Preparation and Some Chemical Properties of Protactinium Metal

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The preparation of protactinium metal by a modified van Arkel technique is described. The product exhibits the body-centred tetragonal structure with a_0 = 3.931(1) and c_0 = 3.236(1) Å. Conditions for conversion of the metal into the tetra- and penta-halides (PaX_4, X = Cl or Br; PaX_5, X = F, Cl, Br, or I) by reactions involving a variety of halogenating agents are described. Reaction with gaseous hydrogen yields either α-PaH_3 (250 °C) or β-PaH_3 (400 °C) which are isostructural with their uranium analogues. The stability of the metal on exposure to the atmosphere has been confirmed.

SMALL quantities of protactinium metal were apparently first obtained by Grosse and Agruss [1] in 1934 by bombarding Pa_2O_5 with 35-keV electrons in a high vacuum and by decomposition of pentahalides on a hot filament.† Neither product was identified with certainty. Subsequently, milligram amounts were obtained by reduction of protactinium tetrafluoride with barium [2,3] or lithium [4] vapour at 1 300—1 400 °C using the double-crucible technique with tantalum crucibles. A refinement of this procedure involved a BaF_2 crucible suspended inside a tantalum crucible with barium reductant at 1 250—1 275 °C,[5,6] the temperature then being increased to 1 600 °C to melt both metal product and the barium fluoride. On cooling, protactinium metal was obtained as a small sphere attached to the bottom of the barium fluoride. Surface-tension effects play a prominent role in this method and individual preparations have been limited to *ca.* 12 mg.[5] Although larger quantities, *ca.* 80 mg, have been prepared by reduction of PaF_4 using calcium [7] or 10% magnesium–zinc alloy [8] the yields were low.

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 mmHg ≈ 13.6×9.8 Pa; 1 Torr = (101 325/760) Pa.

[1] A. V. Grosse and M. Agruss, *J. Amer. Chem. Soc.*, 1934, **56**, 2200.

[2] P. A. Sellers, S. M. Fried, R. E. Elson, and W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1954, **76**, 5935.

[3] B. B. Cunningham, ' Physico-chimie du Protactinium,' Publ. No. 154, C.N.R.S., 1966, p. 45.

[4] R. D. Fowler, B. T. Matthias, L. B. Asprey, H. H. Hill, J. D. G. Lindsay, C. E. Olsen, and R. W. White, *Phys. Rev. Letters*, 1965, **15**, 860.

[5] B. B. Cunningham, *Tagungsber. der 3te Protaktiniumkonferenz*, Schloss Elmau, bei Mittenwald, 1969, BMBW–FBK 71–17, 1972, p. 14–1.

[6] R. L. Dod, Ph.D. Thesis, University of California, Report LBL–659, 1972.

[7] J. A. C. Marples, ' Physico-chimie du Protactinium,' Publ. No. 154, C.N.R.S., 1966, 39; *Acta Cryst.*, 1965, **18**, 815.

[8] J. A. C. Marples, personal communication, 1967.

[9] D. Brown, ' Gmelin Handbook on Protactinium,' System No. 51, 1978, ch. 11.

In view of the small quantities previously available it is hardly surprising that the chemical properties of protactinium metal have not been extensively investigated.[9] Thus, it is known [6] that at >300 °C it reacts with air, carbon dioxide, and water vapour to form Pa_2O_5, whilst reactions with iodine [10] (400 °C) and hydrogen chloride vapour [6] (300 °C) yield the pentaiodide and mainly the tetrachloride, respectively. A product isostructural with β-UH_3 was reported [2] to form on interaction of microgram amounts of protactinium with hydrogen at 250 °C, whereas the products obtained by Dod [6] at 100—300 °C were isostructural with α-UH_3. Further reaction at 400 °C resulted in the formation of an unidentified phase. Similarly, products obtained from reactions with gaseous hydrogen bromide, hydrogen iodide, nitrogen, and ammonia could not be unambiguously identified by *X*-ray powder diffraction, although one product of the reaction with gaseous nitrogen may have been the dinitride, PaN_2.[6] An early report [2] that exposure to air at room temperature led to the formation of oxide films (PaO and PaO_2) was not confirmed by subsequent studies which indicated [6] little noticeable tarnishing even after several months, and provided *X*-ray evidence that there was no reaction even at 100 °C. Apart from the protactinium–iodine reaction, all the above investigations involved only microgram amounts of metallic protactinium.

In view of the limited investigations on the preparation of protactinium metal and the paucity and sometimes conflicting nature of information available on its chemical properties, it was of interest to study these topics further. We now report the preparation of the metal by a modified van Arkel technique together with further observations on its chemical reactions. Whilst this work was in progress we learned from Professor W. Müller [11] that he and his co-workers [12,13] were investigating the preparation of the metal by the same method, which is based on earlier studies by Lorenz *et al.*[14] on Th–Pa mixtures.

RESULTS AND DISCUSSION

Metal Preparation.—Protactinium monocarbide reacts with iodine to yield either PaI_4 or PaI_5, depending on the amount of iodine present in the sealed, evacuated, reaction vessel.[15] When this reaction is performed with only 10% of the stoicheiometric amount of iodine for reaction (1) the

$$2PaC + 5I_2 \longrightarrow 2PaI_5 + 2C \qquad (1)$$

volatile product can be decomposed to yield a deposit of metallic protactinium on a tungsten filament heated to >1 360 °C. The apparatus is shown schematically in Figures 1 and 2. The bulb temperature is maintained at 370—380 °C by a furnace tube and the filament is viewed through 0.5-in diameter holes in the walls of the furnace. The resistance of the filament, and hence its temperature, changes as protactinium is deposited, resulting in slower rates of deposition. An indication of the rate is obtained by continuously monitoring the voltage across, and the current through, the filament and it has been shown that the optimum temperature for deposition is in the range 1 360—1 490 °C (*cf.* the recommended value [16] for the melting point of Pa is 1 572 ± 20 °C). The filament temperature was measured using an optical pyrometer, corrected for protactinium emissivity using the value for thorium [17] (ε 0.36), and adjusted by a Variac at frequent (*ca.* 0.5 h) intervals to maintain a reasonable deposition rate.

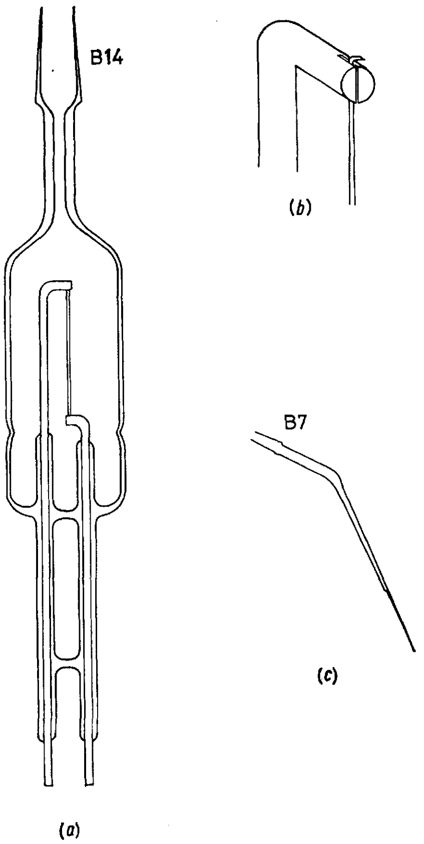

FIGURE 1 (*a*) van Arkel bulb. (*b*) Method of attaching strip filament. (*c*) Iodine bulb

During initial experiments involving both thorium and protactinium, problems were encountered owing to fila-

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

[11] W. Müller, personal communication, 1974.

[12] R. D. Baybarz, J. Bohet, K. Buijs, L. Colson, W. Müller, J. Reul, J. C. Spirlet, and J. C. Toussaint, *Proc. Conf. Transplutonium*, Baden-Baden, 1975, eds. W. Müller and R. Lindner, North-Holland, Amsterdam, 1976, p. 61.

[13] Progress Reports, TUSR–19, 1975, p. 50; TUSR–20, 1976, p. 54; TUSR–21, 1976, p. 63; J. Bohet and W. Müller, *J. Less-Common Metals*, in the press.

[14] R. Lorenz, H. L. Scherff, N. Toussaint, and V. Gos, *J. Nuclear Materials*, 1970, **37**, 203.

[15] D. Brown, G. de Paoli, and B. Whittaker, *J.C.S. Dalton*, 1976, 1336.

[16] F. L. Oetting, M. H. Rand, and R. J. Ackermann, ' The Chemical Thermodynamics of Actinide Elements and Compounds, Part 1—The Actinide Elements,' I.E.A.E., Vienna, 1976.

[17] C. J. Smitholls, ' Metals Reference Handbook,' Butterworth, London, 1949.

ment breakage. This arose when thin tungsten-wire filaments (0.1 mm in diameter) were used and was attributed to ' hot spots ' at the electrode–filament junction which developed as metal was deposited on the central region of the filment. Although these experiments yielded individual quantities of protactinium metal up to 0.2 g, filament lifetimes were unpredictable. A strip filament was subsequently employed [Figure 1(*a*)] with more success and 0.2—0.5 g samples of protactinium metal have been deposited on strips measuring 13—33 × 0.75 × 0.05 mm. No attempt was made to optimise filament dimensions and narrower strips could possibly be employed. In addition it is likely that larger quantities of protactinium can be deposited per unit length of filament. The amounts deposited to date have been in the range 11—15 mg per mm of filament, the resulting ' bars ' being *ca.* 2 mm in diameter.

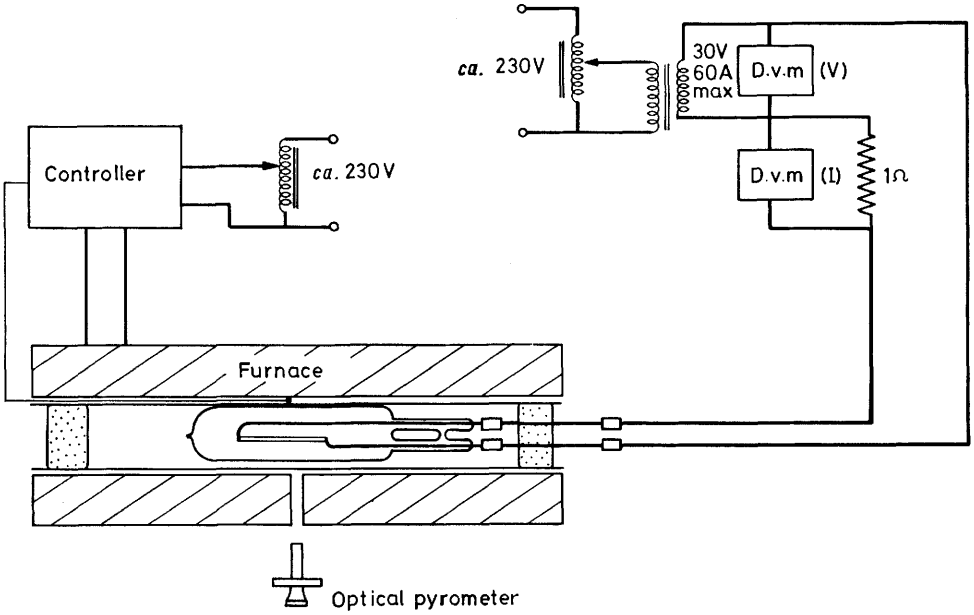

FIGURE 2 Furnace and control system. D.v.m. = Digital voltmeter

Analysis of two products has shown oxygen to be the major light-element impurity (800—900 p.p.m.). These values contrast with the relatively low values for thorium deposited in similar apparatus (80—150 p.p.m.) and are, in fact, higher than the oxygen content of the carbide starting material (460 p.p.m.). This result is not understood at present, particularly as protactinium iodide oxides were not present in the bulbs when deposition was terminated. Analytical data (in p.p.m.) for the two samples of >99.8 (A) and >99.5% (B) purity are: A, O (900), N (40), H(4), C (50), B (100), Mg (200), Mn (100), and Fe (50); B, O (800), N (<10), H (2), Si (1 000), Fe (1 000), Mg (900), Al (500), Cu (200), and Ti (500). The following elements were below the limit of detection: Pb, Cr, Ni, Sb, Sn, Nb, Ag, Zn, Ba, V, W, Mo, Co, and Pt. The higher impurity levels for Si, Fe, Mg, Al, Ca, and Ti in sample B suggest that the starting material was less pure than that for A, and indicate that it is necessary to start with pure carbide since so many other elements are co-deposited under the conditions employed.

The products, however, were radiochemically pure. Thus, α-pulse analysis of one sample *ca.* 2 weeks after preparation showed that only 0.07% of the total α-emission was due to daughter elements. This compares with *ca.* 8% in the starting material and shows that the Th daughter (^{227}Th, $t_{\frac{1}{2}}$ 18.7 d) is not co-deposited, presumably as a consequence of the lower bulb and filament temperatures compared with those normally employed [14,18,19] to produce thorium metal by the van Arkel technique.

The product was silver in colour and malleable. All the samples exhibited only the body-centred tetragonal structure, no lines being present on the *X*-ray powder photographs which could be attributed to the face-centred cubic phase present in Dod's product,[20] obtained after heating to 1 600 °C, and observed in arc-melted samples by other workers.[13,21,22] The unit-cell dimensions of all the preparations were in good agreement [a_0 = 3.931(1), c_0 = 3.236(1) Å] and close to those reported previously for samples obtained by reduction of PaF_4 (refs. 2, 3, 5—7, and 23) and, more recently,[12] by the van Arkel method. According to Zachariasen [23] this unique body-centred tetragonal structure may be considered as a

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[18] D. E. Scaife and A. W. Wylie, *Proc. 2nd Internat. Conf. Peaceful Uses Atomic Energy*, Geneva, 1958, **4**, 215.

[19] D. Brown, T. C. Tso, and B. Whittaker, Report AERE–R 8638, 1976.

[20] J. Fuger and D. Brown, *J.C.S. Dalton*, 1975, 2276.

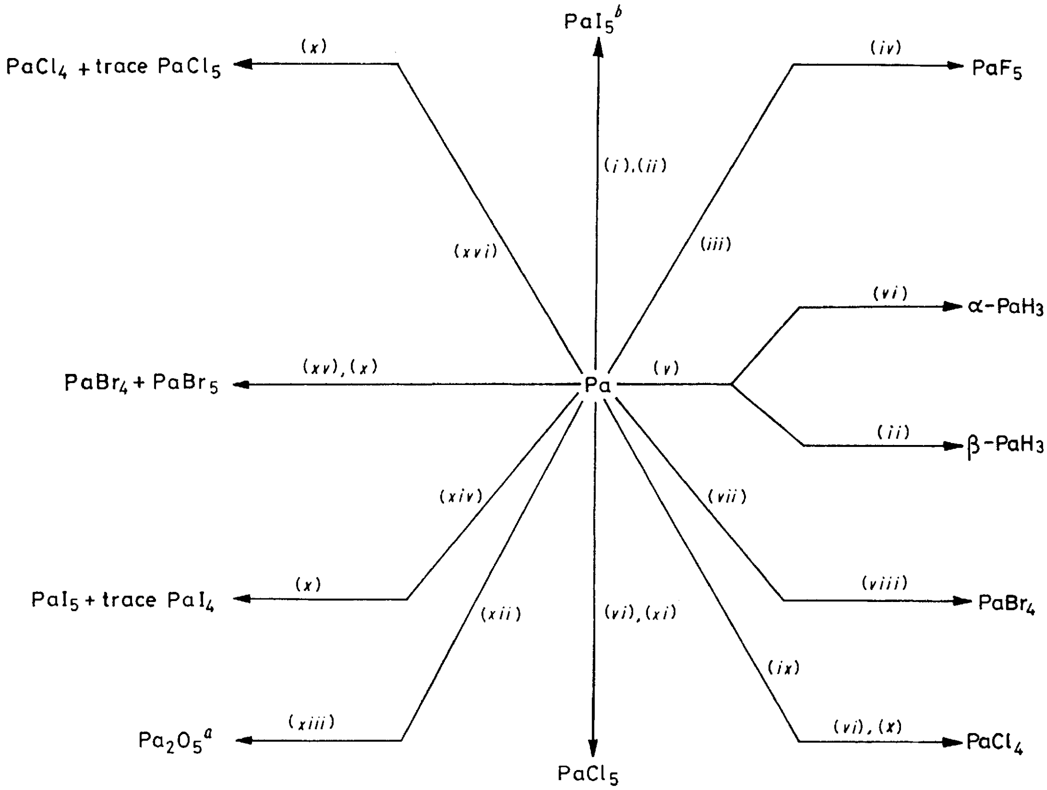
[21] L. B. Asprey, R. D. Fowler, J. D. G. Lindsay, R. W. White, and B. B. Cunningham, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 977.

[22] R. D. Fowler, L. B. Asprey, J. D. G. Lindsay, and R. W. White, ' Low Temperature Physics,' eds. K. D. Timmermans, W. J. O'Sullivan, and E. F. Hammel, 1973, **3**, 257.

[23] W. H. Zachariasen, *Acta Cryst.*, 1952, **5**, 17; 1959, **12**, 698.

body-centred cubic structure compressed along a 4-fold axis. On the basis of the unit-cell dimensions quoted here, each Pa atom has 8 neighbours at 3.216 Å and 2 at 3.236 Å. The metallic radii for co-ordination numbers 10 and 12, respectively, are 1.610 and 1.631 Å. The calculated density is 15.34 g cm^{-3}. A more detailed account of our preparation of protactinium metal will be found in ref. 19, together with a summary of its known physical properties.

Chemical Reactions.—The reactions investigated are shown in the Scheme. Samples (1—3 mg) of the metal exposed to the atmosphere showed no visible signs of attack during periods of up to 2 months. *X*-Ray examination showed no lines attributable to either the monoxide, dioxide, or pentaoxide, in agreement with the observations of Dod [6] but contrary to an earlier report.[2] During analysis for carbon * the metal was heated at 1 100 °C in oxygen; the product was a mixture of the high-temperature orthorhombic and rhombohedral phases [24] of Pa_2O_5.



SCHEME Some chemical reactions of protactinium metal. (*i*) I_2; (*ii*) 400 °C; (*iii*) F_2; (*iv*) 300—400 °C; (*v*) H_2; (*vi*) 350 °C; (*vii*) BBr_3 vapour; (*viii*) 450 °C; (*ix*) BCl_3 vapour; (*x*) 450°C to sublime products; (*xi*) $SOCl_2$ vapour; (*xii*) O_2; (*xiii*) 1 100 °C; (*xiv*) HI; (*xv*) HBr; (*xvi*) HCl

[a] Mixture of the high-temperature orthorhombic and rhombohedral phases; at lower temperature (300 °C) the fluorite phase is obtained according to ref. 6. [b] Previous work reported in ref. 10.

Reaction with an excess of fluorine in a sealed nickel vessel (fluorine pressure 300 mmHg) at 300—350 °C yielded a mixture of Pa_2F_9 and PaF_5; complete conversion into the pentafluoride is achieved at slightly higher temperatures with higher pressures of fluorine. Since it is known [10] that the protactinium–iodine reaction yields the pentaiodide at 400 °C, analogous reactions involving chlorine and bromine were not studied since they will undoubtedly result in the formation of the appropriate pentahalide.

We have confirmed the observation [6] that hydrogen chloride reacts with protactinium at 450 °C to yield mainly the tetrachloride on sublimation of the product in a new vessel at 450—480 °C, and have identified the second product as the pentachloride. Similarly, hydrogen bromide (380 mmHg) reacts with protactinium at 300 °C in a sealed silica vessel, and when the temperature is increased to 450 °C to sublime the products both penta- and tetra-bromide condense in two well separated regions of the vessel. A small amount of protactinium(IV) dibromide oxide, $PaBr_2O$, remains as an involatile residue. The reaction between the metal and an excess of hydrogen iodide commences at *ca.* 280 °C and yields mainly the pentaiodide on sublimation of the product at 450 °C with a relatively small (*ca.* 10%) quantity of PaI_4. This marked increase in the amount of pentahalide is probably due to the instability of HI (ΔH_f 7.4 kJ mol^{-1}) and the ready oxidation of PaI_4 by iodine (*cf.* the difficulty

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* Performed by I. G. Jones, Chemistry Division, A.E.R.E., Harwell.

[24] L. E. J. Roberts and A. Walter, ' Physico-chimie du Protactinium,' Publ. No. 154, C.N.R.S., 1966, p. 51.

in reducing PaI_5 with hydrogen in a sealed vessel[25]). X-Ray examination of partially reacted metal, from reactions involving a deficiency of hydrogen iodide, before sublimation of the products, failed to furnish evidence for the intermediate formation of the tri-iodide,[26,27] which might have been expected as the initial product in direct contact with the excess of metal.

The X-ray powder photograph of one sample of the tetrabromide, recorded within 1 day of preparation, contained reflections extra to those of the normal tetragonal phase[25] which is isostructural with β-$ThBr_4$. On re-examination of the contents of the X-ray capillary and of the bulk sample after several days these had disappeared and only the tetragonal phase was present. A similar observation was made several years ago[28] during the reduction of $PaBr_5$ by aluminium when one product gave an identical X-ray powder pattern. These extra reflections do not coincide with those of monoclinic UBr_4[29] or α-$ThBr_4$,[30,31] and we have been unable to repeat the preparation or to obtain this new phase by rapidly quenching samples from 450 °C to room temperature, or by prolonged heating at 350 °C *in vacuo*. Further work is currently in progress on the possible existence of a second polymorph of $PaBr_4$ and also on the question of dimorphism in the tetrachloride (*cf.* α- and β-$ThCl_4$[32]).

Prolonged treatment of protactinium metal with refluxing thionyl chloride or boron tribromide results in partial (10—20%) conversion into the pentachloride and tetrabromide. Complete conversion is readily achieved by vapour-phase reactions at 350 and 350—450 °C, respectively, using apparatus similar to that described previously for the bromination of Pa_2O_5–C mixtures.[33] Only a trace amount of pentabromide (1—2%) is formed in the BBr_3 reaction. Similarly BCl_3 converts the metal into the tetrachloride at 350 °C with no evidence for the formation of the pentachloride. Apart from the hydrofluorination of Pa_2O_5 in a stream of H_2 and HF, these reactions are the first examples of the direct preparation of protactinium tetrahalides; presumably BI_3 will react similarly to yield PaI_4. In each instance a trace of protactinium(IV) dihalide oxide was also formed and remained at the point of reaction together with a black amorphous powder which was probably boron, possibly mixed with an involatile tungsten halide. The conversion of the metal into the pentachloride by thionyl chloride is in accord with the rapid oxidation of Pa^{IV} in oxygen-free liquid $SOCl_2$.[34]

On contact with an excess of hydrogen at 350 °C protactinium metal was converted into a trihydride isostructural with α-UH_3. At 400 °C the product was isostructural with β-UH_3. The former observation is in agreement with the results of Dod[6] who obtained this product at temperatures up to 300 °C, whilst Sellers *et al.*[2] reported that β-PaH_3 is formed at 250 °C. However, Dod failed to observe the formation of β-PaH_3 at temperatures up to 400 °C. At this temperature he obtained a product with a unique X-ray powder photograph which could not be identified by comparison with data available for other actinoid hydrides. The products of our reactions at 400 °C gave no X-ray reflections other than those of β-PaH_3 and two weak lines attributable in one case to PaO_2 and in another to PaO. Unit-cell dimensions for α- and β-PaH_3 were $a_0 = 4.154$ and 6.646 Å, respectively, in good agreement with the single values reported previously[2,6] for each phase. Thermal decomposition of both phases at *ca.* 300 °C *in vacuo* yielded finely divided metal with unit-cell parameters [$a_0 = 3.928(1)$, $c_0 = 3.240(1)$ Å] close to those of the van Arkel products.

EXPERIMENTAL

All the work was performed in glove-boxes because of the radioactivity associated with ^{231}Pa and its decay products. The metal and all the compounds were handled and dispensed for analysis, X-ray studies, *etc.*, in inert-atmosphere boxes (water and oxygen content $<$20 p.p.m.).

Materials.—Protactinium-231 was available as Pa_2O_5.[35] Graphite (Johnson, Matthey Ltd.; 'Specpure') was used as supplied for the preparation of protactinium monocarbide as described previously.[15] Reagent-grade iodine (B.D.H.) was purified by vacuum sublimation over freshly fired CaO at 150 °C (removal of water) followed by sublimation over dry KI (removal of ICl) and three successive sublimations *in vacuo*. It was loaded into previously degassed bulbs (10^{-5} Torr at 400—500 °C) with fine capillary tips, in an inert-atmosphere box. These were then rapidly pumped to remove the majority of the gas (plus *ca.* 10% of the iodine), dipped into liquid nitrogen, evacuated to 10^{-4} Torr, and sealed [Figure 1(*c*)].

Tungsten-strip filaments (0.7—1.0 mm wide, 0.05 mm thick) were cut from thin sheet (Lamp Metals Ltd.; $>$99.9%, carbon-free) to the required length (13—33 mm). Electrodes were cut from 2 mm diameter tungsten rod; the ends were trimmed and slotted using a diamond circular saw. van Arkel bulbs (Figure 1) were constructed entirely from tungsten sealing glass (Schott–Jena type 8487, W. G. Flaig and Sons Ltd.). Thionyl chloride (B.D.H.) and BBr_3 (Matheson Co. Inc.) were flushed with nitrogen before use. Hydrogen (99.99%, 'Specpure'; B.O.C. Ltd.) and BCl_3 (Matheson) were used as supplied. Hydrogen chloride and HBr (Matheson) were dried over anhydrous $Mg[ClO_4]_2$, and HI (Matheson) over vacuum-dried granular $CaCl_2$.

Metal Preparation.—After testing for leaks, the van Arkel bulbs were degassed at 450—500 °C to 10^{-5} Torr (10—15 h). The carbide was crushed to a fine powder and introduced into the bulb, together with an iodine bulb containing 10% of the quantity of iodine for reaction (1), in an inert-atmosphere box. The bulb and contents were degassed at 350 °C (10^{-5} Torr), allowed to cool, pumped to 10^{-6} Torr, and the

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

[26] V. Scherer, F. Weigel, and M. Van Ghemen, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 589.

[27] D. Brown, B. Whittaker, and G. de Paoli, Report AERE–R 8367, 1976.

[28] D. Brown, unpublished work, 1966.

[29] R. M. Douglass and E. Staritsky, *Analyt. Chem.*, 1964, **29**, 459.

[30] D. E. Scaife, *Inorg. Chem.*, 1966, **5**, 162.

[31] J. T. Mason, M. C. Jha, D. M. Bailey, and P. Chiotti, *J. Less-Common Metals*, 1974, **35**, 331.

[32] J. T. Mason, M. C. Jha, and P. Chiotti, *J. Less-Common Metals*, 1974, **34**, 143.

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

[34] D. Brown and P. J. Jones, *J. Chem. Soc.* (*A*), 1967, 243.

[35] D. Brown and B. Whittaker, Report AERE–R 8315, 1976.

filament degassed by passing a current to heat it to *ca.* 800 °C. After the filament had cooled and the vacuum had returned to 10^{-6} Torr the bulb was sealed and flame-annealed at the point of sealing. It was then gently shaken in order to break the tip of the iodine bulb and release the iodine, and placed in a water-cooled furnace lined with a transparent silica tube (31 mm inside diameter) through which the filament could be viewed *via* a horizontal hole cut through the side of the furnace (Figure 2). Filament temperatures were determined using a Hartmann–Braun optical pyrometer; voltage and current readings were displayed on Fluke type 8000 A digital voltmeters. The furnace temperature was controlled *via* a NiCr–NiAl thermocouple attached to a Eurotherm regulator.

The filament was heated to *ca.* 250 °C below the temperature required for deposition (to prevent iodide condensation on the filament), following which the bulb temperature was then raised to 370—380 °C for iodide formation and volatilisation. The filament temperature was then adjusted until voltage and current readings indicated that metal deposition had commenced. Deposition was monitored by plotting power input against time, and the rate was maintained by increasing the filament current at frequent intervals to hold the ' apparent ' temperature between 1 050 and 1 150 °C. This, after correction using the emissivity value for thorium [17] (ε 0.36), gives a true temperature in the range 1 360—1 490 °C. Deposition times invariably exceeded 8 h and when it was necessary to interrupt an experiment the bulb was allowed to cool before the filament was switched off. On completion of the reaction, excess of iodide was sublimed to one end of the bulb, which was then transferred to an inert-atmosphere box, opened, and the filament removed from the bulb. Yields ranged from 86 to 94%; impurity levels are quoted in the Results and Discussion section. Detailed experimental data for individual preparations are listed in ref. 19.

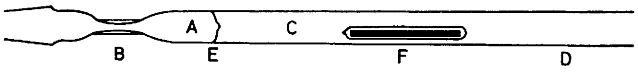

FIGURE 3 Apparatus for metal–gas reactions

Chemical Reactions.—Reactions with the gaseous reagents were carried out in glass vessels shown in Figure 3. These were first sealed on to the manifold of a gas-handling line at D, and volume C was evacuated and filled with hydrogen or the halogenating agent (HCl, HBr, HI, or BCl_3) after which the vessels were drawn off and sealed at D. Thereafter the tubes were handled in inert-atmosphere glove-boxes and small quantities of protactinium metal (10—20 mg), cut from the crystal bar, were loaded into the previously degassed section A. This was evacuated and the tubes were sealed at B. Breakseal E was then broken and F withdrawn to end D by means of a magnet before heating the metal (in A) to the appropriate temperature in a furnace. At the end of the reaction the halide *products*, but not the hydrides, were sublimed at *ca.* 450 °C. Where two products formed these were obtained in well separated regions of the vessel. The reaction between protactinium and fluorine was carried out in a nickel vessel at 300—400 °C, the excess of fluorine being introduced *via* an all-metal vacuum line.

Liquid thionyl chloride and boron tribromide were placed in the side arm of a reaction vessel similar to that described previously [33] for the Pa_2O_5/C–bromine reaction. They were frozen, the vessel was evacuated, and then the liquids were degassed by repeated freezing and pumping, following which the evacuated vessels were sealed. The metal, situated at one end of the vessel, was then heated in the vapour of the halogenating agent and the *products* were sublimed.

Identification of Products.—In view of the small scale of all the reactions, the products were identified by comparison of their *X*-ray powder photographs with existing ones filed at Harwell or, in the case of the hydrides, with published data. The method for loading capillaries and recording the films has been described previously.[19,36] Reflections due to impurities were present on only two films. Thus, one product of β-PaH_3 gave two additional reflections attributable to PaO_2, and a different preparation of the same compound gave two additional reflections due to PaO. The possible existence of a second crystallographic form of $PaBr_4$ is discussed above.

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[36] D. Brown and J. Edwards, *J.C.S. Dalton*, 1972, 1757.