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# ULTRAVIOLET-ACTIVATED SYNTHESIS OF PLUTONIUM HEXAFLUORIDE AT ROOM TEMPERATURE

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## Introduction

Literature reports indicate that pure $PuF_6$ is decomposed by light (1,2). We have also observed that the irradiation of pure, gaseous $PuF_6$ by ultraviolet light at room temperature results in the production of a solid, suggesting the decomposition of $PuF_6$. On the other hand, we have recently observed that the ultraviolet irradiation of mixtures of solid $PuF_4$ and gaseous fluorine at room temperature have resulted in the production of $PuF_6$.

## Experimental

The irradiation of $PuF_4$-fluorine mixtures was carried out in a Monel cell constructed by welding pieces of 1-1/4 in. dia. Monel pipe to form a 90° cross. The four ends of the cross were fitted with synthetic sapphire windows held in place with threaded caps and teflon gaskets. Gases could be introduced to the cell or removed from it through a Hoke No. 1479 valve welded to the cell.

Plutonium tetrafluoride powder was added to the cell through one end, the winow at that end was put into place, and the cell was evacuated and tested for leaks. Gaseous fluorine was then added to the cell to a pressure of 300 mmHg. A thin layer of the plutonium tetrafluoride powder adhering to one of the windows was exposed at room temperature to light of $\sim$3125 Angstrom wavelength from a Bausch & Lomb High Intensity Monochromator with the Bausch & Lomb "Super Pressure Mercury Source" lamp (SP-200).

The energy delivered to the cell by the monochromator was determined using the aqueous potassium ferrioxalate actinometer as described by

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Calvert and Pitts (3). The front window of the actinometer vessel was a sapphire window similar to that of the cell used for ultraviolet-activated synthesis of $PuF_6$. From the actinometric measurements, the light intensity just inside the front window was found to be $4 \times 10^{16}$ quanta/sec. The fraction of light transmitted by the fluorine-$PuF_4$ mixture was assumed to be negligible since the molar absorbancy index of fluorine[4] is sufficiently large that the fraction of 3125 Angstrom light transmitted through a 10-cm path of fluorine alone at 300 mmHg would be negligible.

## Results and Discussion

The production of gaseous $PuF_6$ in the cell was indicated by the appearance of the characteristic absorption spectrum of $PuF_6$ in the near infrared region (8500 to 12000 Angstroms) as measured by a Cary Model 14 spectrophotometer. The pressure of $PuF_6$ produced in the cell was calculated using the measured absorbance, the known values of the molar absorptivity index (5), and the cell length. An irradiation time of 1290 min produced a $PuF_6$ pressure of 5 mmHg. The weight of $PuF_6$ estimated by using this pressure, the ideal gas law, the temperature, and the volume of the cell is 7 mg.

The efficiency of production of $PuF_6$ in this experiment was estimated from the energy input to the cell and the amount of $PuF_6$ produced. Under the conditions of the experiment, the apparent quantum yield for the reaction was $4 \times 10^{-3}$ molecules $PuF_6$/quantum; in other terms, $7 \times 10^{-2}$ kilowatt-hours of energy would be required per gram of $PuF_6$ produced. The experiment described above does not indicate whether the production of $PuF_6$ results from the ultraviolet-activation of $PuF_4$, or fluorine, or both reactants. The efficiency of the reaction might be increased by optimizing the mechanics of exposing this heterogeneous system to light.

The synthesis of $PuF_6$ commonly employed involves the reaction at $>450^\circ C$ of gaseous fluorine or some other oxidative fluorinating agent with solid $PuF_4$ or $PuO_2$. The $PuF_6$ produced must be rapidly quenched to avoid the reverse reaction.

Pure $PuF_6$ is thermodynamically unstable with respect to $PuF_4$ and fluorine at room temperature. The rate of the thermal decomposition of $PuF_6$ to $PuF_4$ and fluorine at room temperature is very low, and therefore, $PuF_6$ is metastable at 25°C. Extrapolation of the experimental equilibrium constants (6) for the reaction of $PuF_4(s) + F_2(g) \rightleftarrows PuF_6(g)$ to 25°C indicates that only 0.004 mmHg of $PuF_6$ would be in equilibrium with 300 mmHg of fluorine. The pressure of $PuF_6$ (5 mmHg) produced in the presence of 300 mmHg of fluorine in the experiment described above is, therefore, considerably greater than the equilibrium value. The results of the experiment suggest that ultraviolet radiation and sufficiently high pressures of fluorine in contact with $PuF_4$ increased the rate of formation of $PuF_6$ above that expected for the thermally activated reaction.

The action of ultraviolet light on the $PuF_4$-fluorine system is similar to the action of gamma radiation on the $PuF_4$-fluorine system (7). Gamma radiation decomposed $PuF_6$ to $PuF_4$ and fluorine. On the other hand, the action of gamma radiation on stetems consisting of solid $PuF_4$ in the presence of 200-700 mmHg of fluorine resulted in the production of $PuF_6$ at pressures in excess of the thermal equilibrium values.

## References

1. B.Weinstock and J.G.Malm, J.Inorg. Nucl. Chem., 2, 380 (1956).
2. J.G.Malm, B.Weinstock and E.E.Weaver, J.Phys. Chem., 62 1506 (1958).
3. J.G.Calvert and J.N.Pitts, Jr., Photochemistry, p. 783, John Wiley and Sons, New York (1966).
4. R.K.Steunenberg and R.C.Vogel, J.Am. Chem. Soc., 78, 901 (1956).
5. M.J.Steindler and W.H.Gunther, Spectrochim. Acta, 20, 1319 (1964).
6. L.E.Trevorrow, W.A.Shinn and R.K.Steunenberg, J.Phys. Chem., 65, 398 (1961).
7. M.J.Steindler and D.V.Steidl in Chemical Engineering Division Summary Report, July-Sept. 1962, USAEC Report 6596, pp. 125-132.