The product of the fluorination of the solid Am(V) compound, when analyzed by X-ray powder diffraction methods, is isomorphous with $KPuF_5$[9] and is assigned the formula $KAmF_5$. It is rhombohedral with $a_0$ = 9.27 kX., $\alpha$ = 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.

The author is indebted to J. P. Nigon of this Laboratory for the purification of the americium used in this study. He wishes to express appreciation to B. B. Cunningham of the Berkeley Radiation Laboratory for the free energy data and for his helpful encouragement. He also wishes to thank J. Singer and F. H. Ellinger of this Laboratory for the X-ray diffraction measurements and E. Staritzky, also of this Laboratory, for the optical crystallographic measurements.

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# NOTES

## Pentafluoropropionyl Hypofluorite

BY ANDREW MENEFEE[1] AND GEORGE H. CADY

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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

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[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).

was boiled with reflux, the condenser being at −78°. The material decomposed slowly during this operation and the decomposition products were measured and analyzed. When attempts were made to conduct the distillation under atmospheric pressure, the material exploded. By conducting the distillation at pressures below 200 mm. (preferably below 100 mm.) it was possible to avoid an explosion. The decomposition was rapid enough, however, to permit the removal of products at a moderate rate. As the pentafluoropropionyl hypofluorite boiled with reflux, the temperature at the bottom of the still was measured with a thermocouple. In this manner pressure *vs.* boiling temperature measurements were made. Values are given in Table I. As the decomposition occurred successive cuts of the products were collected in small glass flasks.

TABLE I

VAPOR PRESSURE OF $CF_3CF_2COOF$

| °C. | Mm. | °C. | Mm. | °C. | Mm. |
|---|---|---|---|---|---|
| −58.4 | 30 | −44.5 | 79 | −29.7 | 167 |
| −54.9 | 37 | −42.7 | 91 | −28.6 | 177 |
| −50.0 | 53 | −41.9 | 96 | −27.3 | 187 |
| −46.8 | 67 | −40.7 | 102 | −25.4 | 208 |

The fluorine content of a middle cut from a distillation was determined by treating the gas with hot potassium and later titrating the fluoride ion in the reaction products. By this method a value of 62.4% fluorine was found. More extensive and complicated analyses of other samples permitted the fluorine content to be calculated. In one run the two middle cuts were found to contain 60.9% and 63.1% F and in another run 62.0% and 62.3% F (theoretical for $C_2F_5$-COOF, 62.6% F).

The more complex analysis involved the following steps: (1) measurement of the weight and volume of the sample, (a) as originally obtained, (b) after contact with and removal from air-free water, (c) after subsequent contact with and removal from sodium hydroxide solution; (2) titration of fluoride ion in the water and in the sodium hydroxide solutions resulting from this contact; (3) titration of the hydroxide ion and the carbonate ion remaining in the alkaline solution; (4) further examination of the part of the gas not absorbed by the water or caustic soda solution. These analyses led to the following conclusions: (1) The first and last fractions of decomposition products from a distillation contained some material, perhaps silicon tetrafluoride, which reacted with water to give fluoride ion. (2) Middle fractions contained only a little of this material and appeared to be uniform in composition, being composed of carbon dioxide (50% by volume) and a gas which was nearly all hexafluoroethane (50% by volume). (3) This fluorocarbon product had a density very close to 138 g. per G.M.V. Upon fractional distillation only hexafluoroethane was detected; however, small amounts of a less volatile fluorocarbon and of carbon tetrafluoride could have been present. When the vapor pressure of the whole fluorocarbon sample was measured using a static method, evidence was found for the presence of a small proportion of a material (probably $CF_4$) more volatile and less dense than hexafluoroethane. When the product boiled away the last part to distil had a density of 143. When the material was frozen and then allowed to warm slowly, it melted over a temperature range from −110 to −102° (melting point of $C_2F_6$, −100.1°).

A mass spectrometer was used to study the somewhat impure hexafluoroethane. Very strong peaks were found which corresponded to $C_2F_8$ and there were very weak lines at masses 150 and 169 which might have come from $C_3F_8$. Since the peaks due to $CF_4$ are also present in the mass spectrum of $C_2F_6$, no conclusion could be drawn about the presence or absence of a small amount of carbon tetrafluoride.

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## Some Physical Properties of the Deutero-germanes[1]

BY ALFRED H. ZELTMANN AND GEORGE C. FITZGIBBON

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Some deutero-germanes have been prepared in this Laboratory and a number of their physical properties measured. The results are summarized in Table I.

TABLE I

PHYSICAL PROPERTIES OF THE DEUTERO-GERMANES

| Compound formula | M.p., °C. | B.p., °C. | $d^t_4$, g. | $t$, °C. | $-\Delta H$, cal./gram mole | $B$ |
|---|---|---|---|---|---|---|
| $GeD_4$ | −166.2 | −89.2 | 1.684 | −160.5 | 3744 | 7.327 |
| $Ge_2D_6$ | −107.9 | 28.4 | 2.184 | −106.4 | 6483 | 7.579 |
| $Ge_3D_8$ | −100.3 | 110.5 | 2.618 | − 99.9 | 7876 | 7.367 |

### Experimental

**Preparation.**—The method of preparation was essentially that of Dennis, *et al.*,[2] used in the preparation of the ordinary germanes.

Deutero-hydrochloric acid, prepared[3a] by slowly adding $D_2O$ to refluxing benzoyl chloride and diluted with $D_2O$ to 4 *N*, was added dropwise to magnesium germanide, $Mg_2Ge$[2,3b] with frequent shaking. The resultant products were carried through a drying and purification train using dry helium gas.

Early runs indicated that thermal exchange of deuterium and hydrogen occurs between germanes and water. To prevent exchange heavy water was used in scrubbing towers which separated DCl and $GeDCl_3$ from the products. The products were then passed in succession over anhydrous calcium chloride and phosphoric acid anhydride to remove $D_2O$ vapor. The products were collected in liquid nitrogen cold traps while the helium was allowed to escape. After collection the products were subjected to a fractionation in an all-glass vacuum system using Stock valves instead of stopcocks where possible.

Purified $GeD_4$ was prepared by maintaining a mixture of germanes at −155° with a Freon cold trap and then pumping a vacuum. While this method caused a loss of some $GeD_4$, it resulted in a purer product. The mixture of germanes was allowed to warm from −155 to −145° and maintained at this temperature where the vapor pressure of $GeD_4$ is about 10 mm. The distilled $GeD_4$ was collected in a bulb cooled with liquid nitrogen. This fractionation was repeated twice or until a satisfactory product resulted as shown by vapor pressure data.

Pure $Ge_2D_6$ was obtained by a similar procedure using the residual mixture of germanes. A vacuum was drawn while maintaining the mixture at −120° to remove any residual $GeD_4$. The mixture was then allowed to warm to −75° while surrounded by a $CHCl_3$-$CCl_4$ eutectic cooling mixture.[4] The distillate was collected in a bulb cooled with liquid nitrogen. This fractionation was also repeated several times.

Pure $Ge_3D_8$ was obtained by maintaining the mixture at −50° with a $CHCl_3$–$CCl_4$ bath while pumping a vacuum. A large portion of the product was lost, but this procedure was necessary in order to remove the last traces of $Ge_2D_6$. The temperature was allowed to increase to −20° and the $Ge_3D_8$ collected in a liquid nitrogen cold trap. This fractionation was repeated several times to yield a satisfactory product. An unidentified oily residue remained.

Mixtures of germanes were detected by taking vapor pressure data on a given sample before and after a fractionation. The fractionation procedure was repeated until separate fractions yielded identical results. Mass spectrometric

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[1] This document is based on work performed for the Atomic Energy Commission at Los Alamos Scientific Laboratory.

[2] L. M. Dennis, R. B. Corey and R. W. Moore, THIS JOURNAL, **46**, 657 (1924).

[3] (a) H. C. Brown and C. Groot, *ibid.*, **64**, 2223 (1942); (b) C. A. Kraus and E. S. Carney, *ibid.*, **56**, 765 (1934).

[4] Amer. Inst. of Physics, "Temperature, Its Measurement and Control," Reinhold Publ. Corp., New York, N. Y., 1941, p. 208.