[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Arsenyl Fluoride

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Arsenyl fluoride, $AsOF_3$, is obtained by fluorinating a mixture containing equimolecular quantities of arsenic trichloride and glassy arsenious oxide. The compound boils at −25.6° and melts at −68.3°. The infrared absorption has a peak at 811 cm.$^{-1}$ which may be attributed to the stretching frequency of the As=O link.

Arsenic differs from phosphorus by having a tendency not to form oxyhalides. No well-defined oxyhalide compound of arsenic, either in the trivalent or in the pentavalent state, is known. The brown colored sticky mass left after refluxing arsenious acid and concentrated hydrochloric acid had been suggested to be AsOCl by previous workers.[2,3] This, however, requires further confirmation.

In this research arsenic(III) oxide, arsenic(V) oxide, arsenious acid, glassy arsenic(III) oxide and a mixture containing equimolecular quantities of glassy arsenic(III) oxide and arsenic trichloride were fluorinated under different conditions. Arsenyl fluoride, whose corresponding phosphorus homolog has been known for a long time, was isolated as a product of the reaction. There was also some evidence for the formation of tetrafluoroarsenic hypofluorite, AsF_4OF. This latter compound, however, was not isolated in the pure state.

Experimental

Preparation.—The arsenic compound to be fluorinated was placed in two nickel boats of approximately 20-cc. capacity each. The boats were placed within a nickel tube capable of being heated to 250°. A stream of a gaseous mixture containing different proportions of nitrogen and fluorine was passed through this tube at different temperatures and the product was passed through glass traps at −183°. The results obtained under various conditions are summarized below.

(1) Arsenic(V) oxide yielded arsenic pentafluoride under all conditions. At a temperature less than 50° arsenic(III) oxide seemed to react with fluorine slowly. Well diluted fluorine at this temperature resulted in the formation of a large amount of arsenic trifluoride. Above 60° the reaction started vigorously and arsenic pentafluoride was the major product.

(2) Glassy arsenic(III) oxide at a temperature of 80° and in the presence of excess of fluorine (the gas leaving the cooled trap contained fluorine) yielded arsenic pentafluoride, containing traces of an oxyfluoride compound of arsenic which may have been tetrafluoroarsenic hypofluorite.

(3) A mixture containing equimolecular quantities of arsenic trichloride and glassy arsenic(III) oxide at a temperature of 180° and in the presence of an excess of fluorine yielded in addition to arsenic pentafluoride, arsenyl fluoride and traces of a red colored compound having a high boiling point.

Eight grams of arsenic(III) oxide placed in a covered porcelain dish was heated for about an hour. The glassy arsenic(III) oxide thus obtained was powdered and mixed thoroughly with 32 g. of arsenic trichloride. Fluorine, diluted with nitrogen, was passed over this mixture at room temperature. After a large part of the chlorine had been replaced by fluorine, the nickel reactor was heated to 180° and 8 to 10 liters of fluorine and 3 liters of nitrogen was passed per hour through the reactor. The material which collected in the cold trap was divided into two parts by distillation. The first portion, which weighed about 40 g., distilled off below −20°. A small sample from this volatile fraction was passed through a gas chromatography column. Four peaks were obtained. The first substance was SiF_4; the second was arsenic pentafluoride; the third was chlorine and the fourth was a substance which boiled near −30° and had a vapor density of about 148 g. per g.m.v. The second fraction of the product weighed about 5 g. In addition to an oily liquid which was recognized as AsF_3, it contained a red colored solid. As some of the compounds of trivalent arsenic have been reported to have red color, *e.g.*, AsI_3, AsP, etc., it may be that this red solid was a lower oxyfluoride of arsenic.

Fluorination of nitrous arsenious oxide yielded a liquid nearly all of which was boiled off at −53.6°. About 2 cc. of liquid boiling at −50 to −50.5° was obtained as the second fraction. The observed molecular weight of this compound was about 174. Mass spectrographic analysis of this compound revealed peaks for mass numbers 148 ($AsOF_3^+$), 129 ($AsOF_2^+$), 110 (AsOF), and 91 (AsO^+); peaks for 132 (AsF_3^+) and 113 (AsF_2^+), however, were much stronger than those for the oxyfluoride fragments. The mass spectrum and the boiling point of this fraction suggest the probable formation of tetrafluoroarsenic hypofluorite, which can be confirmed only after further study.

Separation and Analysis.—The more volatile portion of the product of method 3 was fractionally distilled, yielding arsenic pentafluoride (distilling temperature, −53.6°), chlorine, intermediate mixtures and about 2 ml. of liquid arsenyl fluoride. The latter distilled at about −27°.

As an alkaline solution of potassium hydroxide was admitted to a bulb containing a weighed sample of gaseous arsenyl fluoride a rapid reaction occurred. The solution was removed from the bulb, diluted to 250 ml. and analyzed for arsenic and fluorine. *Anal.* Calcd. for $AsOF_3$: As, 50.66; F, 38.51. Found: As, 49.83, 49.98; F, 38.22, 38.19.

Chemical Properties.—Arsenyl fluoride was found to be a reactive substance. It fumed in air and reacted exothermally with water according to the equations

$$AsOF_3 + H_2O = HAsO_2F_2 + HF \qquad (1)$$

$$AsOF_3 + 2H_2O = H_2AsO_3F + 2HF \qquad (2)$$

The solution was tested for $AsO_3F^=$ as well as $AsO_2F_2^-$ ions.[4,5] The sparingly soluble salts, $KAsO_2F_2$ and $BaAsO_3F$, were obtained from the solution. The yield of $BaAsO_3F$ was less than that of $KAsO_2F_2$. Arsenyl fluoride slowly reacted with mercury and was absorbed to some extent by Kel-F grease. $AsOF_3$ reacted with a solution of potassium iodide instantaneously and iodine was liberated. Approximately two equivalents of iodine were liberated for each mole of $AsOF_3$.

Physical Properties. Molecular Weight.—The average value of the molecular weight from five determinations was 147.8.

Melting Point.—The melting point of the compound was determined using apparatus described previously.[6] The observed value was −68.3°.

The vapor pressure of the compound was determined by measuring the boiling point under various pressures. The results are given in Table I. Extrapolation of the data gave 25.6° as the boiling point of the compound at 760 mm. pressure.

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[2] W. Wallace and F. Penny, *Phil. Mag.*, **4**, 361 (1852).

[3] L. Hurtzig and A. Geuther, *Liebig's Ann.*, **111**, 172 (1859).

[4] G. Mitra, *Science and Culture*, **19**, 216 (1953).

[5] G. Mitra and A. B. Ray, *ibid.*, **20**, 404 (1955).

[6] L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4243 (1951).

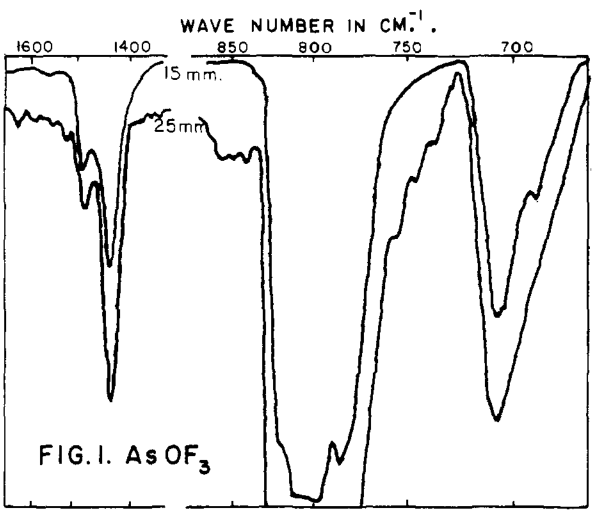

FIG. I. As OF$_3$

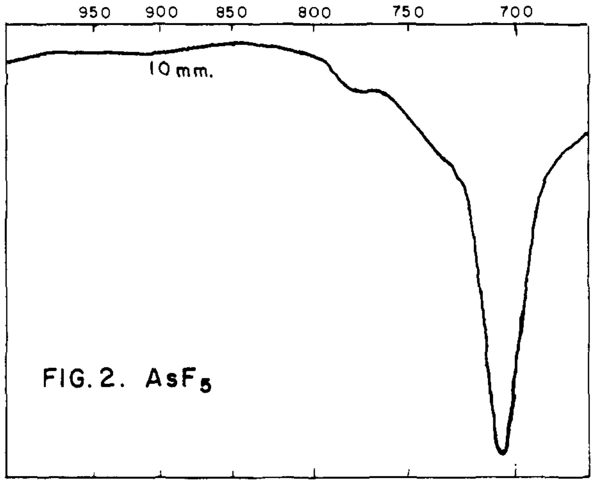

FIG. 2. AsF$_5$

Infrared Spectrum.—The infrared spectrum of the arsenyl fluoride using a 10 cm. long Pyrex glass cell, with sodium chloride windows was taken over the pressure range 2-15 mm. by means of a double beam Perkin-Elmer spectrometer, Model 21. The infrared absorption frequencies for As–F and As–O have not yet been reported. The absorption spectra of $AsOF_3$ and AsF_5 are given in Figs. 1 and 2. The following inferences were drawn.

TABLE I

VAPOR PRESSURE OF ARSENYL FLUORIDE

Temp., °K.	Pressure, mm.	Temp., °K.	Pressure, mm.
210.7	105.5	223.6	228.3
215.3	150.3	226.6	270.2
218.0	168.3	228.1	275.3

(1) AsF_5 at a pressure of 10 mm. gives a peak at 705 cm.$^{-1}$. The Raman spectrum of AsF_3 has been studied,[7] and As–F stretch has been observed in 707 cm.$^{-1}$. A peak has appeared at 703 cm.$^{-1}$ for $AsOF_3$. This is attributed to As–F stretching frequency.

(2) Two other peaks appeared for $AsOF_3$, one at 784 cm.$^{-1}$ and the other at 811 cm.$^{-1}$. These peaks are absent in AsF_5 spectra. Hence they are attributed to As–O link. Raman spectra of various arsenates have been studied.[8,9] Peaks in this region have been reported, *e.g.*, 810 cm.$^{-1}$ for Na_3AsO_4; 815 and 867 cm.$^{-1}$ for H_3AsO_4; 833 and 870 cm.$^{-1}$ for NaH_2AsO_4 and 836 cm.$^{-1}$ for $NaHAsO_4$.

(3) Two other peaks appeared for $AsOF_3$ in the small wave length region, one at 1425 cm.$^{-1}$ and the other at 1480 cm.$^{-1}$. These peaks may have been due to overtones. Further study however is required to confirm the actual nature of these peaks.

Mass Spectrum.—Mass spectrum analysis was made in a Consolidated Engr. Co. Type 21-103 spectrometer. Peaks for mass numbers 148 ($AsOF_3^+$), 129 ($AsOF_2^+$), 110 ($AsOF^+$), 91 (AsO^+), 156 (AsF_4^+), 132 (AsF_3^+), 113 (AsF_2^+) and 94 (AsF^+) were found. No peak for mass number 167 ($AsOF_4^+$) was obtained. The AsF_4^+ peak may have come out of the reaction of the fluoride ion and $AsOF_3$.

It is a pleasant duty of the author to acknowledge indebtedness to Professor G. H. Cady of the University of Washington for his help during the progress of the work. This research was supported in part by the Office of Naval Research.

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[8] Ghose and Das, *J. Phys. Chem.*, **36**, 586 (1932).

[9] Feher and Morgenstern, *Naturwissenschaften*, **25**, 618 (1937).

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Thermal Decomposition of Fluorine Nitrate

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Fluorine nitrate decomposes explosively into NOF and O_2. The slow thermal decomposition at about 100° is represented by the equation $NO_3F \rightarrow NO_2F + {}^1/_2O_2$. This is a first-order reaction, involving a Lindemann-Hinshelwood mechanism, and the rate is described by the equation $K_\infty = 5.80 \times 10^{13} \exp(29700/RT)$ sec.$^{-1}$. Although the experiments do not clearly indicate any one mechanism, it may be that the rate controlling step is $NO_3F \rightarrow NO_3 + F$, and that this is followed by $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$ and $NO_2 + F \rightarrow NO_2F$.

Fluorine nitrate has been known from the time of its discovery[1] to be unstable and explosive. The present investigation has shown that the rate of thermal decomposition may be followed easily in the vicinity of 100° and at fairly low pressures. The reaction has been studied under various conditions of temperature and pressure and in the presence of added foreign gases.

Experimental

Materials.—Potassium nitrate of "reagent grade" which contained less than 0.001% potassium nitrite was used. It was powdered, dried at 130-150°, and then stored in a vacuum desiccator. Fluorine in cylinders was obtained from the Pennsylvania Salt Manufacturing Company and was used without treatment except to pass the gas through a Monel Metal trap cooled with Dry Ice. Water-pumped nitrogen was passed through silica gel, Anhydrone (magnesium perchlorate) and a trap cooled with Dry Ice. Other

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