[CONTRIBUTION FROM UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

New Compounds of Quadrivalent Americium, AmF_4, $KAmF_5$[1]

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Two new compounds, $KAmF_5$ and AmF_4, were prepared by reaction of fluorine gas with Am(III), Am(IV) or Am(V) compounds. The fluorinations proceed readily at 500° and one atmosphere of fluorine.

The known oxidation states of americium are (III),[2a] (IV),[2a] (V)[2b] and (VI),[3] of which (III), (V) and (VI) have been found in solution. The only compound of Am(IV) known prior to this work has been the dioxide, AmO_2.[2a,4] The composition of this compound was found to be $AmO_{1.98 \pm 0.02}$.[5]

At the time this work was carried out, thermal data derived from the heat of solution of AmO_2 indicated that the free energy for the reaction $AmF_3(c) + 1/2F_2(g) = AmF_4(c)$ was -10.5 kcal./mole at 298°K., or -0.5 kcal./mole at 1000° K.[6] More recent work indicates that the free energy of the above reaction may be considered more negative, of the order of -22 kcal./mole at 1000°K.[7]

Similar calculations indicate that AmF_5 may be capable of existence at 298°K. and one atmosphere of fluorine gas, but not at much higher temperatures. Since the values used in the calculations are obtained indirectly, the successful production of AmF_4 would serve as a check on the general validity and order of magnitude of these thermodynamic quantities. Previous attempts to prepare AmF_4 by treatment of the Am(III) fluoride with fluorine gas at elevated temperatures yielded no tetrafluoride.[8]

Experimental

Purity of the Americium Stock.—The americium stock solutions used in this study were purified by J. P. Nigon. Spectrochemical analysis of this stock by Oliver Simi of this Laboratory showed no amounts of cations above the limits of detection.

Preparation of Starting Materials.—Americium dioxide was prepared by precipitation of the Am(III) oxalate from a solution 0.1 *M* in nitric acid and 0.1 *M* in ammonium oxalate. This oxalate was heated in a stream of oxygen to 350° for one hour to convert to black AmO_2.

Americium trifluoride was prepared by precipitation from a solution 1 *M* in nitric acid and 2 *M* in hydrogen fluoride. This precipitate was washed with water, then with acetone and dried on a water-bath at 85°. The material prepared in this way appears to be much more reactive than that prepared by treatment with gaseous hydrogen fluoride at 600–700°.

The preparation of $NaAmO_2(C_2H_3O_2)_3$ was carried out in the manner previously described.[3] The compound was washed with acetone and air-dried.

The solid Am(V) compound was prepared by oxidation with NaOCl in saturated K_2CO_3 solution.[9] This compound was washed with water until partial peptization occurred, then twice with acetone and dried on a water-bath.

Tank fluorine was used with no further purification.

Apparatus.—The fluorination was carried out in a 1 inch i.d. nickel tube 12 inches in length. The inlet end of this tube was welded to a 3 inch length of 0.25 inch nickel tubing which, in turn, was silver soldered to the copper tubing supplying the gases used. A brass flange with screw threads was silver soldered to the exit end of the tube. A threaded brass cap with a Teflon gasket was used to close the end of the tube, and a small Hoke valve was connected to this to allow sealing off of the system.

The sample, in the form of a powder, was placed in a small nickel holder to which was affixed a long nickel wire as a handle. This container was inserted through the exit end of the reaction tube to the heated zone near the inlet.

The nickel reaction tube was heated at the inlet end by means of a 4 inch nichrome heating element. The temperature was measured by means of a Cr–Al thermocouple between the heating element and the nickel tube. A Micro-max recorder–controller was used to control the temperature.

The connecting tubing was of copper with either flared or silver soldered connections. Small brass Hoke diaphragm needle valves controlled gas flow, except for fluorine, where Monel valves with Teflon seats were used. A Welch Duo-Seal mechanical pump without trap was used to establish a vacuum in the system. The pressure was read by means of a thermocouple gage.

Procedure.—The substance to be fluorinated was placed in the nickel sample holder and this placed in the nickel reaction tube. The system was then evacuated to 20 μ or less, fluorine gas added to 1 atmosphere and allowed to flow through the apparatus at about 3 cc. per minute, while the temperature was raised to 500° over a period of about 0.5 hour. The heating was continued for one to two hours, after which the tube was allowed to cool slowly in the stream of fluorine. Argon was added and allowed to flow through rapidly for 10–20 minutes. The system was then opened and the sample removed.

Results

X-Ray powder patterns of the product of fluorination of either AmF_3 or AmO_2 show it to be isomorphous with UF_4, NpF_4 and PuF_4.[10,11] It is monoclinic with $a_0 = 12.47$ kX., $b_0 = 10.45$ kX., $c_0 = 8.18$ kX., $\beta = 126 \pm 1°$. The salt is microcrystalline, tan in color, and in large aggregates has an orange cast. No single crystals exceeding 3 μ have been made. In common with UF_4[12] and PuF_4,[10] the compound is biaxial negative with a moderate optic axial angle. The refractive indices are slightly higher than those of the corresponding PuF_4. Upon addition of water to the compound, there is a slow evolution of gas, and the tetrafluoride is converted into very fine-grained birefringent aggregates which give the characteristic absorption spectrum of Am(III).

(1) This work was sponsored by the AEC.

(2) (a) B. B. Cunningham and L. B. Asprey, AECD-2946 (1950); see also B. B. Cunningham, "The Transuranium Elements," National Nuclear Energy Series, McGraw-Hill Book Co., Inc., N. Y., 1949, Vol. 14B, Part II, p. 1363–1370; (b) L. B. Werner and I. Perlman, THIS JOURNAL, **73**, 495 (1951); see also AECD-2898 (1950).

(3) L. B. Asprey, S. E. Stephanou and R. A. Penneman, *ibid.*, **73**, 5715 (1951).

(4) First identified by W. H. Zachariasen from X-ray diffraction studies.

(5) L. B. Asprey, UCRL-329 (1949).

(6) L. Eyring, H. R. Lohr and B. B. Cunningham, THIS JOURNAL, **74**, 1186 (1952).

(7) Private communication from B. B. Cunningham.

(8) S. Fried, THIS JOURNAL, **73**, 416 (1951).

(9) J. P. Nigon, R. A. Penneman, E. Staritzky, T. K. Keenan and L. B. Asprey, *J. Phys. Chem.*, in press.

(10) W. H. Zachariasen, MDDC-1152 (1947).

(11) W. H. Zachariasen, "The Transuranium Elements," National Nuclear Energy Series, McGraw-Hill Book Co., New York, N. Y., 1949, Vol. 14B, Part II, pp. 1462–1472.

(12) E. Staritzky, to be published shortly.

The product of the fluorination of the solid Am(V) compound, when analyzed by X-ray powder diffraction methods, is isomorphous with $KPuF_6$[9] and is assigned the formula $KAmF_6$. It is rhombohedral with a_0 = 9.27 kX., α = 107° 35′. No evidence of the formation of AmF_5 was obtained at 500°, although it may be stable at lower temperatures.

The fluorination of the Am(VI) compound resulted in an X-ray pattern which could not be interpreted.

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NOTES

Pentafluoropropionyl Hypofluorite

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Fluorine replaces the hydrogen in trifluoroacetic acid forming trifluoroacetyl hypofluorite.[2] It has now been found that pentafluoropropionyl and probably heptafluorobutyryl hypofluorites may be formed by similar reactions.

Pentafluoropropionyl hypofluorite, C_2F_5COOF, is a colorless gas which rapidly liberates iodine from a solution of potassium iodide. When at a pressure of a few millimeters of mercury and at temperature ranging from −40° to above 25°, it decomposes at a moderate rate forming carbon dioxide and hexafluoroethane. It also decomposes explosively. From vapor pressures at temperatures below −25° it is estimated that the substance has a normal boiling point of about 2°. The compound appears to be less stable than trifluoroacetyl hypofluorite.

By use of the same technique as that employed for reaction of trifluoroacetic acid with fluorine, with the exception that the trap containing the acid was kept at room temperature, it was found that only very small yields of explosive products were obtained from pentafluoropropionic acid and heptafluorobutyric acid. When the procedure was modified by placing about 2 ml. of water in the reaction vessel (Part C of the figure in reference 1) and by removing trap A, the yield of explosive product was greatly increased. The apparatus for condensing and distilling the product was also improved by replacing trap W (ref. 1) and still U by a U-tube trap surmounted by a reflux condenser. This device could be used to collect the crude product and later to purify it by distilling away the products more volatile than pentafluoropropionyl hypofluorite.

Preparation.—A stream of dry nitrogen flowing at a rate of about 5 l. per hour bubbled through pentafluoropropionic acid at approximately 25° and carried the vapor of this acid into a 900-ml. polyethylene reaction vessel where this gas stream mixed and reacted with a stream of fluorine flowing at a rate of approximately 1.5 g. per hour. A 2-ml. volume of water was present in the bottom of the reaction vessel. The gases passed through a polyethylene trap cooled to −78°, where much of the hydrogen fluoride by-product condensed. Gases from this trap passed through a 20-ml. glass trap, referred to above, cooled to −183°. Later this trap was used as the pot of a still and the distilling material was caused to reflux by a condenser cooled by solid carbon dioxide. Under these conditions about 0.53 g. of pentafluoropropionyl hypofluorite was obtained in three hours from 4.9 g. of pentafluoropropionic acid. The actual production must have been higher than this, because some of the hypofluorite apparently condensed and was lost in the trap cooled to −78°. In two different runs this trap collected enough of the product to explode with moderate violence.

After stopping the flow of fluorine and pentafluoropropionic acid, the system was flushed with dry nitrogen. Two different procedures were used to obtain the liquid form of the compound in high concentrations and to permit its identification.

Identification.—In the first of the two procedures the liquid oxygen in the Dewar flask surrounding the trap was removed. After the trap had warmed to about −90°, solid carbon dioxide was used to keep the trap cool. While the temperature rose, gases escaped from the trap, but nearly all of the pentafluoropropionyl hypofluorite remained as a colorless liquid. With the liquid held at −78° successive portions of gas were withdrawn from the trap in the manner described in reference 1. At first the removal of each portion reduced the pressure in the system. After numerous samples had been withdrawn, however, the pressure remained constant, at about 6 mm., approximately the vapor pressure of the hypofluorite at −78°. When stored in the line, this vapor decomposed slowly. Before decomposition it could be exploded with the help of a "leak-tester" Tesla coil, the pressure rising to about 12 mm. When the material behaved in this manner, it was assumed that the liquid in the trap was highly concentrated pentafluoropropionyl hypofluorite. By allowing the temperature of the trap to rise to about −60° pressures of the vapor higher than 6 mm. were obtained.

Samples of material were then evaporated from the trap simply by opening a stopcock to permit vapor to flow successively into different glass flasks attached to mercury manometers. Samples were taken rapidly one immediately after the other to reduce the extent of decomposition of the hypofluorite due to standing in the system. The pressure of each sample rose rapidly at first due to the decomposition of the pentafluoropropionyl hypofluorite, and within about 30 minutes it increased to about 1.7 times the original value. After this the decomposition continued more and more slowly, but eventually the pressure nearly doubled. Typical values for the increase factor were: 1.87, 1.92, 1.88, 2.06. From densities of the samples, it was possible to calculate the molecular weight of the hypofluorite. Since the initial pressures were small and rather difficult to measure, the molecular weights were not very precise; typical values: 185, 186, 178, 193, 185, 170, 189, 170, 191, 175, 183, 177 (average, 182). The theoretical value for C_2F_5COOF is 182.02.

In the second identification procedure the hypofluorite

(1) An abstract of the M.S. Degree thesis of Andrew Menefee, 1953.

(2) G. H. Cady and K. B. Kellogg, THIS JOURNAL, **75**, 2501 (1953).