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PREPARATION OF SOME PROTACTINIUM COMPOUNDS AND THE METAL

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Protactinium was discovered in 1917 by Rahn and Mietner and independently about the same time by Soddy and Cranston. It was not until 1928 that the first compound was reported. Von Grosse reported the preparation of Pa_2O_5 by heating either the hydrated oxide or the oxalate. The formula was derived by analogy with niobium and tantalum; no experimental evidence was given to support this formula. The first preparation of the metal was reported in 1934 by Von Grosse. He reported two preparations, one from the oxide on a copper target by bombardment with 35-KEV electrons in a high vacuum and the other by the decomposition of the vapors of the chloride, bromide, or iodide on a wolfram filament at elevated temperatures and a pressure of 10^{-5} to 10^{-6} mm of Hg.

Preparation of protactinium compounds has been reported by various investigators. The compounds are summarized in Table 1.

Further work on protactinium compounds by us has resulted in the preparation and identification of the metal, a hydride, tetrafluoride, monoxide, dioxide, and an oxysulfide. A nitride and a volatile fluoride, bromide, and iodide have been prepared but not definitely identified.

The protactinium oxide hydrate that was used in the above preparations was spectrographically pure. A description of the purification of this material is given in ANL-4411, 4469, and 4490.

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Table I
Some Compounds of Protactinium

Compound	Formula	Description	Workers
pentoxide	Pa_2O_5	white	Von Grosse, 1934; Elson, Fried, Sellers, Zacharaisen 1950
phosphate	$\text{Pa}_3(\text{PO}_4)_5$	-	" "
pentachloride	PaCl_5	white	" " " " "
pentiodide	PaI_5	-	" "
pentafluoride hydrate	$\text{PaF}_5 \cdot \text{XH}_2\text{O}$	white	" "
potassium-fluoride	K_2PaF_7	white	" "
dioxide	PaO_2	black	" " "
tetrachloride	PaCl_4	greenish yellow	" " "
pentabromide	PaBr_5	-	" "

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Oxides

Several workers have reported the preparation of protactinium pentoxide. Von Grosse reported the preparation of protactinium pentoxide by the heating of the hydrated oxide or oxalate. However, the composition of this oxide was proven by Elson, Fried, Sellers, and Zachariasen to be ca. $\text{PaO}_{2.25}$ by x-ray analysis. We also reported the preparation of a cubic form of Pa_2O_5 formed by heating the dioxide to 1100°C in oxygen and a second form of the pentoxide, orthorhombic and isostructural with U_2O_5 , Th_2O_5 , and Nb_2O_5 , which resulted in the course of an attempt to prepare a fluoride by the action of BrF_3 on $\text{PaO}_{2.25}$ at 400°C .

The first preparation of the dioxide was reported by us. It was prepared as a film on the walls of a capillary in an attempt to reduce the white volatile chloride with zinc at 400°C . This oxide was black and had the fluoride structure and was thus isostructural with the dioxides of the other Vf -elements from thorium to americium.

Since this compound was expected to be an important intermediate in the preparation of other tetravalent protactinium compounds, it was necessary to devise a method in which the product could be obtained free.

Our first approach, which failed, was to reduce the $\text{PaO}_{2.25}$ with H_2 in a quartz capillary at temperatures up to 1100°C . We then attempted to reduce the $\text{PaO}_{2.25}$ by the action of active metals such as Mg and Al; this attempt also failed.

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Surprisingly vigorous measures were required to reduce the oxide completely to PaO_2 . It was found necessary to treat the precipitated oxide, in a suitable crucible (thoria), with hydrogen at a temperature of 1750°C . Under these conditions the dioxide was formed, having the fluorite structure and the expected lattice dimensions; it was thus isostructural with thorium, uranium, neptunium, and plutonium dioxides. A comparison of the unit cell dimensions is shown in Table II.

TABLE II

Unit Cell Dimensions of the Dioxides of the T-Elements from Thorium to Plutonium.

Substance	a
ThO_2	5.585 Å
PaO_2	5.518
UO_2	5.457
NpO_2	5.425
PuO_2	5.386

The PaO_2 was a black solid substance and was not readily soluble in dilute or concentrated sulfuric acid, hydrochloric, or nitric acids. It was, however, soluble in hydrofluoric acid. The dioxide reacts with COCl_2 to produce " PaOCl_2 ".

The monoxide was prepared in our first attempt to prepare the metal by the reduction of PaF_5 with barium. Probably the metal was prepared, but on exposure to air slow oxidation took place on the surface of the metal, resulting in PaO and PaO_2 . This was evidenced by x-ray analysis, which showed a few faint diffraction lines due to the metal and the remainder due to PaO and PaO_2 . PaO has the PaO_2 type of structure and is thereby isostructural with UO_2 . The unit

cell dimension is $a = 4.985 \pm 0.005 \text{ \AA}$
 $= 4.975 \pm 0.005 \text{ kX}$

The monoxide is slowly oxidized by air to Pa_2O_5 .

The precipitated oxide hydrate was heated in vacuum at intervals of 100°C and the composition and structure after each treatment were determined by x-ray analysis. The changes are described by the following scheme:

Tetrafluoride

Protactinium tetrafluoride was successfully prepared in the nickel apparatus shown in Fig. 1.

Fig. 1

The apparatus is designed with a double set of valves. One set for regulating the flow of the gases and the other for stopping the flow of gases without interfering with the regulating valves.

Our first attempt to prepare the tetrafluoride by the action of a mixture of $\text{H}_2 + \text{HF}$ on $\text{PaO}_{2.25}$ was not successful. A platinum boat containing the $\text{PaO}_{2.25}$ was placed in the nickel furnace. The gas flow was carefully regulated and the temperature was gradually raised to 600°C and maintained for one quarter of an hour. The

system was then cooled while still containing the flow of hydrogen, ^{was continued}
On opening the apparatus one discovered that the protactinium had disappeared from the boat. Probably a volatile fluoride was formed and had condensed on the cool portion of the apparatus.

Protactinium tetrafluoride was successfully prepared by the above procedure using PaO_2 in place of $\text{PaO}_{2.25}$. The tetrafluoride has been definitely identified from its x-ray diffraction pattern. The substance has the ZrF_4 type of structure and is thus isostructural with ThF_4 , UF_4 , NpF_4 and PuF_4 . The unit cell dimensions are intermediate between those reported for ThF_4 and UF_4 .

PaF_4 is a reddish brown solid not readily reactive toward air. It reacts when heated with moist O_2 to form an oxide and it is reduced to the metal by the action of barium at 1400°C .

Protactinium oxysulfide

We have successfully prepared PaOS from PaCl_5 by the action of H_2S and CS_2 . An all glass apparatus designed for the preparation of neptunium chloride was used for the experiment and is shown in Fig. 2.

Fig. 2

The $\text{PaO}_{2.25}$ as a pellet was transferred to a capillary, suitable for use in x-ray analysis, and attached to the system as shown above. The oxide was chlorinated with carbon tetrachloride by the usual procedure.

The chloride being volatile was sublimed out of the heated zone. The furnace was cooled and placed over the " PaCl_5 ". The H_2S was passed thru CS_2 and then thru two cold traps at -50°C to remove water. The gases were then admitted into the system to a pressure of 650 mm. The temperature of the furnace was gradually raised to 900°C over a period of one hour. The light yellow product was proved by x-ray analysis to be PaOS which is isostructural with ThOS , UOS and NpOS .

The dimensions of the tetragonal unit cell containing two molecules are given in Table III.

TABLE III

Substance	a_1	a_3
ThOS	$3.963 \pm 0.002\text{\AA}$	$6.746 \pm 0.004\text{\AA}$
PaOS	3.832 ± 0.001	6.704 ± 0.004
UOS	3.843 ± 0.001	6.694 ± 0.001
NpOS	3.825 ± 0.002	6.654 ± 0.010

The unit cell dimensions of PaOS are slightly smaller than one should have expected. It is probable that some of the metal sites are vacant and that the actual composition is $\text{Pa}_{0.95}\text{OS}$. This would imply that a small fraction of the protactinium atoms are in the pentavalent state.

Protactinium Metal

We believed that once the compound PaF_4 was obtained ~~that~~ there would be a fair chance of making the metal. The only other

fluoride that had been prepared was a volatile compound, presumably PaF_3 . This fluoride and other halides would be unsatisfactory for the production of the metal because of their volatility and reactivity toward air. The melting point of protactinium was estimated to be approximately 1400°C by interpolating between the melting points of thorium and uranium. Therefore, it seemed that the reduction of a protactinium compound would have to be made at approximately this temperature in order to obtain a fused piece of the metal. Accordingly, PaF_4 was treated with barium metal at approximately 1500°C using the "double crucible" system, shown in Fig. 3:

Fig. 3

The PaF_4 was placed in the inner crucible, and the inner crucible and barium were then placed in the outer crucible, and the system was assembled as shown above. The system was evacuated to about 10^{-6} mm of Hg, and the temperature gradually raised to 1500°C . The reaction yielded shiny malleable globules of protactinium metal. The X-ray diffraction pattern of a flattened piece of the metal proved it to have tetragonal crystal structure. The calculated density was 15.71 g/cm^3 .

Protactinium Hydride

Protactinium hydride was prepared from protactinium metal and hydrogen by the micro-technique shown in Fig. 4.

The metal and mercury were placed in the capillary as shown in Fig. 4 and the system was evacuated. Very pure hydrogen was admitted *a pressure of* to about 500 mm of *Hg* ~~pressure~~. The ground glass joint was then turned thru an angle to permit the mercury to form a plug in the capillary. Additional hydrogen was admitted to move the mercury plug a distance into the capillary. The joint was then *turned* ~~reverted~~ to its original position. The furnace was placed over the metal and the temperature gradually raised until the plug of mercury began to move toward the furnace indicating the uptake of hydrogen by the metal. The hydride was formed at 250°C. The metal crumbled somewhat upon reacting with hydrogen. X-ray analysis proved the product to be PaH_3 , analogous to UH_3 .

Protactinium Nitride " PaN_2 "

We have prepared probably PaN_2 by the action of NH_3 *on* ~~in~~ " PaCl_5 " and *on* ~~in~~ PaCl_4 . The " PaCl_5 " was prepared with CCl_4 by the usual

procedure. Triple distilled NH_3 was admitted into the system to a pressure of 340 mm of Hg, and the temperature of the furnace was gradually raised to 800°C during a period of one hour. The product obtained was a bright yellow solid and was not volatile at 800°C in vacuum. The product according to x-ray analysis seemed to be PaH_2 , isostructural with UH_2 , but the possibility of oxygen atoms being present in the crystals could not be ruled out.

Since the " PaCl_3 " used may have contained some PaOCl_2 , or possibly PaOCl_3 , we decided to use as a starting material PaCl_4 of definitely known composition. The product obtained was bright yellow, was not volatile at 800°C in vacuum, and gave the same x-ray diffraction pattern as the product obtained from " PaCl_3 ".

Bromides

We have prepared volatile bromides of protactinium by several procedures. Two volatile compounds were obtained from each reaction. These bromides as yet have not been identified. The reactions involved: 1) protactinium oxide and aluminium bromide, 2) the oxide and hydrogen bromide, 3) the oxide and carbon tetrachloride, 4) the oxide, hydrogen bromide, and thionyl bromide, and 5) protactinium pentachloride, hydrogen bromide, and thionyl bromide.

Iodides

We have prepared volatile iodides which as yet have not been identified. Two volatile iodides were obtained from each of the following reactions: 1) the oxide and AlI_3 in a bomb at 800°C and 2) the metal and iodine at approximately 600°C .

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