[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON AND THE UNIVERSITY OF NEW ENGLAND]

Fluorine Fluorosulfonate

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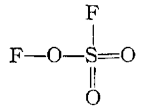
The compound fluorine fluorosulfonate, SO_3F_2, has been prepared by the fluorination of sulfur trioxide in the presence of silver difluoride and excess fluorine at 220°. Its structure has been confirmed by chemical reactions and by infrared spectra. The vapor shows strong absorption at 1501, 1248, 879, 852, 789 and 575 cm.$^{-1}$. The substance, which is a highly reactive oxidizing agent, is a gas with an odor like that of oxygen difluoride. It condenses as a colorless liquid which boils at −31.3° and melts at −158.5°.

Discussion

Most of the known hypofluorite type compounds have been formed either by replacement of the hydrogen atoms present in the molecules of strong acids or by the addition of fluorine across the double bond of a carbonyl group. Although previous attempts to prepare sulfur hypofluorite-type compounds by the reaction of fluorine with sulfuric acid had been unsuccessful, it was thought that sulfamic acid might react differently and moreover that the hydrogen atoms of the amino group might be replaceable.

Fluorination at temperatures greater than 200° resulted in the formation of a new substance with the formula SO_3F_2. The molecular weight and chemical composition of this new compound suggested that it should also be formed by the reaction of fluorine with sulfur trioxide. This proved to be the more satisfactory method of preparation, giving 60% of the theoretical yield. The remainder of the product was essentially sulfuryl fluoride. The reaction is analogous to the addition of halogen acids to sulfur trioxide with the formation of fluorosulfonic[2] or chlorosulfonic acids.[3]

The molecular weight, chemical composition, chemical behavior, synthesis from sulfur trioxide and fluorine, and its infrared spectrum all indicate that the new substance is a fluorine derivative of fluorosulfonic acid with the formula



$$F{-}O{-}\overset{\displaystyle F}{\underset{\displaystyle \overset{\|}{O}}{S}}{=}O$$

It reacts with sodium hydroxide solution in the cold, in accordance with the equation

$$SO_3F_2 + 2OH^- \longrightarrow SO_3F^- + F^- + H_2O + {}^1/_2O_2 \quad (1)$$

When the compound reacts with potassium iodide solution, two equivalents of iodine are liberated for every mole of fluorine fluorosulfonate consumed, in accordance with the equation

$$SO_3F_2 + 2I^- \longrightarrow SO_3F^- + F^- + I_2 \quad (2)$$

Since the hydrolysis of the fluorosulfonate ion to sulfate ion does not involve an oxidation–reduction process, the same amount of iodine would be liberated if the reaction were written as

$$SO_3F_2 + H_2O + 2I^- \longrightarrow SO_4^= + 2F^- + 2H^+ + I_2 \quad (3)$$

That the latter reaction was not significant was shown by using a neutral potassium iodide solution, titrating the free iodine liberated and then determining the amount of hydrogen ion by adding potassium iodate and titrating the very small quantity of iodine liberated by the reaction

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \quad (4)$$

The fluorine fluorosulfonate molecule has either no symmetry, or only one plane of symmetry, belonging to either the C_1 or C_s point groups. In either event, all vibrations are allowed in the infrared and Raman spectra. To assist in the assignment of observed absorption frequencies to particular modes of vibration, a comparison was made with the previously unreported spectrum of the similarly constituted methyl fluorosulfonate. The spectra of these compounds and that of dimethyl ether are reproduced in Figs. 1, 2 and 3.

As is to be expected, the methyl fluorosulfonate and dimethyl ether have many common absorption frequencies. By eliminating these from the spectrum of the methyl ester one can make the following inferences.

(1) The strong bands at 1501 and 1248 cm.$^{-1}$ in the fluorine fluorosulfonate spectrum correspond to S–O stretching frequencies. These values are in good agreement with the values of 1502 and 1269 cm.$^{-1}$ reported for S–O stretching frequencies in sulfuryl fluoride.[4]

(2) In the methyl ester these characteristic vibration frequencies are displaced to lower values, *viz.*, 1465 and 1235 cm.$^{-1}$, and the first one masks the 1459 cm.$^{-1}$ frequency that would be expected from the –OMe group.

(3) Since the 879 cm.$^{-1}$ frequency of the fluorine fluorosulfonate is the only one absent from the spectrum of the methyl ester, it is assumed to be due to the O–F stretch, although with oxygen difluoride[5] and trifluoromethyl hypofluorite[6] O–F absorption frequencies occur at 928 and 945 cm.$^{-1}$, respectively.

(4) Since absorption due to totally symmetric S–F stretch occurs at 848 cm.$^{-1}$ in sulfuryl fluoride,[4] the 852 cm.$^{-1}$ band of fluorine fluorosulfonate and the 840 cm.$^{-1}$ band of methyl fluorosulfonate may be assigned to S–F stretch.

(5) The bands at 789 and 787 cm.$^{-1}$ are to be associated with the S–O stretch of the S–O–F and S–O–Me groups, respectively (see Figs. 1 and 2).

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(2) (a) O. Ruff, *Ber.*, **47**, 652 (1914); (b) W. Traube and W. Lange, *ibid.*, **57**, 1038 (1924).

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(6) The bands at 575 and 520 cm.$^{-1}$, present in the fluorine and methyl derivatives of fluorosulfonic acid, are due to O–S–O bending. A band in the same region occurs in the spectrum of sulfuryl fluoride, at 544 cm.$^{-1}$.

Experimental Details

Preparation from Sulfamic Acid.—Undiluted fluorine, always present in excess, was passed over 14 g. of sulfamic acid in a 12″ long shallow nickel tray enclosed in an electrically heated nickel tube. At first the temperature was maintained near 180° but the amount of product formed was very small until the temperature was raised above 200°, the decomposition temperature of sulfamic acid. The most readily condensable portion of the product was light yellow in color, but the intensity of this color decreased after each distillation to other parts of the system. This yellow product apparently was very unstable and it was not identified.

The 8 g. of product was distilled in a vacuum-jacketed fractionating column having a small volume and low liquid hold-up: 5.9 grams (about 75%) proved to be sulfuryl fluoride, this being confirmed by molecular weight, boiling point, infrared spectrum and a mass spectrogram. The remaining 25% (2.1 g.) was extremely reactive, igniting hydrocarbon stopcock greases, reacting readily with the mercury in manometers connected to the system and burning insulation from thermocouple wires. (The latter were eventually coated with a tetrafluoroethylene resin, using du Pont Teflon primer 850–201 followed by two coats of Teflon clear finish 852–201.) An analysis for sulfur and fluorine, coupled with a molecular weight of 118, indicated an SO_3F_2 molecule. This suggested that the material might be formed in high yield by the reaction of fluorine with sulfur trioxide. Such proved to be the case.

Preparation from Sulfur Trioxide.—A flask containing anhydrous polymerized sulfur trioxide was connected to the system, and the vapor swept into a catalytic fluorination apparatus, like that of Kellogg and Cady,[7] by a stream of nitrogen flowing at a rate of 5 liters per hour. Fluorine, also diluted with nitrogen, was passed into the reactor which was maintained at 220° and the gaseous products condensed in traps cooled with liquid oxygen; 14.3 grams of product was obtained from 13.8 g. of sulfur trioxide. On fractionation 8.4 g. of pure material, boiling in the range $-31.6 \pm 0.1°$, was obtained. The distillation curve showed two distinct plateaus, the first occurring at $-55.4°$ which corresponds to the boiling point of sulfuryl fluoride.

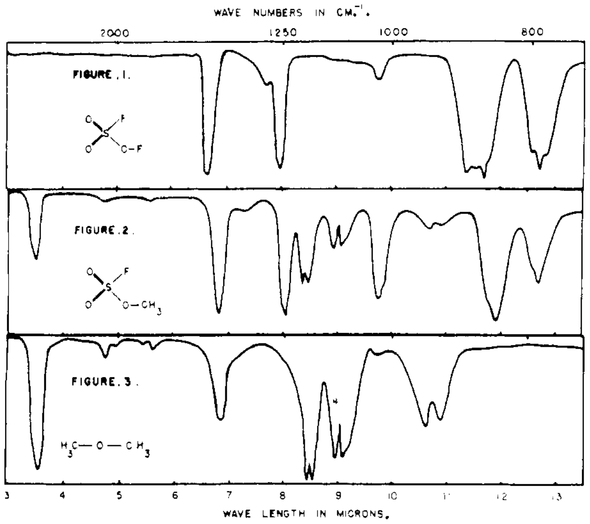
Vapor Density.—Small samples of the gas at pressures ranging from 60 to 250 mm. at room temperature were used for vapor density measurements. The values obtained from 8 determinations ranged from 117 to 119.5 with an average value of 118.6 g. per gram molecular volume. The theoretical molecular weight of SO_3F_2 is 118.

Analysis.—A known volume of standard potassium hydroxide was allowed to react with a known weight of the gas. The reaction was accompanied by fuming. After prolonged shaking to ensure completeness of reaction and saturation of the solution with the residual gas, the volume of the residual gas was found to be approximately half that of the original sample. This is what might be expected in accordance with the equation 1. The residual gas, after drying, was found to be oxygen.

The total solution was then diluted to 250 cc. Titration of aliquots showed that the cold hydrolysis had consumed two equivalents of alkali per mole. Barium chloride, when added to this solution, formed only the faintest precipitate.

Prolonged boiling of further aliquots of the alkaline solution showed that further hydrolysis, again requiring two equivalents of alkali per mole, occurred. The addition of barium chloride solution now gave an immediate precipitate of barium sulfate.

Similarly prepared solutions were analysed for sulfate ion by precipitate with barium chloride. The fluoride ion was determined on separate aliquots by titration with thorium nitrate, using sodium alizarin sulfonate as indicator.[8] The fluoride ion was separated from the interfering sulfate ions by distillation from a perchloric acid solution at 132° prior to titration.



Figs. 1, 2 and 3.—Infrared spectra of fluorine fluorosulfonate (top), methyl fluorosulfonate (middle) and dimethyl ether (bottom). Gas pressures were 10 mm. in a 10 cm. cell with sodium chloride windows.

Anal. Calcd. for SO_3F_2 (118): S, 27.1; F, 32.2. Found: S, 26.1, 27.03, 26.6, 26.4; F, 31.5, 31.3, 32.0, 31.4.

In a similar manner, potassium iodide solution was introduced into a bulb containing a weighed sample of the gas. Iodine was liberated freely and the gas was completely dissolved. The iodine liberated was titrated with standard sodium thiosulfate solution. Considering the gas to be ideal, the number of equivalents of iodine liberated per mole of gas was found in two cases to be 1.97 and 1.98 (the theoretical for SO_3F_2 is 2.00).

Density.—This was determined by use of a pycnometer having a capillary neck graduated in hundredths of a cc. The bulb was filled with a weighed sample of the compound and the temperatures recorded when the liquid level corresponded with the various capillary markings. The observed densities at −74.05, −69.7 and −65.5° were 1.7844, 1.7698 and 1.7564 g. per cc., respectively. The temperature dependence of the density σ is given by the equation

$$\sigma_T = 0.00325T + 2.4314$$

From the densities the volume coefficient of expansion at −70° is calculated to be 0.00181 per degree.

Vapor Pressure and Boiling Point.—Vapor pressures were measured by determining the boiling point of the compound under pressures ranging from 11 to 780 mm. Apparatus like that of Kellogg and Cady[7] was used. Some of the data are given in Table I in which values included in parentheses are not experimental and have been computed from the equation

$$\log_{10}P(\text{mm}). = 6.56476 - \frac{6.2687 \times 10^2}{T} - \frac{6.3906 \times 10^4}{T^2}$$

in which the temperature T is given in degrees absolute. The boiling point of −31.3° obtained from this equation is

Table I

Vapor Pressures of Fluorine Fluorosulfonate

T, °A.	$P_{\text{exptl.}}$ (mm.)	T, °A.	$P_{\text{exptl.}}$ (mm.)
179.6	10.95	213	164.1
184.4	17.92	(216.3)	(200)
(184.8)	(20)	219.4	240.9
193	39.83	227.6	377.4
(195.9)	(50)	232.2	477.9
196.7	53.16	240.5	712.3
201.5	75.67	241.8	753.7
(205.5)	(100)	(241.9)	(760)
206.6	108	242.3	777.7

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[7] K. B. Kellogg and G. H. Cady, This Journal, **70**, 3986 (1948).

[8] R. H. Kimball and L. E. Tufts, *Ind. Eng. Chem., Anal. Ed.*, **19**, 150 (1947).

considered to be a better value than −31.6° observed as the compound was distilled.

Between 40 and 760 mm., the deviation of the calculated vapor pressures from the experimentally observed pressures is less than 0.5%.

The latent heat of vaporization at the boiling point calculated from the above data using the Clapeyron equation is 5350 cal. per mole. This corresponds to a Trouton constant of 22.15.

Melting Point.—The melting point, −158.5°, was determined from a warming curve using apparatus built by Burger[9] following the design described by Sturtevant.[10] The latent heat of fusion was estimated to be approximately 1900 cal. per mole.

Infrared Spectrum.—The infrared absorption spectra of the substances in the vapor phase were measured over the range 2–15 μ by means of a double-beam Perkin–Elmer spectrometer, Model 21, employing a rocksalt prism and a 10 cm. Pyrex glass cell, with sodium chloride windows sealed to the cell with fluorocarbon wax. To eliminate reaction with the glass walls of the cell, a thin coating of aluminum oxide–phosphoric acid cement was applied to the inside of the cell and caused to set by slow heating with an infrared lamp. For the very reactive fluorine fluorosulfonate, the spectrum was recorded at pressures ranging from 2 to 10 mm.

The region from 15 to 25 μ was studied, using a cell with KBr windows, at a maximum pressure of 10 mm. and a CsBr prism. The pressure limitation was due to reaction of the compound with the windows, resulting in the liberation of free bromine and other reaction products. This interaction was much more pronounced when KI windows were used in an attempt to locate absorption bands in the 25–40 μ region. Brown stains appeared on the windows, presumably due to the formation of triiodide ions. These stains could be removed readily by pumping. After using KBr or KI cell windows for scanning the 15–40 μ regions, the spectrum in the 2–15 μ region was observed on the same sample to ensure that the compound had not completely reacted.

Fluorosulfonic Acid and Methyl Fluorosulfonate.—The acid was prepared by condensing sulfur trioxide and excess hydrogen fluoride in a nickel vessel, allowing it to stand overnight, evaporating off the excess hydrogen fluoride and distilling at atmospheric pressure, while excluding water vapor from the system. Methyl fluorosulfonate was prepared by passing dimethyl ether into fluorosulfonic acid and distilling under reduced pressure.[11]

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[CONTRIBUTION NO. 691 FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY]

The Preparation of Monobromosilane and Organic Silyl Derivatives

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A method is described for preparing mono- and dibromosilane in quantity. New organic silyl derivatives have been prepared from monobromosilane and their physical constants reported. The infrared spectra of these derivatives are also included and discussed.

Introduction

The chemistry of the methyl radical has received much study, but the analogous silyl radical (SiH_3–) has been given little attention. The first silyl compounds were prepared by Stock and Somieski[1] by halogenating silane with hydrogen halide gas in the presence of an aluminum halide catalyst. This type of reaction does not occur with carbon compounds but proceeds stepwise in the case of the silicon hydrides as shown by the equations

$$SiH_4 + HX \xrightarrow{AlX_3} SiH_3X + H_2$$

$$SiH_3X + HX \xrightarrow{AlX_3} SiH_2X_2 + H_2, \text{ etc.}$$

Some silyl derivatives have been prepared using vacuum line techniques by treating monohalogenated silanes with amines,[2] zinc alkyls,[1c] silver cyanide,[3] phosphorus and sulfur.[4] Using these techniques, Burg and Kuljian[5] synthesized silyl-aminoboron compounds, and Van Artsdalen and Gavis[6] tried unsuccessfully to prepare the silyl Grignard compound by monobromosilane reacting with magnesium. A number of organosilanes also have been made by reduction of the corresponding trihalosilanes with lithium aluminum hydride.[7]

The initial purpose of this work was to prepare a monohalogenated silane in sufficient quantity to make possible further study of the silyl radical. Previously, the extent of such experimentation has been limited by the necessity of using vacuum line techniques or by the availability of the proper trihalosilanes. Monohalogenated silanes can theoretically be prepared by selective reduction of the corresponding tetrahalide, as indicated by Hurd.[8] We have attempted partial reduction of silicon tetrachloride (always present in excess) using lithium aluminum hydride and calcium hydride as reducing agents, with incompatible solvents for the hydride and the silicon tetrachloride, and using low temperatures. All attempts failed to give any monochlorosilane. This is in agreement with the re-

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