

ene (66%), 4-methyl-2-pentanone to 1-chloro-2,4-dimethyl-1-pentene (60%), benzaldehyde to β -chlorostyrene¹⁸ (76%).

(4) **Reaction of Triphenylphosphine with Hydrogen Bromide.**—Triphenylphosphine (3.06 g., 0.0116 mole) was dissolved in 60 ml. of ether, and hydrogen bromide was bubbled into the solution. The white solid which resulted was filtered, washed with ether and dried. A 96% yield (3.85 g.) was obtained. The product was very soluble in methylene chloride and was recrystallized from methylene chloride by adding ether. The resulting triphenylphosphonium bromide decomposed between 170–198°.

Anal. Calcd. for $C_{18}H_{15}BrP$: C, 62.99; H, 4.70. Found: C, 63.20; H, 4.69.

In addition, 0.2228 g. of the solid was placed in 30 ml. of water and stirred for a short time. The triphenylphosphine was filtered off and washed. The filtrate and washings re-

(18) *n*^{25D} 1.5728. *Anal.* Calcd. for C_8H_7Cl : C, 69.33; H, 5.09. Found: C, 69.50; H, 5.25.

quired 5.54 ml. of 0.1164 *N* NaOH for titration of the HBr formed in the decomposition of triphenylphosphonium bromide. Calcd. for $C_{18}H_{15}BrP$: HBr, 23.58. Found: HBr, 23.42.

The tetraphenylborate, $[(C_6H_5)_3PH][B(C_6H_5)_4]$, could be prepared by mixing concentrated solutions of triphenylphosphonium bromide and sodium tetraphenylborate in methanol. The resulting white crystals decomposed beginning ca. 170° to a brown melt at 200°.

Anal. Calcd. for $C_{42}H_{38}PB$: C, 86.59; H, 6.23. Found: C, 86.89; H, 6.69.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY,^{1a} ARGONNE, ILLINOIS]

Reactions of Sulfur Tetrafluoride with Oxides, Oxyfluorides, and Fluorides of Uranium and Plutonium^{1b}

BY CARL E. JOHNSON, JACK FISCHER AND MARTIN J. STEINDLER

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Some quantitative and qualitative observations concerning the reaction of sulfur tetrafluoride with various fluorides, oxyfluorides and oxides of uranium and plutonium are presented. The reaction of sulfur tetrafluoride with plutonium hexafluoride in which plutonium hexafluoride is reduced to plutonium tetrafluoride is reported.

The previously known synthesis of sulfur tetrafluoride from sulfur and cobalt trifluoride² or elemental fluorine³ gave mixtures from which sulfur tetrafluoride could be isolated only with difficulty. It has now been found⁴ that sulfur tetrafluoride can be prepared readily by the reaction of sodium fluoride with sulfur dichloride in refluxing acetonitrile or by fluorination of sulfur, with chlorine and sodium fluoride at elevated temperatures and pressures.

Recently sulfur tetrafluoride has been reported to be a unique fluorinating agent in that it provides a direct and simple method for the synthesis of inorganic fluorides⁵ and the preparation of uranium hexafluoride from uranium trioxide.⁶

Experimental

Materials.—Uranium trioxide used in these experiments was obtained by thermal decomposition of $UO_4 \cdot 2H_2O$. It is necessary to dehydrate the $UO_4 \cdot 2H_2O$ above 300° to insure complete conversion to uranium trioxide. It was necessary to store the uranium trioxide in a desiccator to prevent its hydration. Chemical analyses were obtained

on the uranium trioxide; found 82.7% U, 16.7% oxygen; calculated 83.2% U, 16.8% oxygen.

The uranyl fluoride used was purchased from General Chemical Company. X-Ray diffraction analyses indicated anhydrous uranyl fluoride⁷ to be the predominant species present. Chemical analyses of the material gave the results: 76.8% U, 12.4% F and 10.8% oxygen. Calculated, 77.3% U, 12.3% F and 10.4% oxygen. The U_3O_8 used was "primary standard" material purchased from National Bureau of Standards and was used as received. The uranium dioxide used was material produced by the Argonne Chemical Engineering pilot plant group. Chemical analyses indicated it contained 87.2% U and 11.5% oxygen which compared favorably with the calculated content of 88.2% U and 11.8% oxygen. The uranium tetrafluoride was Mallinckrodt Chemical Works production grade material which was analyzed as containing 74.8% U and 25.2% F. The uranium hexafluoride used in the experiments was purchased from Oak Ridge National Laboratory. Prior to use the uranium hexafluoride was purified by distillation and fractionation to remove any hydrogen fluoride. The vapor pressure at zero degrees was determined and found to be 17.4 mm. The literature value⁸ is given as 17.6 mm.

The plutonium dioxide used was obtained from Los Alamos. The material was ignited at high temperature with no noticeable weight loss. By analysis the plutonium content was 87.5% Pu compared to a calculated content of 88.2% Pu. The plutonium tetrafluoride was obtained from Rocky Flats. Chemical analysis indicated 75.8% Pu and 24.2% F. The calculated content is 75.9% Pu and 24.1% F. The plutonium hexafluoride used was prepared by the reaction of plutonium tetrafluoride with fluorine. The gaseous plutonium hexafluoride formed was trapped at -80° and residual fluorine was removed. The vapor pressure of plutonium hexafluoride was determined to be 17.8 mm. at zero degrees. The literature value⁸ is 17.9 mm.

Prior to use commercial high purity fluorine, obtained from the Pennsylvania Salt Manufacturing Co., was passed

(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission at the Argonne National Laboratory, operated by the University of Chicago under Contract No. W-31-109-eng-38. (b) Presented at ACS Meeting, New York City, N. Y., September, 1960, paper #71.

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through a sodium fluoride bed at 100° to remove hydrogen fluoride.

Sulfur tetrafluoride was obtained from E. I. du Pont de Nemours and Co. in 500 cc. steel cylinders. Non-condensable gases were removed by distillation. Infrared analysis, made by comparing our scans with those in the literature,⁹ of the purified gas indicated only trace amounts of thionyl fluoride as an impurity presumably arising from the reaction of sulfur tetrafluoride with trace amounts of moisture. The sample was analyzed chemically by treating the gas with potassium. The excess potassium reacted with ethyl alcohol and the alkaline solution was diluted to volume with water. Fluorine was determined by thorium nitrate titration of F⁻ ion and sulfur by reaction of SO₃²⁻ ion with iodine and titration of the excess iodine to the starch endpoint with sodium thiosulfate. Sample I, 70.3% F, 28.8% S; Sample II, 69.8% F and 30.0% S. The calculated values are 70.4% F and 29.6% S.

The vapor pressure of sulfur tetrafluoride was measured at -77.3° and found to be 57.5 mm. compared with the literature value of 58.0 mm.³ Vapor density determinations of sulfur tetrafluoride gave a value for the molecular weight of 108.3 ± 0.1 compared with the calculated molecular weight of 108.07.

Apparatus and Procedure.—A 1.236 liter nickel vessel heated by a resistance wound furnace was used to study the stoichiometry of the reactions involving uranium compounds. The reaction vessel was connected to a service manifold equipped with a supply of sulfur tetrafluoride, a source of vacuum, thermocouple gauge and a cold trap. Also connected to the manifold were a Booth-Cromer¹⁰ pressure transmitter and an infrared cell. Packless (Hoke 413) diaphragm valves were used throughout the system. The entire manifold was heated by resistance wire to facilitate the movement of uranium hexafluoride in the system. The reaction vessel was equipped with a Teflon gasketed, flared entry port for the insertion of solids. A calibrated thermocouple positioned in a thermocouple well in the vessel was used for measuring temperature. The infrared cell was fabricated from nickel and fitted with silver chloride windows. The volume of the system was calibrated to allow quantitative measurements of the gases.

A Beckman IR-4 infrared spectrophotometer equipped with NaCl and KBr optics was used for qualitative analysis of gaseous species.

A typical stoichiometry experiment was carried out as follows: the equipment was first evacuated to a pressure of one micron or less. The closed reaction vessel was removed from the manifold and placed in a dry box where a weighed quantity of the solid reactant was added. After replacing the vessel on the manifold and evacuating to a pressure of one micron or less, a measured quantity of sulfur tetrafluoride was added. The vessel was closed and brought to temperature. At the end of the reaction period a sample of gas was taken for infrared analysis. The remainder of the gaseous products were condensed, weighed and hydrolyzed for chemical analysis. In order to remove any unreacted uranium compound an excess of fluorine was introduced into the heated vessel. The uranium hexafluoride produced was trapped at -80°, hydrolyzed and chemically analyzed. Before the vessel could be used for another experiment it had to be flushed a few times with sulfur tetrafluoride to remove fluorine that had adsorbed on the interior surface of the vessel. Heating and evacuation were insufficient to remove adsorbed fluorine. Chemical reaction with sulfur tetrafluoride to form sulfur hexafluoride appeared to insure complete removal of the fluorine.

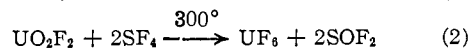
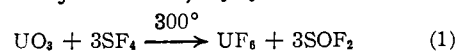
The special equipment and manipulators required for the safe handling of plutonium compounds are a consequence of the combined radioactivity and high toxicity of plutonium. Furthermore, plutonium dioxide and plutonium tetrafluoride were utilized in the form of finely divided solids and plutonium hexafluoride as a volatile solid. Therefore special apparatus and techniques were necessary to handle the plutonium compounds. The details of the equipment and experimental procedures are given in detail elsewhere.¹¹

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Results

Reaction of Sulfur Tetrafluoride with: Uranium Trioxide, Uranyl Fluoride, U₃O₈.



The reaction of sulfur tetrafluoride with uranium trioxide yielded uranium hexafluoride and thionyl fluoride as products as shown in equation 1. This was confirmed both by chemical analysis and infrared analysis of the gaseous products. Analytical data are contained in Table I indicating that three moles of sulfur tetrafluoride are required for each mole of uranium trioxide.

TABLE I
REACTION BETWEEN SF₄ AND UO₃ AT 300°

Initial SF ₄ mmole × 10 ³	Initial UO ₃ mmole × 10 ³	Reacted SF ₄ mmoles × 10 ³	Reacted UO ₃ mmole × 10 ³	Reacting ratio SF ₄ :UO ₃
11.8	5.24	11.2	3.59	3.12:1
12.8	3.37	10.0	3.25	3.08:1

Kinetic rate studies have indicated that the reaction has an appreciable rate at 300°. There were no experiments done above 425° as the stability of uranium trioxide is doubtful above this temperature. Examination of the uranium trioxide after momentary contact with sulfur tetrafluoride has definitely established that anhydrous uranyl fluoride is an intermediate in the reaction.

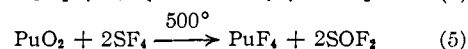
In experiments with uranyl fluoride and sulfur tetrafluoride, as shown in equation 2, only uranium hexafluoride and thionyl fluoride were found as products. The chemical analysis resulted in a mole ratio of 2/1 sulfur tetrafluoride to uranyl fluoride as indicated in Table II. The stoichiometry found adds support to the thesis that uranyl fluoride is the first step intermediate in the reaction between uranium trioxide and sulfur tetrafluoride.

TABLE II
REACTION BETWEEN SF₄ AND UO₂F₂ AT 300°

Initial SF ₄ mmoles × 10 ³	Initial UO ₂ F ₂ mmole × 10 ³	Reacted SF ₄ mmoles × 10 ³	Reacted UO ₂ F ₂ mmole × 10 ³	Reacting ratio SF ₄ :UO ₂ F ₂
8.02	3.25	6.40	3.08	2.08:1
6.97	4.85	6.85	3.44	1.99:1

The reaction of sulfur tetrafluoride with U₃O₈ resulted in the formation of uranium hexafluoride and uranium tetrafluoride as the uranium products and thionyl fluoride as the sulfur product as shown in equation 3. The sulfur product was identified by infrared analysis. Chemical analysis of the uranium product indicated that a ratio of two moles of uranium hexafluoride and one mole of uranium tetrafluoride were formed for each mole U₃O₈ used.

Reaction of Sulfur Tetrafluoride with: Uranium Dioxide, Plutonium Dioxide



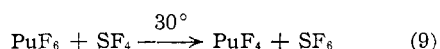
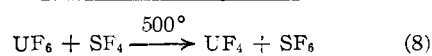
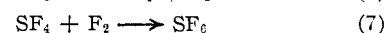
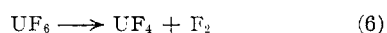
(11) M. J. Steindler, D. V. Steidl and R. K. Steunenberg, The Fluorination of Plutonium Tetrafluoride, ANL-5875, June 1958.

The experimental apparatus was modified slightly for these experiments in that a flow system was used rather than a closed vessel as specified previously. For the reaction with uranium dioxide, as shown in equation 4, weight change in addition to chemical analysis indicated that the reaction becomes significant only at temperatures above 450°. Smith¹² indicated complete conversion of uranium dioxide to uranium tetrafluoride in 10 hr. at 350° and 300 atmospheres pressure. In our experiments no perceptible change had occurred in 1 hr. at 350° and atmospheric pressure. In 1 hr. at 500°, an 85.5% conversion of uranium dioxide to uranium tetrafluoride was found.

In experiments with plutonium dioxide, as shown in equation 5, weight change and X-ray diffraction analyses were used to follow the extent of the reaction. Plutonium dioxide presents a parallel to uranium dioxide in that no detectable reaction occurred in 1 hr. at 375°. In 1 hr. at 600°, 45% of the plutonium dioxide was converted to plutonium tetrafluoride.

Reaction of Sulfur Tetrafluoride with: Uranium Tetrafluoride, Plutonium Tetrafluoride.—Under the experimental conditions of large excesses of sulfur tetrafluoride and temperatures up to 600°, no apparent reaction occurred between either uranium tetrafluoride or plutonium tetrafluoride and sulfur tetrafluoride. Sulfur tetrafluoride is not capable of acting as an oxidizing agent in these systems.

Reaction of Sulfur Tetrafluoride with: Uranium Hexafluoride, Plutonium Hexafluoride



The extent of the reaction of uranium hexafluoride with sulfur tetrafluoride, equation 8, was observed by the change in pressure. Infrared analysis of the gas showed the presence of sulfur hexafluoride. No reaction was observed at 300°.

(12) W. C. Smith, E. I. du Pont de Nemours and Co., private communication.

At 500° there is an observable rate of reaction. At this temperature, however, the stability of uranium hexafluoride in nickel equipment is somewhat doubtful.¹³ The apparent reaction of sulfur tetrafluoride, equation 7, may be due to the presence of fluorine originating from the thermal decomposition of uranium hexafluoride, equation 6. The above equations are not intended to imply that uranium tetrafluoride is the sole uranium product of decomposition. Intermediates such as U_4F_{17} and UF_5 also may be formed.

It was observed that plutonium hexafluoride definitely reacts with sulfur tetrafluoride, as shown in equation 9. The extent of the reaction was calculated by assuming that all the plutonium hexafluoride distilled from a supply vessel into the reaction vessel would appear as plutonium tetrafluoride when the reaction was completed. The amount of plutonium tetrafluoride formed was measured by weight gain of the reaction vessel. Calculations of this type indicated a minimum of 98% reaction. Chemical analysis of the solid reaction product for fluorine and plutonium gave an atom ratio of fluorine to plutonium of 4.14/1.

The gaseous product of the reaction was also identified. The pressure of the gaseous product was measured and found to be equal to that of the original sulfur tetrafluoride pressure. The sulfur fluoride gases were separated from one another by selective hydrolysis in water of the excess sulfur tetrafluoride. Results indicated 1.14 millimoles of sulfur hexafluoride present compared to 1.17 millimoles of plutonium hexafluoride initially used. Vapor density determination on the gaseous residue of the hydrolysis indicated a molecular weight of 143.4 for the gas compared to 146.0 for sulfur hexafluoride.

In summary, in all the reactions studied, we have found sulfur tetrafluoride to be a good fluorinating agent. Under no circumstances did sulfur tetrafluoride act as an oxidizing agent and in reaction with plutonium hexafluoride it acted as a reducing agent.

Acknowledgments.—The authors wish to acknowledge the assistance of T. Gerding and D. Steidl in the experimental determinations.

(13) A. E. Florin, Los Alamos, private communication.