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[54] PHOTOCHEMICAL PREPARATION OF PLUTONIUM PENTAFLUORIDE

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[58] **Field of Search** ..... 423/251; 204/157.1 R

[56] **References Cited**

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[57] **ABSTRACT**

The novel compound plutonium pentafluoride may be prepared by the photodissociation of gaseous plutonium hexafluoride. It is a white solid of low vapor pressure, which consists predominantly of a face-centered cubic structure with $a_o = 4.2709 \pm 0.0005$ Å.

4 Claims, No Drawings

PHOTOCHEMICAL PREPARATION OF PLUTONIUM PENTAFLUORIDE

This invention is the result of a contract with the Department of Energy (Contract No. W-7405-ENG-36).

BACKGROUND OF THE INVENTION

The invention described herein relates to the compound plutonium pentafluoride (PuF_5) and a photochemical method for preparing it.

Plutonium hexafluoride (PuF_6) has a substantial vapor pressure at or near room temperature and is therefore a useful feed material in a process for plutonium isotope separation based on an isotope-selective, laser-induced photodissociation reaction.

It is well known in the literature that the thermal decomposition of PuF_6 results in the formation of PuF_4 and F_2. Alpha particle irradiation produces the same products. In either instance, the net result is as shown in equation (1).

$$PuF_6(g) \xrightarrow{\Delta \text{ or } \alpha} PuF_4(s) + F_2(g) \quad (1)$$

In a laser-induced isotope separation process, however, photodissociation to PuF_5 would be preferable, since less energy is required to abstract one fluorine atom than two.

Thermodynamic considerations suggest that PuF_5 should be capable of existence. Heretofore, however, all efforts to isolate it have been unsuccessful.

SUMMARY OF THE INVENTION

We have now found that when gaseous PuF_6 is irradiated with radiation of a wavelength less than 520 nm, a white solid product is formed which has been identified as PuF_5. The PuF_5 is readily formed when the PuF_6 is irradiated using a nitrogen laser at 337.1 nm.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Plutonium pentafluoride, a white solid product of low vapor pressure, is formed by the photochemical reduction of gaseous PuF_6 using a nitrogen laser at 337.1 nm. Similar results are also obtained by using a nitrogen-pumped dye laser with an output at 480 nm for the photodecomposition of PuF_6. The stoichiometry of the reaction in equation (2)

$$PuF_6(g) \xrightarrow{h\nu} PuF_5(s) + \tfrac{1}{2} F_2 \quad (2)$$

was determined by measuring the pressure in a nickel cell equipped with quartz windows while simultaneously irradiating with a nitrogen laser (or the dye laser). A Validyne pressure transducer which had been calibrated against a quartz spiral manometer was used for the pressure measurements. The pressure decrease indicated by equation (2) was observed on a strip chart recorder and the extent of the pressure loss was proportional to the irradiaton time, at least until the window was screened by the formation of the deposit. The production of F_2 as indicated by equation (2) was supported by data obtained by cooling the gas to $-78°$ C. in a dry ice trap and removing the non-condensible gas at this temperature. (Boiling point of $F_2 = -188°$ C.) The quantity of plutonium hexafluoride lost was then determined by warming the gas to room temperature and measuring the pressure difference.

Experimental evidence for the nitrogen laser preparation of PuF_5 is given in the Table. When Cell I which consisted of quartz and nickel was used, the laser was not focused. When Cell II which consisted of sapphire and nickel was used, the laser was focused. Both cells were conditioned with F_2 and with PuF_6 prior to irradiation. The percentages of PuF_5 and PuF_4 in the solid product were calculated from stoichiometry, i.e., loss of PuF_6 and formation of F_2. The data of the Table show that under certain conditions the stoichiometry of equation (2) was closely followed.

TABLE

Cell	Irradiation Time (Min.)	Initial Pressure of PuF_6 (Torr)	Pressure After Laser Irradiation (Torr)	Pressure After Fluorine Removal (Torr)	Percentage of PuF_5 in Solid Product	Percentage of PuF_4 in Solid Product
I	14.0	74.50	72.43	69.90	90.0	10.0
I	29.0	70.20	66.20	62.15	99.4	0.6
I	75.0	52.67	49.12	45.55	99.7	0.3
I	84.0	44.00	37.60	31.20	100.0	0.0
II	98.0	59.72	56.23	51.15	81.4	18.6
II	125.0	43.81	38.70	28.49	66.7	33.3

A powder x-ray diffraction pattern of the white solid photodecomposition product was initially amorphous; however, after the solid was heated at 125° C. for 65 hours a crystalline product was obtained. Analysis of the x-ray data indicated the presence of two crystal phases. The predominate phase which constituted about 85% of the product had a face-centered cubic structure with $a_o = 4.2709$ Å ± 0.0005 Å. The second phase was not identified. Neither phase had the structure parameters which are associated with the compounds PuF_3, PuF_4 or PuF_6.

An infrared examination was made of the solid PuF_5 deposit which had formed with laser irradiation on windows of AgCl and also on windows of NaCl. The spectral absorption features were very similar in these two cases. A single absorption peak centered at 617 cm^{-1} was found. The full width at half maximum of this peak was about 15 cm^{-1}. When PuF_4 was formed by the thermal decomposition of PuF_6 and deposited on AgCl windows, no absorption was noted in the 600 to 700 cm^{-1} region.

To permit an infrared spectral comparison to be made between PuF_5 and UF_5, the latter compound was deposited photochemically by the reduction of UF_6 on a KCl window. A broad infrared absorption peak with a maximum at 505 cm^{-1} was observed; this absorption is very similar to that observed for PuF_5 at 617 cm^{-1}.

Nitrogen pumped dye lasers with outputs at 480, 500 and 520 nm were found to decompose PuF_6 photochemically with decreasing efficiency, and a practical threshold energy is that corresponding to the 520 nm wavelength. A dye laser with an output of 560 nm did not

reduce PuF_6 when used as the single source of radiation; however a photodecomposition occurred when this wavelength was combined with a dye laser with an output of 794 nm. In the experimental arrangement used, both dyes were pumped with the same nitrogen laser so that appropriate synchronization was assured.

PuF_6 was also photochemically decomposed in an all quartz cell of 1 cm path length with the nitrogen laser. After removing the excess PuF_6, a white deposit remained which has been identified above as PuF_5. The deposit was dissolved rapidly and completely in an aqueous solution mixture of saturated $Al(NO_3)_3$ and 0.1M HNO_3. A pink color characteristic of PuO_2^+ was observed initially. A spectrophotometric examination of the solution indicated the presence of both PuO_2^+ and Pu^{+4} ions, both products of the disproportionation of the PuO_2^+ ion.

The foregoing examples are merely illustrative of preferred embodiments of the invention and do not limit in any way the scope of the invention. It will be understood that the scope of the invention is as set forth in the Summary of the Invention and encompassed by the broad claims appended hereto.

What we claim is:

1. As a composition of the matter, the compound PuF_5.

2. A method of preparing PuF_5 which comprises irradiating PuF_6 with radiation having a wavelength less than 520 nm and an intensity sufficient to photodissociate said PuF_6 to PuF_5.

3. The method of claim 2 wherein said radiation has a wavelength of about 337 nm.

4. The method of claim 2 wherein said radiation has a wavelength of about 480 nm.

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