigated the direct conversion of the mono-

¹ D. Brown, J. F. Easey, and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 1698.

² D. Brown, J. Hill, and C. E. F. Rickard, *J. Chem. Soc. (A)*, 1970, 476.

³ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 262.

⁴ D. Brown and B. Whittaker, unpublished work.

⁵ W. Müller and M. Bohet, unpublished work.

carbide into protactinium halides. Our results indicate that it is an excellent starting material for the preparation of the pentahalides (PaX_5 ; $\text{X} = \text{Cl}, \text{Br}, \text{and I}$) and that it will prove useful in the reduction of these compounds to tetrahalides.

RESULTS AND DISCUSSION

The only report concerning the preparation of protactinium carbides is that of Lorenz *et al.*⁶ who reduced the pentaoxide using an excess of carbon at temperatures of up to 2 200 °C. Using a similar technique we have obtained the monocarbide mixed with excess of carbon at 1 700 °C. The true composition of this material, confirmed by ignition to the pentaoxide, is 'PaC·3.4C'. X-Ray powder studies showed only the presence of the face-centred-cubic phase expected for the monocarbide by analogy with other actinoid carbides, and for convenience we shall refer to this material as protactinium monocarbide. Our unit-cell dimension, $a_0 = 5.060 \pm 0.002$ Å, is in excellent agreement with the published value. No attempt was made to obtain other carbides since we were primarily interested in the chemical reactions of the monocarbide. It is an air-stable material which is converted smoothly into the pentaoxide as the temperature is raised slowly to 750 °C in the atmosphere.

The reaction between the monocarbide and an excess of iodine at 350–400 °C in an evacuated sealed silica tube yields protactinium pentaiodide. A double-furnace technique similar to that used for the preparation of UI_4 ⁷ was employed. The carbide was heated at 350 °C for several hours with the cooler end of the tube at 180–200 °C to maintain an adequate vapour pressure of iodine. The product was isolated in high yield by vacuum sublimation (10^{-4} mmHg) at *ca.* 350 °C.* The reaction, which is simpler than those involving halogen exchange and far superior to any involving the pentaoxide, is suitable for the preparation of gram amounts of the pentaiodide.

When stoichiometric amounts of protactinium monocarbide and pentaiodide (1 : 4 mol ratio) were heated in an evacuated tube completely enclosed in a furnace at 600 °C the product was the dark green tetraiodide which was isolated by vacuum sublimation at *ca.* 450 °C. Attempts to obtain PaI_3 by increasing the amount of monocarbide and heating the mixture at 600 °C for several hours were unsuccessful, the product again being the tetraiodide. The same product was also obtained when the monocarbide was heated with a deficiency of mercury(II) iodide *in vacuo*. The temperature was increased and held at 500 °C for several hours when the tetraiodide deposited as crystals in the centre of the tube. No evidence for the formation of the tri-iodide was found on X-ray powder-diffraction analysis of the carbide–

* 1 mmHg $\approx 13.6 \times 9.8$ Pa, 1 Torr = (101 325/760) Pa, 1 ton ≈ 1.02 Mg.

⁶ R. Lorenz, H. L. Scherff, and N. Toussaint, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2381.

⁷ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.*, 1965, 350.

⁸ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 719.

carbon residue. A small quantity (*ca.* 1%) of PaI_2O was formed in this reaction.

Protactinium tetraiodide has previously been prepared by reduction of the pentaiodide using aluminium.⁸ The PaC– PaI_5 reaction is more attractive since it does not involve the introduction of another element. Reactions involving reduction of the pentaiodide with resublimed zinc have proved unsatisfactory. Thus, at 500–550 °C the product was mainly the pink di-iodide oxide, PaI_2O , whilst even at 410 °C a dark mirror formed along most of the length of the tube, resulting in a low yield of the tetraiodide mixed with ZnI_2 . The problem appears to be the low melting point of zinc (419.5 °C), although the extensive formation of PaI_2O at 550 °C is not fully understood since the tetraiodide is stable when heated to 800 °C in a sealed evacuated silica tube.

Protactinium monocarbide is unreactive towards refluxing thionyl chloride, refluxing boron tribromide, and bromine at room temperature. However, conversion into PaCl_5 is readily achieved when the carbide is heated at 200–250 °C in SOCl_2 vapour using apparatus similar to that described earlier³ for the $\text{Pa}_2\text{O}_5/\text{C}$ –bromine reaction. Trace amounts of adsorbed SOCl_2 were removed from the product by resubliming it in a clean evacuated tube. This reaction has advantages over the alternative protactinium(v) hydrous oxide–thionyl chloride reaction; thus it occurs at an appreciably lower temperature, and the carbide is an easier material to handle than the low-fired or vacuum-dried hydrous oxides. Direct conversion of the monocarbide into $\beta\text{-PaBr}_5$ was achieved by heating it at 350 °C in bromine vapour using similar apparatus to that for the chlorination. The product was removed from the excess of carbon by sublimation at 450 °C.

Although the chlorination and bromination reactions involved only 20 mg of carbide they could easily be employed for gram amounts of material. In addition, it is probable that the monocarbide can be used as an alternative to aluminium for the reduction of PaCl_5 and PaBr_5 to the corresponding tetrahalides.

Physical Properties of the Halides.—Unit-cell dimensions in an orthorhombic space group have been obtained from two single-crystal studies on PaI_5 ; ^{9–11} the results differed in the values of a_0 and c_0 and it was concluded, after an attempt to solve the structure and that of the apparently isostructural tantalum analogue, that the crystals examined were twinned.^{10,11} Few X-ray powder-diffraction lines are observed on photographs of the pentaiodide. The values listed in Table 1 for our new preparations are in complete agreement with those recorded earlier, but not published, for products from the protactinium–iodine and halogen-exchange reactions. The tetraiodide also gives only weak X-ray powder photographs but they are (Table 1) adequate to

⁹ R. D'Eye, A. Fox, A. G. Maddock, and D. Toms, quoted in D. Brown and A. G. Maddock, *Quart. Rev.*, 1963, **17**, 289.

¹⁰ D. Brown, J. F. Easey, D. G. Holah, and C. E. F. Rickard, *Proc. 3rd Internat. Protactinium Conf.*, Schloss Elmau, 1969, Report BMBW–FB 71–17, 1971, 25–1.

¹¹ J. F. Easey, Ph.D. Thesis, Leicester University, 1968.

show that it is not isostructural with either thorium or uranium tetraiodide.

Attempts to obtain Raman shifts for the dark penta- and tetra-iodide were unsuccessful. Infrared results for these compounds are listed in Table 2 together with

TABLE 1
X-Ray powder-diffraction results for PaI_5 and PaI_4

PaI_5		PaI_4	
$\sin^2\theta_{\text{obs.}}$	Relative intensity *	$\sin^2\theta_{\text{obs.}}$	Relative intensity *
0.0576	s	0.0104	s
0.0585	w+	0.0165	s
0.0958	m+	0.0604	w
0.1330	s	0.0622	w
0.1360	s	0.0645	w
0.1587	m	0.0895	w—
0.1861	w—	0.0952	w—
0.1905	m+	0.1019	m
0.1946	w	0.1728	m+
0.2281	w+	0.1817	w
0.3215	w		
0.3267	w—		
0.3359	w—		
0.3591	w—d		
0.3668	w—		

* s = Strong, m = medium, w = weak, and d = diffuse.

TABLE 2
Infrared and Raman vibrations (cm^{-1}) *

PaCl_5		PaBr_5		PaI_5	PaI_4
I.r.	Raman	I.r.	Raman	I.r.	I.r.
365s	376s	250 (sh)	245m	180s	174s
326s	324w	240 (sh)	225s	144w	132 (sh)
260 (sh)	139w	232s	210s	112w	120s, b
220vs, b		202m		55w	100 (sh)
188 (sh)		150m			56s
115m					
84w					

* s = Strong, m = medium, w = weak, sh = shoulder, and b = broad.

Raman and i.r. data for the pentabromide and pentachloride. The Raman results for the last compound are similar to those reported previously.¹² In view of the seven-co-ordinate chain structure of PaCl_5 and the dimeric six-co-ordinate structure of $\beta\text{-PaBr}_5$ the observed vibrations have not been assigned.

EXPERIMENTAL

Apparatus and Chemicals.—The study was made in glove-boxes because of the radioactivity associated with ^{231}Pa . The halides were handled in inert-atmosphere boxes (water and oxygen content <20 p.p.m.). The Pyrex and silica apparatus was heated under a continuous vacuum before use. Commercially available carbon, iodine, and bromine were used as supplied; zinc metal was sublimed before use. Protactinium-231 was available from a batch of material which has recently been recovered and purified.⁴ Spectrographic analysis showed it to be >99.6% pure. The pentaoxide, obtained in the established manner by ignition of the hydrous oxide at 750 °C, was characterised by X-ray powder-diffraction analysis. X-Ray powder photographs, Raman spectra, and i.r. spectra were recorded as described previously.¹³

Protactinium Monocarbide.—Protactinium pentaoxide

(0.5 g, purity >99.6%) was intimately ground with twice the stoichiometric quantity of spectra-grade graphite for the reaction $\text{Pa}_2\text{O}_5 + 7\text{C} \rightarrow 2\text{PaC} + 5\text{CO}$, and 1 wt. % of a binder (Apiezon vacuum wax). Carbon tetrachloride was added to assist dispersal of the binder during grinding. The mixture was vacuum dried (10^{-4} Torr) and pelletised using a pressure of 2 ton cm^{-2} . The pellets were heated in a graphite susceptor, the temperature being increased to 1700 °C over a period of 2 h using a radio-frequency vacuum furnace. Carbon monoxide evolution, which commenced at ca. 1100 °C, was virtually complete at 1500 °C.

Protactinium Penta-iodide.—Protactinium monocarbide (0.39 g) and an excess of iodine were heated together in an evacuated sealed silica tube for several hours. The temperature of the carbide was maintained at 350 °C while the cool end of the tube was situated in a second furnace at 180–200 °C. The product was sublimed from the region of the carbide at 350 °C following which the reactants were again heated in the two furnaces to ensure complete reaction. The yield of resublimed penta-iodide was >90% (Found: I, 73.1; Pa, 26.6. PaI_5 requires I, 73.3; Pa, 26.7%).

Protactinium Tetra-iodide.—The penta-iodide (0.1 g) was heated with a small excess of monocarbide for the reaction $4\text{PaI}_5 + \text{PaC} \rightarrow 5\text{PaI}_4 + \text{C}$, the evacuated silica container being completely enclosed in a furnace at 500–600 °C for several hours. The green-black product was sublimed away from the carbon and excess of carbide and resublimed in a clean evacuated tube (10^{-4} mmHg) at 450 °C, yield >80% (Found: I, 68.1; Pa, 31.55. PaI_4 requires I, 68.7; Pa, 31.25%). Similar reactions involving sufficient monocarbide to achieve reduction to protactinium tri-iodide also yielded PaI_4 . The same product was obtained when PaC (0.025 g) and sufficient mercury(II) iodide for the formation of PaI_3 were heated together at 500 °C; the tetra-iodide was sublimed from the reaction mixture at 450 °C.

Protactinium Pentabromide and Pentachloride.—The monocarbide (0.02 g) was heated at one end of an evacuated sealed tube in bromine (350 °C) or thionyl chloride vapour (200–250 °C). The product sublimed to the centre of the tube which was opened after condensing the excess of halogenating agent into a side-arm (*cf.*, apparatus for $\text{Pa}_2\text{O}_5/\text{C}$ -bromine reactions³). Protactinium penta-bromide and -chloride were identified by X-ray powder photography after resublimation of the products in clean evacuated tubes.

Analysis.—Protactinium was weighed as Pa_2O_5 following ignition (750 °C) of the hydrous oxide precipitated on the addition of 10% aqueous ammonia-acetone to the frozen halide (by liquid-nitrogen). The mixture was allowed to warm to room temperature in a stoppered tube and the hydrous oxide then isolated by filtration through a silica crucible. Iodide in the supernatant was precipitated after acidification with dilute nitric acid and weighed as silver iodide. The composition of the monocarbide-carbon mixture was determined by ignition to Pa_2O_5 .

We thank Mr. N. Bridger and Mr. F. Ewart (Appl. Chem. Div., Harwell) for provision of carbothermal reduction apparatus and instruction in its use, and Mr. A. M. Deane (Chem. Div., Harwell) for provision of spectral facilities.

[5/2289 Received, 24th November, 1975]

¹² J. McCordick, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 665.

¹³ D. Brown, P. E. Lidster, and B. Whittaker, Report AERE-R 8035, 1975.