The Preparation and Properties of N-Fluoroformyliminosulfur Difluoride, $SF_2=NCOF$[1]

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The inorganic isocyanates derived from silicon, phosphorus, and sulfur have been found to react readily with sulfur tetrafluoride to give, in common, the novel compound, N-fluoroformyliminosulfur difluoride, $SF_2=NCOF$, the preparation and properties of which are described.
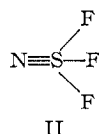
Introduction

Compounds containing the iminosulfur difluoride structure have come to be known only in recent years. Smith, *et al.*,[2-4] obtained organoiminosulfur difluorides upon sulfur tetrafluoride fluorination of several organic compounds containing carbon–nitrogen multiple bonds. Tullock[5] obtained trifluoromethyliminosulfur difluoride by the reaction between an inorganic thiocyanate, chlorine, and a metal fluoride.

Previously Glemser, *et al.*,[6,7] had reported on a compound SNF_3 which they had obtained upon fluorination of a mixture of SNF and SN_2F_2 with AgF_2 and by the thermal decomposition of SN_2F_2. At the time of its discovery, Glemser, *et al.*, assigned the iminosulfur difluoride structure (I) to the molecule simply on the basis of hydrolysis experiments. In subsequent years,
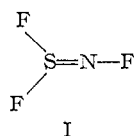
however, serious doubts have arisen as to the existence of I; first because Glemser[8] himself has not been able to repeat the preparation of SN_2F_2 from which I was prepared and second because Glemser[9] obtained from the reaction between N_4S_4 and AgF_2 a molecule with the same empirical formula as I for which structure II

has been assigned unequivocally on the basis of detailed spectroscopic studies.[8,10,11]

We have now obtained a new iminosulfur difluoride N-fluoroformyliminosulfur difluoride, $SF_2=NCOF$, from the reaction between sulfur tetrafluoride and the inorganic isocyanates derived from silicon, phosphorus, and sulfur. The molecular weight, elemental analyses, mass spectral data, F^{19} nuclear magnetic resonance spectrum, and infrared spectrum have all been found to be consistent with the assigned structure.

Experimental

Caution.—Fluoroformyliminosulfur difluoride appears to be highly toxic. Suitable safety precautions must be observed in its preparation and subsequent handling.

Apparatus.—The reactions were carried out in either a glass vacuum system or a nickel reactor of approximately 100-ml. capacity. Since sulfur tetrafluoride attacks Pyrex glass at elevated temperatures to give thionyl fluoride and silicon tetrafluoride, the nickel reactor is the preferred vessel for carrying out reactions above room temperature. Sulfur tetrafluoride was measured out in a calibrated all-metal vacuum system into a stainless steel cylinder and weighed on a high capacity high precision Mettler automatic balance (Model K-7). An all-glass high vacuum system was employed for the final purification and handling of the purified compound. An auxiliary vacuum system which was constructed with the liberal use of ball and socket joints so that it could be readily disassembled for cleaning purposes was employed for charging the metal reactor, for removing the volatile reaction products of the reaction, and for the preliminary purification of the product by fractional distillation condensation. All stopcocks and ground glass joints were greased with Kel-F No. 90 grease manufactured by the Minnesota Mining and Manufacturing Co. Hoke stainless steel cylinders equipped with Hoke 300 series needle valves were employed for storage of the highly volatile reaction products.

Materials.—Sulfur tetrafluoride (Matheson 90–94%) was used without further purification since thionyl fluoride was the only impurity which could be detected in the infrared spectrum of the material. Phosphorus triisocyanate was prepared from phosphorus trichloride and sodium cyanate according to the literature[12]; b.p. 64.8–65° (9.5 mm.). Phosphorus fluorodiisocyanate was prepared by the fluorination of phosphorus triisocyanate with antimony(III) fluoride according to the method of Anderson[13] and purified by vacuum fractionation in the high vacuum line. Methanesulfonyl isocyanate was prepared from methanesulfonic anhydride and silver cyanate according to the method

(1) Work supported by the Advanced Research Projects Agency, Office of the Secretary of Defense. Taken in part from the thesis submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy by Calvin S. Kobayashi. Presented before the Symposium on Covalent Inorganic Fluorine Compounds, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

(2) W. E. Smith, C. W. Tullock, E. L. Muetterties, W. R. Hasek, F. S. Fawcett, V. A. Engelhardt, and D. D. Coffman, *J. Am. Chem. Soc.*, **81**, 3165 (1959).

(3) W. E. Smith (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,862,029 (Nov. 25, 1958).

(4) W. E. Smith, C. W. Tullock, R. N. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 551 (1960).

(5) C. W. Tullock (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,833,422 (April 21, 1959).

(6) O. Glemser and H. Schroeder, *Z. anorg. allgem. Chem.*, **284**, 97 (1956).

(7) O. Glemser and H. Haeseler, *ibid.*, **287**, 54 (1956).

(8) O. Glemser and H. Richert, *ibid.*, **307**, 328 (1961).

(9) O. Glemser and H. Richert, *ibid.*, **307**, 313 (1961).

(10) K. Ramaswamy, K. Sathianandan, and F. F. Cleveland, *J. Mol. Spectry.*, **9**, 107 (1962).

(11) W. H. Kirchhoff and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **84**, 334 (1962).

(12) Belgian Patent 591,707 (to Imperial Chemical Industries, Ltd.) (May 1960).

(13) H. H. Anderson, *J. Am. Chem. Soc.*, **69**, 2495 (1947).

of Field and Settlage.[14] Silicon tetraisocyanate[15] was prepared by the reaction of silicon tetrachloride with silver cyanate. It was vacuum distilled directly into weighed ampoules equipped with break-off seals; b.p. 57° (2.5 mm.).

Reaction of Silicon Tetraisocyanate with Sulfur Tetrafluoride. —The evacuated nickel reactor was charged with $Si(NCO)_4$ (2.4070 g., 0.012 mole), then with SF_4 (5.75 g., 0.053 mole), while maintaining the reactor at $-78°$ with a Dry Ice–trichloroethylene bath. The charged reactor was placed in a 3-in. tube furnace and heated to 123° over a 6.5-hr. period. The furnace temperature was maintained above 100° for approximately 4 hr. The reactor was cooled to room temperature and connected to the evacuated auxiliary vacuum system. The volatile contents of the reactor were then allowed to vaporize into the vacuum system which had in series two U-tubes chilled to $-78°$ followed by a nickel cylinder of approximately 130-ml. capacity chilled to $-196°$. Between 3 and 4 ml. of a yellow liquid was obtained in the first $-78°$ U-tube. The more volatile fraction which passed through the first $-78°$ U-tube likewise passed through the second $-78°$ U-tube and condensed out in the liquid nitrogen chilled nickel cylinder. The infrared spectrum of the most volatile fraction which was obtained at 260 mm. pressure revealed that it consisted mostly of SiF_4 and SOF_2 with trace quantities of COF_2 and an isocyanate. There was also evidence for the presence of minute quantities of some unidentified compounds. Sulfur tetrafluoride was found definitely to be absent. The fraction which condensed out at $-78°$ contained mostly SF_2=NCOF with SOF_2 and SiF_4 as contaminants. The presence of a trace of isocyanate contamination was also evident. The $-78°$ fraction was purified by passing it through a series of U-tubes cooled successively to -45, -78, and $-196°$. The fraction which was retained in the $-45°$ tube was further fractionated until a fraction was obtained which remained colorless upon storage at room temperature and exposure to fluorescent light; yield of crude product 3.8609 g. (60%). A light tan amorphous solid (0.2074 g.) remained in the reactor. During the early stages of the purification by means of fractional distillation condensation, a yellow, dense vapor permeated the vacuum system and deposited a light yellow film on the glass walls of the auxiliary vacuum system. This yellow vapor, which dissolved in stopcock grease, diminished in quantity, however, and finally disappeared after several fractionations. Furthermore, during the early stages of the fractionation process, a yellow solid residue also remained behind in the U-tube containing the parent fraction. This yellow nonvolatile residue, which appeared to form as the result of the decomposition of one or more reactive materials, gave upon pyrolysis volatile products which could be removed from the vacuum system with pumping. The purification steps were continually followed by means of infrared spectra and vapor pressure measurements.

Reaction of Methanesulfonyl Isocyanate with Sulfur Tetrafluoride.—Methanesulfonyl isocyanate (2.3416 g.) was allowed to react with sulfur tetrafluoride (2.17 g.) in the auxiliary vacuum system shown in Figure 1. A weighed quantity of methanesulfonyl isocyanate contained in an ampoule with a break-off seal was introduced through joint J_1 of the vacuum system and condensed out in the 50-ml. capacity reaction vessel. The stainless steel cylinder containing the weighed quantity of sulfur tetrafluoride was then connected to the vacuum system at J_1 and sulfur tetrafluoride was introduced in small portions with stopcocks S_3, S_5, and S_6 closed. The contents of the reaction vessel were stirred with a magnetic stirrer while being heated to 170° with an oil bath. Stopcock S_6 was periodically opened in order to allow the volatile reaction products to be transferred to the fractionation train which consisted of three U-tubes chilled in order to -78, -78, and $-196°$. The process of admitting SF_4 to the reaction vessel and removing the volatile reaction products as well as unreacted SF_4 was repeated until all the SF_4 had been allowed to come into contact with CH_3-
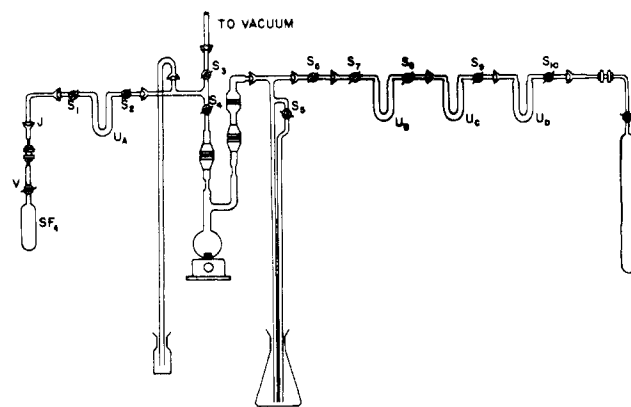

Figure 1.—Auxiliary vacuum system.

SO_2NCO in the reaction vessel. The fraction which condensed out in the liquid nitrogen chilled U-tubes was mostly SOF_2, SiF_4, SF_4, trace quantities of SF_2=NCOF, and an isocyanate impurity. Additional infrared absorption bands revealed the presence of trace quantities of other impurities as well. Volatile components of the brownish yellow liquid fraction which condensed out in the first $-78°$ trap consisted mainly of SF_2=NCOF, SOF_2, and SiF_4. Trace quantities of an isocyanate were also present along with unidentified compounds giving infrared absorption bands in the C—F, C=N, and C≡N regions. The vapor phase infrared spectrum of this fraction did not reveal the presence of CH_2SO_2F, which was expected to be one of the reaction products. This fraction also contained one or more components which attacked Kel-F 90 stopcock grease as evidenced by the development of a yellow coloration at the stopcocks exposed to it. Upon further fractionation, yellow, purple, as well as black films deposited on the walls of the U-tube containing the various fractions, presumably due to further reaction of reactive species present in the mixture. The least volatile fraction consisted of a considerable amount of unreacted CH_3SO_2NCO as evidenced by its liquid phase infrared spectrum. Methanesulfonyl fluoride also appears to be present in this least volatile fraction. No further attempts were made to isolate and purify the SF_2=NCOF obtained from the reaction since the presence of highly reactive chemical species made the purification extremely tedious.

Reaction of Phosphorus Fluorodiisocyanate.—Phosphorus fluorodiisocyanate (1.9 g., 0.014 mole) was allowed to react with sulfur tetrafluoride (2.7 g., 0.025 mole) in the auxiliary vacuum system described above (Figure 1). Sulfur tetrafluoride was allowed to come into contact with phosphorus fluorodiisocyanate in several portions in the manner described for the reaction of methanesulfonyl isocyanate with sulfur tetrafluoride. The temperature of the reactor was initially maintained at $-78°$ using a Dry Ice–trichloroethylene bath. As the reactants came into contact with each other at this temperature, reaction set in immediately as evidenced by fizzing on the walls of the reactor and by the development of a yellow coloration. As the addition of sulfur tetrafluoride was continued, the yellow material initially formed acquired a rust coloration. After a while the entire contents of the reactor solidified. However, as the addition of sulfur tetrafluoride was continued further with constant stirring, the contents of the reactor became liquid again. Upon continued addition of sulfur tetrafluoride, the entire contents of the reactor solidified into a rust-colored solid mass. The solid in the reactor decomposed upon heating with a Bunsen burner, giving off a gaseous material. The arrangement of U-tubes for trapping out volatile materials was similar to that employed for the previous reaction. In this reaction, however, the stainless steel cylinder shown in Figure 1 was connected to the condensation train and along with U_D was cooled to $-196°$. A dark rust-colored solid deposited in all three U-tubes of the condensation train. Since this occurred in spite of the presence of a sintered

(14) L. Field and P. H. Settlage, *J. Am. Chem. Soc.*, **76**, 1222 (1954).

(15) J. S. Forbes and H. H. Anderson, *ibid.*, **62**, 761 (1940).

glass disk between the reactor and the condensation train, it is apparent that volatile materials which had passed through the sintered glass disk had reacted and deposited solids in the condensation train. The reaction was carried out over a period of 4 hr. The fraction which condensed out in the −78° U-tubes consisted essentially of SF₂=NCOF, an isocyanate (or isocyanates), PF₅, SiF₄, SF₄, and SOF₂ as revealed by its vapor phase infrared spectrum. The fraction which condensed out in the stainless steel cylinder consisted mostly of PF₅ with lesser quantities of SiF₄, SOF₂, PF₃, SF₄, POF₃, and trace quantities of an isocyanate and SF₂=NCOF. The presence of COF₂ could not be detected even in trace amounts. Even after repeated fractionation in the high vacuum system, an isocyanate impurity and PF₅ could not be completely removed. The yield of partially purified SF₂=NCOF was 0.2479 g. No attempts were made to characterize the solid materials which formed in the reaction, because of their high reactivity.

Reaction of Phosphorus Triisocyanate with Sulfur Tetrafluoride.—Phosphorus triisocyanate (8.03 g., 0.051 mole) was allowed to react with sulfur tetrafluoride (2.76 g., 0.026 mole). Since P(NCO)₃, upon cooling below its melting point, −2°, polymerizes readily to give a solid mass, the depolymerization of which entails the application of heat with subsequent partial decomposition, it cannot be admitted to a vacuum system by conventional vacuum techniques which necessitate cooling, if it is desired to employ it in a pure state. In order to avoid the aforementioned difficulty, the reaction with sulfur tetrafluoride was carried out in an atmosphere of carefully dried nitrogen in the apparatus described in Figure 2. After evacuating and flaming
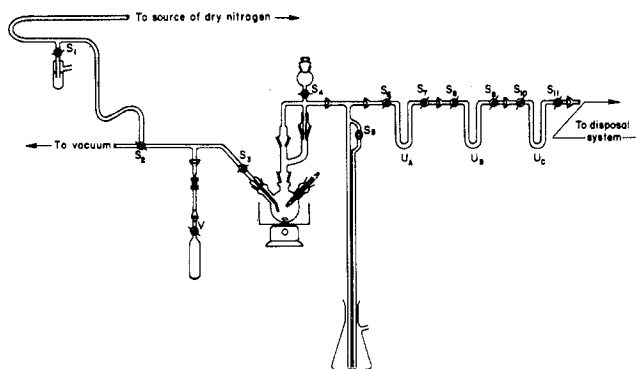

Figure 2.—Auxiliary vacuum system.

out the apparatus, high purity nitrogen which had been dried by passage through Drierite, P₂O₅, and Linde Molecular Sieve 4A was admitted to the apparatus until atmospheric pressure was attained. The addition funnel was then charged with a weighed amount of P(NCO)₃ through a serum stopple by means of a hypodermic syringe. The funnel was stoppered and its contents were emptied into the reaction vessel. With a slight flow of nitrogen gas being allowed through the apparatus, the U-tubes in the condensation train were chilled to −78, −78, and −196°. Sulfur tetrafluoride was then introduced carefully by cracking valve V. Reaction commenced immediately as SF₄ came into contact with the P(NCO)₃, which was being stirred with a magnetic stirrer and chilled in an ice–water bath. An orange liquid appeared as the temperature rose to 37°. As the reaction proceeded further the formation of a white solid was noticed. Stirring was continued for an additional 0.5 hr. after the addition of SF₄ had been completed and the temperature of the reaction flask had returned to 25°. The reaction vessel at this point contained a mixture of a white solid, a light yellow solid, and a light yellow liquid. The infrared spectrum of all fractions revealed the presence of SF₂=NCOF. The amount of SF₂=NCOF present, however, was small compared to the amount of SF₄ and SOF₂ present. A small amount of pure SF₂=NCOF was obtained upon repeated fractionation in the high vacuum line. Yellow solids had condensed out throughout the reactor and con-

densation train. No attempt was made to characterize these solids.

Chemical Analysis.—The chemical analysis of SF₂=NCOF was carried out in the Microanalytical Laboratory at Purdue University under the direction of Dr. C. S. Yeh.

Anal. Calcd. for CF₃NOS: F, 43.51; N, 10.69; S, 24.42. Found: F, 42.68; N, 10.69; S, 23.96.

Molecular Weight.—The molecular weight was determined by the vapor density method and from the molecule ion peak of the compound in its mass spectrum: from vapor density measurement, 128; from mass spectral data, 131 (calcd. for SF₂=NCOF, 131).

Melting Point.—The melting point was determined in the high vacuum system employing a conventional plunger type apparatus described by Sanderson.[16] The temperature measurement was made with a calibrated platinum thermohm in conjunction with a high precision resistance recorder (Leeds and Northrup No. 69812, Type G); m.p. −94.7 ± 0.1°.

Vapor Pressure and Boiling Point.—The vapor pressure measurements were carried out in a high vacuum system employing conventional mercury manometers. The values obtained were 0.1 mm. at 195°K., 0.2 mm. at 220.3°K., 3.0 mm. at 227.8°K., 7.8 mm. at 242.4°K., 14.3 mm. at 250.4°K., and 61.2 mm. at 273.1°K. The vapor pressure can be expressed by the following equation between 0 and −52.7°.

$$\log P \text{ (mm.)} = -1950/T + 8.9406$$

The extrapolated boiling point is 48.8°. The molar heat of vaporization calculated from the Clausius–Clapeyron equation is 8.92 kcal. and the Trouton constant is 27.8 cal./deg.

Mass Spectrum.—The mass spectrum was obtained with a Bendix time-of-flight Model 12-101 mass spectrometer at an ionization voltage of 50 v. Table I shows the relative intensities of the fragments observed.

Ultraviolet Spectrum.—The ultraviolet spectrum of SF₂=NCOF was obtained as an isooctane solution in a silica cell of 1-cm. optical path length. The silica cell was connected to the high vacuum system by means of a graded quartz to Pyrex seal and the cell was charged completely under vacuum. A single broad peak was observed with λ_max at 290 mμ.

Infrared Spectrum.—The infrared spectrum in the 2–15 μ region (Figure 3) was obtained with a Perkin-Elmer Model 137 Infracord spectrometer. That in the 15–25 μ region (Figure 4)
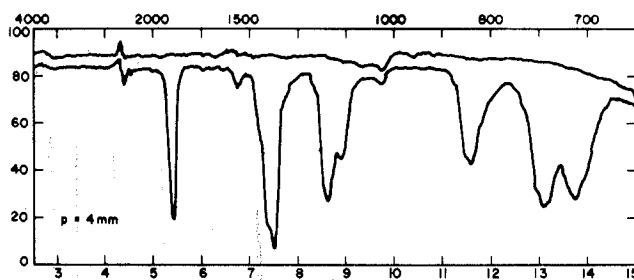

Figure 3.—Infrared spectrum of SF₂=NCOF.

was obtained with a Beckman IR5A spectrophotometer equipped with CsBr optics. The strong absorption at 1850 cm.⁻¹ is characteristic of the C=O stretching vibration in the −COF group.[17] The broad absorption centered at 1350 cm.⁻¹ was attributed to the S=N stretching vibration since the organoiminosulfur difluorides have been found to absorb in the 7.15–7.35 μ (1400–1360 cm.⁻¹) region.[4] The absorptions in the 1100–1200 cm.⁻¹ region have been attributed to C–F vibrations because bis(monofluorocarbonyl) peroxide, (FCO)₂O₂,[18] has C–F stretching vibra-

(16) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 96.

(17) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

(18) A. J. Arvia and P. J. Aymonino, *Spectrochim. Acta*, **18**, 1299 (1962).

Table I

Mass Spectrum of SF$_2$=NCOF

m/e	Relative intensity	Species
12	1.0	C$^+$
14	1.2	N$^+$
16	2.8	O$^+$
18	4.0	H$_2$O$^+$ (background)
19	0.5	F$^+$
26	0.6	CN$^+$
28	12.2	CO$^+$, N$_2^+$, Si$^+$
29	1.4	
30	2.7	
31	4.5	
32	12.2	S$^+$
33	2.3	
34	0.8	^{34}S$^+$
41	1.1	
42	7.3	CON$^+$
43	3.7	
44	25.1	CO$_2^+$
46	80.0	SN$^+$
47	89.8	COF$^+$
48	21.1	^{34}SN$^+$, SO$^+$
51	14.3	SF$^+$
52	1.1	^{34}SO$^+$
57	1.8	
58	1.1	SNC$^+$
61	0.8	NCOF$^+$
64	21.6	SO$_2^+$ (?)
65	29.7	SFN$^+$
67	4.5	^{34}SFN$^+$
70	41.2	SF$_2^+$
84	2.2	SF$_2$N$^+$
85	1.6	SiF$_3$ (?)
86	2.2	SOF$_2^+$ (?)
89	3.3	SF$_3^+$ (?)
93	8.0	SFNCO$^+$
112	100.	SF$_2$NCO$^+$
131	72.0	SF$_2$NCOF$^+$ (molecule ion)

Figure 4.—Infrared spectrum of SF$_2$=NCOF.

Freon-11 (CCl$_3$F), and the values obtained in c.p.s. were converted to chemical shifts expressed in p.p.m. relative to CF$_3$-COOH. There were two fluorine resonances of relative intensity 2:1 assignable to SF$_2$[20-22] and N-C(O)F[23] fluorine atoms. The former occurred at −118.2 p.p.m. and the latter at −96.7 p.p.m. No fine structure due to spin–spin splitting was observed in the spectrum which was obtained at room temperature.

Hydrolysis Experiments.—N-Fluoroformyliminosulfur difluoride hydrolyzed readily in dilute potassium hydroxide to give SO$_3^{-2}$, NH$_3$, CO$_3^{-2}$, and F$^-$. Thus
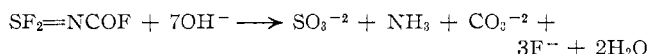
$$SF_2=NCOF + 7OH^- \longrightarrow SO_3^{-2} + NH_3 + CO_3^{-2} + 3F^- + 2H_2O$$

(20) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 340.

(21) R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, 1, 756 (1962).

(22) Although Smith, *et. al.*,[4] reported that the F^{19} resonance for the fluorine atoms in the –N=SF$_2$ grouping in α,α-difluorobenzyliminosulfur difluoride occurred at 4028 c.p.s., they failed to give the experimental conditions which were employed for their measurements. However, if we were to assume that their measurements had been made at 40 Mc./sec. with CF$_3$COOH as the reference standard, we arrive at a chemical shift value of −107 p.p.m., which is in good agreement with what we have observed for the –N=SF$_2$ grouping in SF$_2$=NCOF.

(23) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, 84, 4275 (1962).

tions at 1178 and 1221 cm.$^{-1}$. The strong bands at 727 and 764 cm.$^{-1}$ have been assigned to S–F stretching vibrations since the stretching vibrations of SOF$_2$ occur at 748 and 808 cm.$^{-1}$.[19]

N.m.r. Spectrum.—The F^{19} nuclear magnetic resonance measurements were made with a Varian Associates HR-60 nuclear magnetic resonance spectrometer at 56.4 Mc./sec. The chemical shifts were measured by substitution relative to

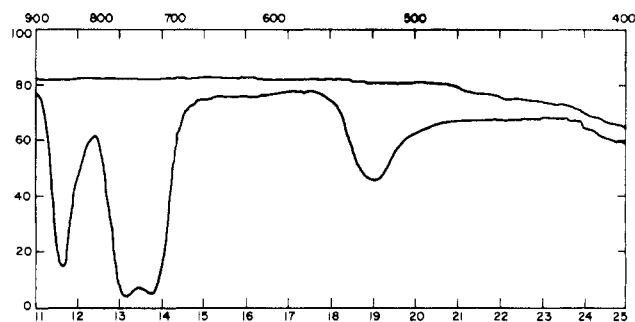(19) J. K. O'Loane and M. K. Wilson, *J. Chem. Phys.*, 23, 1313 (1955).