Such a rate law is consistent with scheme I provided there is a pre-equilibrium between the phosphonate and its conjugate acid and that the degree of protonation is small.[19] Another possibility consistent with the rate law is a one-step mechanism, i.e., protonation of the phosphonate accompanied by a simultaneous fission of the phosphorus hydrogen bond.[19] No distinction can be made between the above alternatives from the present data. The detailed mechanism of the formation of the phosphite form is being investigated by a study of kinetic isotope effects.

The non-acid-catalyzed term, k_w, in equation 1 represents a spontaneous dissociation of the P–H bond, presumably favored by the high dielectric constant of water and its basic properties.

From Table III it is seen that the values of k_H and k_w for the exchange reaction are larger than the corresponding values for the oxidation reaction.

(19) A. A. Frost and R. G. Pearson. "Kinetics and Mechanism." John Wiley and Sons, Inc., New York. N. Y., 1953. Chap. 9.

This difference is partly due to the different temperatures at which the experiments were carried out. A further cause for the discrepancy may be due to differences in medium between the two sets of experiments. The dialkyl phosphonate concentration was less than 0.1% by volume in the case of the oxidation reaction mixtures studied by Nylen,[15] as compared to 15–25% by volume in the case of the exchange reaction. It should also be noted that the exchange was studied in D_2O solution and the oxidation results are for H_2O solutions. Considering the differences in the temperature and the nature of the medium, the agreement between the values of the catalytic constants obtained from both reactions is reasonably good.

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

Some Reactions of Peroxydisulfuryl Difluoride

By JEAN'NE M. SHREEVE[1] AND GEORGE H. CADY

The reactions of peroxydisulfuryl difluoride with several substances have been examined. Three new fluorosulfonates, octafluorobis-(fluorosulfonato)-cyclopentane $(C_5F_8(SO_3F)_2)$, tetrafluorobis-(fluorosulfonato)-ethane $(C_2F_4(SO_3F)_2)$ and tetrafluorobis-(fluorosulfonato)-sulfur (VI) $(SF_4(SO_3F)_2)$ were produced by direct combination of peroxydisulfuryl difluoride with perfluorocyclopentene (C_5F_8) and tetrafluoroethylene (C_2F_4) at room temperature and with sulfur tetrafluoride (SF_4) at 128° respectively. These new compounds have been characterized. Structures have been confirmed by mass, nuclear magnetic resonance and infrared spectra. A white solid, dioxobis-(fluorosulfonato)-molybdenum(VI) $(MoO_2(SO_3F)_2)$, was obtained with either molybdenum hexacarbonyl or molybdenum metal.

It has been shown that peroxydisulfuryl difluoride reacts with some substances to give fluorosulfonates.[2-3] The reactions of $S_2O_6F_2$ with several additional substances have now been studied, and it has been found that the peroxide acts in three ways: (1) as an oxygenating agent through the addition of oxygen to the central atom of the reacting species, e.g., with CO, PF_3, SOF_2, $COCl_2$, CCl_4 or S; (2) as a fluorosulfonating agent, e.g., with HgO, KCl, ICl, C_5F_8, C_2F_4, or SF_4; (3) as an oxygenating and fluorosulfonating agent by adding oxygen and fluorosulfonate groups to the central atom, e.g., SOClF, Mo or $Mo(CO)_6$. Pyrosulfuryl fluoride $(S_2O_5F_2)$ is obtained as a product of reactions of types 1 and 3.

Experimental

Preparation of Peroxydisulfuryl Difluoride.—Peroxydisulfuryl difluoride can be prepared by reaction of fluorine with an excess of sulfur trioxide at about 250°, by the combination of fluorine fluorosulfonate with sulfur trioxide at 300°[4] or by the electrolysis of fluorosulfonic acid.[5] The catalytic fluoronation of sulfur trioxide vapors by fluorine in the presence of a heated catalyst of copper ribbon coated

(1) Department of Chemistry, University of Idaho, Moscow, Idaho.

(2) John E. Roberts and George H. Cady. J. Am. Chem. Soc., **81**, 4166 (1959).

(3) John E. Roberts and George H. Cady. ibid., **82**, 352, 353 (1960).

(4) F. B. Dudley and G. H. Cady, ibid., **79**, 513 (1957).

(5) F. B. Dudley, Thesis, University of New England, Australia (1960).

with silver difluoride provided an easy and simple method to prepare the easily purified product.

Fluorination of sulfur trioxide carried by a stream of dry nitrogen with a slight excess of fluorine in the presence of a silver difluoride catalyst in a "catalytic reactor"[6] at 155° produced the $S_2O_6F_2$, which was purified by prolonged pumping at −78° to remove the contaminants silicon tetrafluoride, sulfuryl fluoride and fluorine fluorosulfonate. In a 15 hr. run using a nitrogen flow of 8 liters per hour and a catalyst contact time of about 15 minutes, a 96 g. sample of product was obtained. It contained 97% peroxydisulfuryl difluoride. In another run, 26.1 g. of sulfur trioxide yielded 31.6 g. of $S_2O_6F_2$ (yield, 97% theoretical).

Storage of the compound in a glass vessel at −78° was satisfactory. Although the glass container apparently was not attacked at room temperature, a nonvolatile oily material was slowly formed in the $S_2O_6F_2$. Apparently this did not introduce contaminants into the $S_2O_6F_2$ distilled from the vessel. The yellow oil was not identified.

Materials.—The Swarts reaction[7] provided a general method for the conversion of chlorides to the corresponding fluorides by reaction of the former with antimony(III) fluoride in the presence of antimony(V) chloride as a catalyst. Thionyl fluoride and thionyl chlorofluoride were obtained using thionyl chloride while phosphorus(III) fluoride was prepared from phosphorus(III) chloride. Tetrafluoroethylene was produced by the pyrolysis of Teflon (polytetrafluoroethylene) in an iron vessel at 550°. Sulfur tetrafluoride was used directly from a cylinder supplied by E. I. du Pont de Nemours and Co., Inc. All other materials were of reagent grade.

(6) K. B. Kellogg and G. H. Cady, J. Am. Chem. Soc., **70**, 3086 (1948).

(7) H. S. Booth and F. C. Mericola, ibid., **62**, 640 (1940).

General Methods.—Infrared spectra were studied using a Perkin–Elmer Model 21 Infrared Spectrometer with a sodium chloride prism. The gaseous samples were contained in a 10 cm. glass cell with silver chloride windows.

Nuclear magnetic resonance spectra were obtained through the use of a Varian Model 4311 B high resolution spectrometer with a 40 or 60 megacycle oscillator. For some of the samples areas of the absorption peaks were used as a quantitative measure for fluorine.[8]

Mass spectra were recorded using a Consolidated Engineering Corporation type 21–103 mass spectrometer.

Vapor densities were determined using Regnault's method with a glass flask of 252 ml. volume. Single capillary pycnometers were used for liquid densities. Melting points were obtained by warming the solid at a rate of about $0.2°$ per minute in a 1-propanol bath which had been cooled by adding solid carbon dioxide. Because of the tendency for the compounds to supercool, freezing points were not found by cooling.

Vapor pressures were determined using a method previously described.[8]

Elemental analyses were obtained for $C_5F_8(SO_3F)_2$ and $C_2F_4(SO_3F)_2$ after heating the material with potassium at $450°$ for 30 hr. Basic hydrolysis of $SF_4(SO_3F)_2$, KSO_3F, $I(SO_3F)_3$ or $MoO_2(SO_3F)_2$ was used to obtain aqueous solutions for analysis. Sulfur was determined iodometrically as sulfide when the potassium fusion technique was employed. The technique involving basic hydrolysis allowed sulfate to be precipitated as barium sulfate. Fluorine, after distillation,[9] was precipitated as lead chlorofluoride, dissolved, and chloride was determined by the Volhard method. After hydrolysis of $MoO_2(SO_3F)_2$, molybdate was removed[10] before sulfate precipitation as barium sulfate. Molybdenum was determined gravimetrically as the 8-hydroxyquinolate.

Since $S_2O_6F_2$ and its compounds attack glass only slowly if at all, all reactions studied were carried out in Pyrex glass vessels, unless otherwise specified. Because of the ease of hydrolysis of $S_2O_6F_2$, all reactions were run under high vacuum conditions.

Procedure 1 for the reaction of $S_2O_6F_2$ with an equimolar amount of the reacting compound was as follows: (a) The reacting compound was added to a 500 ml. Pyrex glass bulb to give a pressure of about 125 mm. (b) The $S_2O_6F_2$ was slowly introduced at room temperature. (When reaction occurred at this temperature it was accompanied by the production of a fleeting brown color in the area of mixing and was exothermic.) (c) After cooling to room temperature, separation of reaction products was effected successfully using fractional codistillation.[11]

Procedure II, usually used with materials which did not react at room temperature, was as follows: (a) An equimolar mixture of $S_2O_6F_2$ and the reacting compound was placed in a nickel reactor previously described.[8] (b) As the temperature was slowly increased from $26°$ to $200°$, temperature and pressure were recorded frequently. (c) A plot of this temperature–pressure relationship, if different from that expected for an ideal gas, was regarded as an indication that reaction had occurred. (d) The mixture was cooled, removed from the reactor by condensing in a tube at $-183°$ and later separated by fractional codistillation.

Identification of previously known reaction products, after separation, was made using vapor density and infrared spectra determinations.
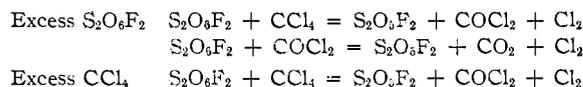
Reactions Involving Oxygenation by $S_2O_6F_2$. Reaction with Carbon Monoxide.—In an attempt to prepare carbonyl bis-(fluorosulfonate) the reaction between $S_2O_6F_2$ and CO was examined using procedures 1 and 2. Two compounds were found. The more volatile one was CO_2 (mol.wt. 46.2, infrared $4.35\ \mu$) and the less volatile was $S_2O_5F_2$ (mol. wt. 183, infrared 6.65, 8.05, 11.45, 12.10 and $13.60\ \mu$) which indicated that the reaction $CO + S_2O_6F_2 = CO_2 + S_2O_5F_2$ had occurred at room temperature.

Reaction with Carbonyl Chloride.—A second attempt to make carbonyl bis-(fluorosulfonate) and also chlorine fluorosulfonate led to the study of the reaction between carbonyl chloride and $S_2O_6F_2$. No reaction occurred at room tem-

perature. However, a green gas was produced by ultraviolet irradiation. Three products were identified: CO_2 (mol. wt. 46.3, infrared $4.35\ \mu$); Cl_2 (mol. wt. 70.5, green) and $S_2O_5F_2$ (mol. wt. 182.9, infrared as above). This indicated that the reaction $COCl_2 + S_2O_6F_2 = CO_2 + S_2O_5F_2 + Cl_2$ had occurred.

Reaction with Molybdenum Hexacarbonyl.—When an excess of peroxydisulfuryl difluoride was distilled onto 0.100 g. of sublimed molybdenum carbonyl in a 500 ml. bulb and the mixture allowed to warm to room temperature, an exothermic, rapid reaction occurred producing 0.108 g. of a gas identified as carbon dioxide (theoretical weight of CO_2 obtainable, 0.100 g). Pyrosulfuryl fluoride ($S_2O_5F_2$) was also a gaseous product. In addition to the gases a white solid ($MoO_2(SO_3F)_2$) and a nonvolatile liquid, to be discussed later, were produced.

Reaction with Carbon Tetrachloride.—Unsuccessful attempts were made to prepare chlorine fluorosulfonate by the reaction of $S_2O_6F_2$ with various chlorides including anhydrous carbon tetrachloride. No immediate reaction was noted but on standing at room temperature, a green gas was formed. Four products were identified as: CO_2 (infrared $4.35\ \mu$); Cl_2 (green); $COCl_2$ (infrared 5.48, $11.75\ \mu$) and $S_2O_5F_2$ (infrared as above). These indicated that the following reactions had occurred

Excess $S_2O_6F_2$ $S_2O_6F_2 + CCl_4 = S_2O_5F_2 + COCl_2 + Cl_2$

$$S_2O_6F_2 + COCl_2 = S_2O_5F_2 + CO_2 + Cl_2$$

Excess CCl_4 $S_2O_6F_2 + CCl_4 = S_2O_5F_2 + COCl_2 + Cl_2$

Reaction with Sulfur.—An excess of peroxydisulfuryl difluoride was distilled onto finely divided, vacuum-dried sulfur, and the mixture was irradiated with ultraviolet light for an extended period. A color change from yellow to orange to white to medium blue to green was observed. Volatile products were identified as follows: SO_2 (mol. wt. 60); $S_2O_5F_2$ (infrared as above) and $S_3O_8F_2$ (mol. wt. 262, infrared 6.70, 8.00, 8.18, 11.50, 12.65μ). Two equations may be written: $S + 2S_2O_6F_2 = SO_2 + 2S_2O_5F_2$ and $SO_2 + S_2O_6F_2 = S_3O_8F_2$. The second of these reactions had previously been recognized. No explanation has been found for the color change, which appeared to be a surface effect.

Reaction with Phosphorus(III) Fluoride.—The reaction of $S_2O_6F_2$ and PF_3 was found to be extremely vigorous and exothermic. Products found were: POF_3 (infrared 6.15, 7.08, 7.42, 10.11, 10.58, 11.45μ) and $S_2O_5F_2$ (infrared as above). The same products were obtained by mixing at $0°$ followed by ultraviolet irradiation, $PF_3 + S_2O_6F_2 = POF_3 + S_2O_5F_2$.

Reaction with Thionyl Fluoride.—A temperature vs. pressure plot obtained from heating a mixture of SOF_2 and $S_2O_6F_2$ to $200°$ was identical with that expected for increasing the temperature of an ideal gas at constant volume. Examination of the products showed small amounts of SO_2F_2 (infrared 6.65, 7.85, 11.50μ) and $S_2O_5F_2$ (infrared as above). Most of the reactants remained unchanged. A slow oxidation of thionyl fluoride to sulfuryl fluoride had occurred with no pressure change according to $SOF_2 + S_2O_6F_2 = SO_2F_2 + S_2O_5F_2$.

Reactions Involving Fluorosulfonation by $S_2O_6F_2$.—The second type of reaction displayed by peroxydisulfuryl difluoride was fluorosulfonation where the $S_2O_6F_2$ molecule was split into two fluorosulfonate groups which then either: (1) replaced volatile anions from the reacting compound; (2) added across carbon–carbon double bonds; or (3) added to the central atom of the reacting compound increasing its oxidation number.

Reaction with Mercury(II) Oxide.—A slight excess of peroxydisulfuryl difluoride was distilled onto 0.2536 g. (1.170 mmoles) of yellow mercury(II) oxide which had been dried at $300°$. No reaction occurred at room temperature, but on heating at $150°$ for 24 hr., a white solid was obtained according to the reaction $HgO + 2S_2O_6F_2 = Hg(SO_3F)_2 + O_2 + S_2O_5F_2$. After volatile materials had been removed, the remaining mercury bis-(fluorosulfonate) weighed 0.3490 g. (1.164 mmoles). On addition of water, the yellow solid $Hg_3F_4(OH)_2 \cdot 3H_2O$, noted by Roberts and Cady[2] on hydrolyzing $Hg(SO_3F)_2$, was produced. Because $Hg(SO_3F)_2$ had been previously synthesized and characterized, no further study was undertaken.

Reaction with Potassium Chloride.—An excess of peroxydisulfuryl difluoride was distilled onto 0.0620 g. (0.832 mmole) of powdered potassium chloride which had been

(8) Wayne P. Van Meter and George H. Cady, J. Am. Chem. Soc., **82**, 6005 (1960).

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

(10) D. A. Lambie and W. R. Schoeller, Analyst, **65**, 281 (1940).

(11) G. H. Cady and D. P. Siegwarth, Anal. Chem., **31**, 618 (1959).

TABLE I
DENSITIES OF $C_5F_8(SO_3F)_2$

Temp., °C.	10.0	20.0	29.4	40.1	47.7
Density, g./cc.	1.917	1.895	1.874	1.850	1.831

TABLE II
VAPOR PRESSURES OF $C_5F_8(SO_3F)_2$

P, mm.	Temp., °K.	P, mm.	Temp., °K.
24.9	334.4	321.9	392.8
45.0	343.4	349.8	395.1
65.1	351.8	429.4	401.7
83.4	357.2	459.9	403.7
107.1	362.8	519.6	407.6
129.4	367.5	571.6	411.2
151.8	371.6	645.2	415.1
186.5	376.8	755	420.0
226.0	383.0	(760)	(421.2)
280.9	388.6	798	422.6

dried at 130°. When the bulb was allowed to warm to room temperature, bubbles could be seen leaving the surface of the solid. Subsequently, a green gas formed by the reaction $2KCl + S_2O_6F_2 = 2KSO_3F + Cl_2$ was observed. After the reaction had become complete, the excess unchanged $S_2O_6F_2$ and chlorine were distilled away leaving 0.1158 g. (0.838 mmole) of a white solid, KSO_3F. When the potassium fluorosulfonate was subjected to basic hydrolysis at 100° for 48 hr., 1.98 g. equivalents of base were consumed per mole of compound. (Theor., 2.00 g. equivalents.) Sulfur found: 22.9%; calculated: 23.2% for KSO_3F.
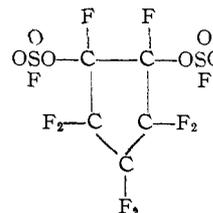
Reaction with Iodine Monochloride.—Addition of peroxydisulfuryl difluoride to ICl resulted in a vigorous reaction producing swirling smoke in the reaction flask and green gaseous chlorine. A red-orange liquid was formed which upon the addition of more $S_2O_6F_2$ lightened in color. When the excess $S_2O_6F_2$ was removed, the liquid crystallized to a yellow solid, $I(SO_3F)_3$.[3] The compound was analyzed for sulfur. Sulfur found: 23.42, 22.68%. (Theor. 22.68%.) The equation for the reaction is $2ICl + 3S_2O_6F_2 = 2I(SO_3F)_3 + Cl_2$.

Reaction with Perfluorocyclopentene to give Octafluorobis-(fluorosulfonato)-cyclopentane.—Peroxydisulfuryl difluoride, in excess, reacted vigorously with perfluorocyclopentene according to the equation $C_5F_8 + S_2O_6F_2 = C_5F_8(SO_3F)_2$. On occasion, when the $S_2O_6F_2$ was added too rapidly, flashes of light were observed. After the reaction was complete, the remaining $S_2O_6F_2$ was removed by first pumping while the products were maintained at −20°, and second by a stream of dry helium passing through the remaining material at −20° for 4 hr. Nearly pure octafluorobis-(fluorosulfonato)-cyclopentane was obtained.

Properties of Octafluorobis-(fluorosulfonato)-cyclopentane. (a) Molecular Weight.—Experimental measurements gave an average molecular weight of 410 ± 10 compared to a calculated 410.2 for $C_5F_8(SO_3F)_2$. The error was rather large because of the low vapor pressure (3 mm.) of the compound at room temperature. **(b) Density.**—The density of $C_5F_8(SO_3F)_2$ was determined at five different temperatures. The interpolated value at 25° was 1.886 g./cc. The volume coefficient of expansion, calculated from the data, was 1.17 × 10⁻³ at 25°. **(c) Melting point.**—The melting point was not found since all attempts to crystallize the compound resulted in a glass. **(d) Vapor Pressure and Boiling Point.**—The vapor pressure values of the compound over the temperature range 61.2 to 149.4° which are given in Table II indicated a boiling point of 148.0°, a molar heat of vaporization of 10.2 kcal. and a Trouton constant of 24.3. **(e) Infrared Spectrum.**—Figure 1 shows the spectrum of $C_5F_8(SO_3-F)_2$ obtained in the range 2 to 15 μ at 3 mm. pressure. Some of the bands of the product were identified by comparison with those of the reactants.[4,12,13] Strong bands at 1496 cm.⁻¹ (6.68 μ) and 1253 cm.⁻¹ (7.97 μ) were attributed to S–O stretch and at 853 cm.⁻¹ (1173 μ) to S–F stretch and at 1217 cm.⁻¹ (8.22 μ) to C–F stretch. Weak bands at 1310 cm.⁻¹ (7.63 μ) and at 1152 cm.⁻¹ (8.68 μ) were also attributed to

(12) R. N. Haszeldine, J. Chem. Soc., 4423 (1952).

(13) P. Torkington and H. W. Thompson, Trans. Faraday Soc., 41, 236 (1945).
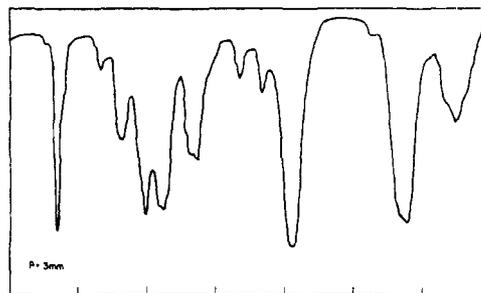
Fig. 1.—Infrared spectrum of $C_5F_8(SO_3F)_2$.

C–F stretch. Unidentified bands occurred at 1365 cm.⁻¹ (7.32 μ), 1069 cm.⁻¹ (9.35 μ), 990 cm.⁻¹ (10.11 μ) and 803 cm.⁻¹ (12.47 μ). **(f) Mass Spectrum.**—The principal peaks in the spectrum for mass numbers above 55 corresponded to the ions: SO_2^+, SOF^+, CF_3^+, SO_2F^+, $C_3F_3^+$, $C_2F_3O^+$, $C_2F_4^+$, $C_3F_3O^+$, $C_2F_5^+$, $C_3F_5^+$, $C_4F_5O^+$, $C_3F_7^+$, $C_4F_7^+$, $C_4F_7O^+$ and $C_5F_8^+$. A parent peak ($C_5F_8(SO_3F)_2^+$), although very weak, was noted at mass number 410. **(g) Nuclear Magnetic Resonance Spectrum.**—A comparison of areas under absorption peaks for $C_5F_8(SO_3F)_2$ and for $S_2O_6F_2$ gave 2.3 for the number of S–F bonds per molecule of $C_5F_8(SO_3F)_2$. Ther atio of S–F/C–F was 1/3.9 compared to theoretical 1/4. **(h) Elementary Analysis.**—Sulfur found: 14.9%; calculated: 15.6%. The sample was treated by potassium fusion in preparation for analysis. It apparently did not react with water.

$$\begin{array}{ccc} & F & F & \\ O & | & | & O \\ OSO-C & -C-OSO \\ F & | & | & F \\ & F_2-C & C-F_2 \\ & & \diagdown\diagup & \\ & & C & \\ & & | & \\ & & F_2 & \end{array}$$

Reaction with Tetrafluoroethylene to Form Tetrafluorobis-(fluorosulfonato)-ethane.—Since peroxides act as initiators for the polymerization of C_2F_4 to polytetrafluoroethylene, only low pressures of C_2F_4 were used during the reaction $S_2O_6F_2$ was always present in excess. The reaction was extremely vigorous and was carried out by slowly adding tetrafluoroethylene to $S_2O_6F_2$ containing 10% nitrogen by volume to reduce the reaction rate. Although $S_2O_6F_2$ was present in excess at all times to insure minimum polymerization of C_2-F_4, the entrance to the reaction vessel and other parts of the vacuum line soon were coated with a white solid. When the addition of C_2F_4 was very slow, a white smoke was observed which gradually condensed into fine droplets which very slowly enlarged and collected at the bottom of the vessel. A slightly more rapid addition resulted in a large temperature rise and quantities of brown color (probably due to SO_3F radicals). Separation and identification of products indicated the following reactions: $C_2F_4 + S_2O_6F_2 = C_2F_4(SO_3F)_2$ and $C_2F_4 + 2S_2O_6F_2 = 2COF_2 + 2S_2O_5F_2$. Polymeric products were not identified. The products, carbonyl fluoide and pyrosulfuryl fluoride, of the second reaction constituted only about 5% of the total product. After the sample had been purified by fractional codistillation, a portion was subjected to gas chromatography using a tricresyl phosphate-fire brick column at 72°. Since a single peak was obtained, it was concluded that the distilled material was over 99% pure.

Properties of Tetrafluorobis-(fluorosulfonato)-ethane. (a) Molecular Weight.—Molecular weight determinations on the sample gave an average of 298 compared to a calculated value of 298.15 for $C_2F_4(SO_3F)_2$. **(b) Density.**—The density of $C_2F_4(SO_3F)_2$ was determined at the four temperatures given in Table III. The density at 25° by interpolation was

TABLE III
DENSITIES OF $C_2F_4(SO_3F)_2$

Temp., °C.	1.0	12.5	24.3	35.4
Density, g./cc.	1.839	1.811	1.780	1.750

1.778 g./cc. The volume coefficient of expansion, calculated from the data of Table III, was 1.49 × 10⁻³ at 25°.
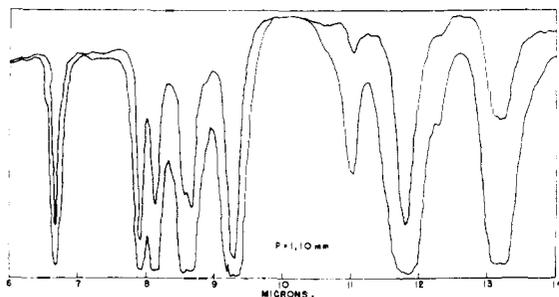
Fig. 2.—Infrared spectrum of $C_2F_4(SO_3F)_2$.

(c) **Melting Point.**—$C_2F_4(SO_3F)_2$ melted at $-27.8°$. (d) **Vapor Pressure and Boiling Point.**—The vapor pressures given in Table IV indicate a normal boiling point of 102.7°. From the Clausius-Clapeyron equation, the molar heat of vaporization was 9.1 kcal. and the Trouton constant 24.1.

TABLE IV

VAPOR PRESSURES OF $C_2F_4(SO_3F)_2$

P, mm.	Temp., °K.	P, mm.	Temp., °K.
21.8	295.8	424.1	359.0
46.0	306.9	496.8	363.7
82.7	318.0	561.1	367.0
124.5	327.4	641.4	370.9
177.8	336.0	693.8	373.2
242.6	343.5	743	375.7
293.6	348.6	(760)	(375.9)
371.3	355.1	787	377.2

(e) **Infrared Spectrum.**—The infrared spectra obtained at 1 and 10 mm. are given in Fig. 2. By comparing the frequencies of the tetrafluorobis-(fluorosulfonato)-ethane with those of the reactants,[4,13] the molecular motions for some of the bands were assigned. Strong bands at 1496 cm.$^{-1}$ (6.68 μ) and 1263 cm.$^{-1}$ (7.92 μ) were attributed to S–O stretch, while those at 906 cm.$^{-1}$ (11.04 μ) and 846 cm.$^{-1}$ (11.81 μ) were due to S–F motions. A C–F stretch was responsible for the band at 1163 cm.$^{-1}$ (8.60 μ). Other strong bands occur at 1230 cm.$^{-1}$ (8.13 μ), 1077 cm.$^{-1}$ (9.28 μ) and 758 cm.$^{-1}$ (13.20 μ). (f) **Nuclear Magnetic Resonance Spectrum.**— Using perfluorocyclopentane (C_5F_{10}) as a standard, the number of C–F bonds found per molecule of $C_2F_4(SO_3F)_2$ was 3.4 (theor. 4.0). The experimental number of S–F bonds was 1.8 (theor. 2.0) when $S_2O_6F_2$ was used as the standard. (g) **Elementary Analysis.**—Sulfur content found was 20.6% compared to 21.5% calculated. The sample was prepared for analysis by heating with potassium. (h) **General.**— Tetrafluorobis-(fluorosulfonato)-ethane was observed to be a colorless liquid which dissolved Kel-F stopcock grease but was inert toward mercury and glass and, for at least short periods of contact, toward water. The properties were consistent with the structure

$$\begin{array}{ccc} O & F & F & O \\ \| & | & | & \| \\ FSOC & - & COSF \\ \| & | & | & | \\ O & F & F & O \end{array}$$
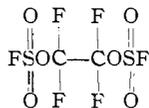
Reaction with Sulfur Tetrafluoride to Form Tetrafluorobis-(fluorosulfonato)-sulfur(VI).—Peroxydisulfuryl difluoride did not react with sulfur tetrafluoride at room temperature. To study the effect of increasing temperature, equivalent amounts of SF_4 and $S_2O_6F_2$ were treated as described under Procedure 2 above. At 85°, the pressure began to fall gradually. At 106°, the decrease was very rapid. In subsequent runs the reactor was maintained at 128° while equal pressures of the reactants were added and allowed to remain until the pressure stopped decreasing. An 86% yield of tetrafluorobis-(fluorosulfonato)-sulfur(VI) was obtained based on the reaction $SF_4 + S_2O_6F_2 \xrightarrow{128°} SF_4(SO_3F)_2$. This indicated that the SF_4 as received was at least 86% pure. SOF_2 was the main contaminant in the SF_4 as shown by vapor density and infrared spectrum determinations. The more volatile SOF_2 was removed by distillation leaving pure $SF_4(SO_3F)_2$ which required no further purification.
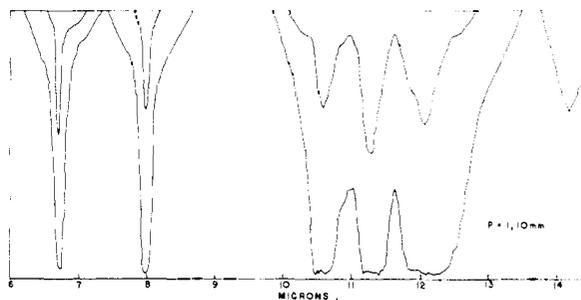
Fig. 3.—Infrared spectrum of $SF_4(SO_3F)_2$.

Properties of Tetrafluorobis-(fluorosulfonato)-sulfur(VI). (a) **Molecular Weight.**—Molecular weight determinations on the sample gave an average of 306 compared to 306.12 for $SF_4(SO_3F)_2$. (b) **Density.**—Densities were measured at the three temperatures given in Table V. From these data the extrapolated density at 25° was found to be 1.984 g./cc.

TABLE V

DENSITIES OF $SF_4(SO_3F)_2$

| Temp., °C.	0.0	10.6	22.9
Density, g./cc.	2.049	2.022	1.989

The volume coefficient of expansion was calculated from the data of Table V to be 1.34×10^{-3} at 25°. (c) **Melting Point.**—The melting point found for $SF_4(SO_3F)_2$ was $-62.9°$. (d) **Vapor Pressure and Boiling Point.**—A normal boiling point of 116.6° was obtained from the vapor pressures given in Table VI. The molar heat of vaporization from vapor pressure data was 9.3 kcal. and the Trouton constant 23.9.

TABLE VI

VAPOR PRESSURES OF $SF_4(SO_3F)_2$

P, mm.	Temp., °K.	P, mm.	Temp., °K.
22.9	305.8	330.8	363.7
30.7	310.5	415.6	370.8
45.2	317.7	455.4	373.9
60.0	322.8	532.1	378.1
89.2	331.2	634.8	384.2
99.7	333.6	690.1	386.9
149.8	343.5	724.2	388.6
189.1	349.6	(760)	(389.8)
232.2	354.4	769	390.4
272.4	359.0	800	391.5

(e) **Infrared Spectrum.**—Infrared spectra obtained at 1 and 10 mm. are given in Fig. 3. A comparison of the spectrum of $SF_4(SO_3F)_2$ with those of the reactants[4,14] enabled identification of the molecular motions responsible for some of the bands. S–O stretch appeared at 1491 cm.$^{-1}$ (6.71 μ) and 1251 cm.$^{-1}$ (7.99 μ) while S–F stretch at 887 cm.$^{-1}$ (11.28 μ) and 839 cm.$^{-1}$ (12.06 μ). Other bands occurred at 943 cm.$^{-1}$ (10.60 μ) and 704 cm.$^{-1}$ (14.20 μ). (f) **Mass Spectrum.**—The mass spectrum of $SF_4(SO_3F)_2$ above 56 included the following ions: SO_2^+, SOF^-, SF_2^+, SO_3^+, SO_2-F^+, SF_3^+, SF_3O^+ and SF_4^+. No peaks for masses greater than that of SF_4^+ were noted. (g) **Nuclear Magnetic Resonance Spectrum.**—The n.m.r. spectrum shown in Fig. 4 was run at 23° and a frequency of 40 megacycles. In the figure a large gap due to chemical shift between the $>SF_4$ fluorine atoms and the $-SO_3F$ fluorine atoms was eliminated; therefore, the chemical shift between these groups was much larger than it appears to be. The shift from the center of the $>SF_4$ spectrum to the center of the $-SO_3F$ spectrum was 1227 cycles per second. Numbers written below the $> SF_4$ part of the spectrum indicate the observed separations in cycles per second. The two clusters of peaks suggested that two pairs of structurally different fluorine atoms were present in the $>SF_4$ group. Since the clusters were not triplets, it appeared that the spin–spin

(14) R. E. Dodd, L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1956).
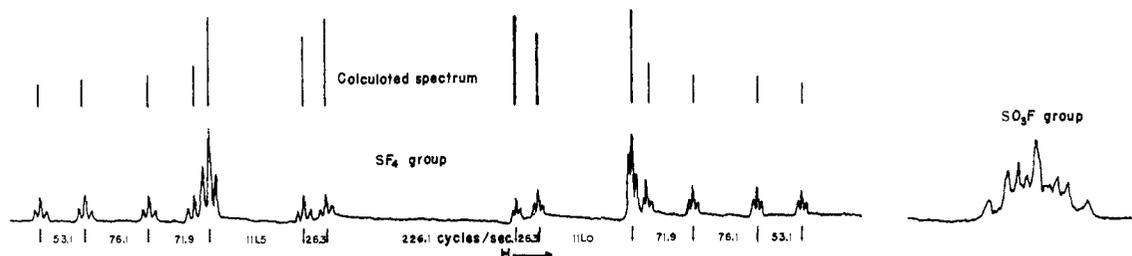
Fig. 4.—N.m.r. spectrum of cis-SF₄(SO₃F)₂.

coupling constant, J, and the chemical shift, δ, were of the same order of magnitude. Professor Kenneth B. Wiberg, a colleague of the authors, has kindly applied his computer program to the problem and has calculated the theoretical spectrum for the $>SF_4$ group based upon a value of δ of 501 cycles per second. Various values of J were tried, the best agreement with the experimental spectrum being obtained for J 156 cycles per second. The calculated spectrum is shown as lines in Fig. 4. Agreement between theory and experiment was good enough to validate the assumed structure of the $>SF_4$ group. It was therefore concluded that the fluorosulfonate groups occupied cis positions in an octahedral structure about the sulfur atom. If the fluorosulfonate groups had been trans, the fluorine atoms of the $>SF_4$ group probably would have been identical. Spin-spin splitting due to the fluorine atoms of the fluorosulfonate groups caused the "lines" of the $>SF_4$ group to have the triplet structure observable in Fig. 4. (h) **Elementary Analysis.**—When the compound was hydrolyzed in sodium hydroxide solution at 100°, it was found that 11.6 g. equivalents of base (theor. 12.0) were consumed per mole as shown in the equation

$$SF_4(SO_3F)_2 + 12\ OH^- = 3\ SO_4^{--} + 6F^- + 6\ H_2O$$
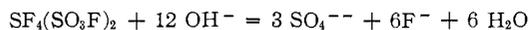
The sulfur and fluorine contents of the compound (as found in the hydrolyzed product) were: S, 30.4%; F, 37.6% (Theor. S, 31.4%; F, 37.2%). (i) **General.**—The compound was found to be a clear, colorless liquid which was inert toward mercury but apparently attacked glass slowly and was dissolved readily in Kel-F stopcock grease. The properties were consistent with the structure
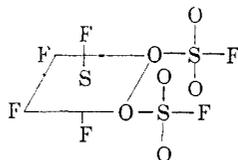
Reactions Involving Both Fluorosulfonation and Oxygenation.—With some compounds peroxydisulfuryl difluoride acted both as an oxygenating and a fluorosulfonating agent through the addition of one or more oxygen atoms and one or more fluorosulfonate groups to the central atom of the reacting species.

Reaction with Thionyl Chlorofluoride.—Thionyl chlorofluoride is the only known thionyl compound which contains two different groups attached to the central atom. Although it seemed that $S_2O_6F_2$ might replace the chlorine with a fluorosulfonate group and give rise to a second such compound, this was not found to be the case.

The reaction was quite exothermic and the gas in the bulb acquired a slight greenish tinge. Products found were chlorine (green, mol. wt. 72) and $S_2O_5F_2$ (infrared as above) indicating the reaction: $2\ SOClF + 3S_2O_6F_2 = 4S_2O_5F_2 + Cl_2$.

Reaction with Molybdenum Hexacarbonyl or Molybdenum Metal to Form Dioxobis-(fluorosulfonato)-molybdenum(VI).—As was mentioned earlier, the reaction of $S_2O_6F_2$ with $Mo(CO)_6$ proceeded rapidly and was accompanied by the quantitative displacement of the carbonyl groups to form carbon dioxide and by evolution of heat. As the reaction progressed, the white carbonyl, which had been sublimed into the reaction vessel, gradually became emerald green. Finally a bright orange liquid and a white solid were produced. On occasion, if the gaseous products were not almost continuously removed, the bulb containing the reaction mixture was completely destroyed due to the

sudden and rapid release of carbon monoxide and carbon dioxide. This removal required frequent cycles of holding the vessel at $-78°$ while the gas was pumped away and then warming the bulb to room temperature to allow the reaction to continue.

Because of the inconvenience associated with this reaction, the reaction of excess $S_2O_6F_2$ with molybdenum metal was tried. It was found that at room temperature the reaction occurred slowly but that at 60-85°, the metal was rather rapidly converted to a white solid and a solution of a bright orange substance in liquid $S_2O_6F_2$. The reaction was allowed to occur in a 50 or 100 ml. Pyrex glass bulb equipped with a 2 mm. Kern stopcock attached to a 10/30 inner standard taper joint. Two break seals also were attached to the bulb. Finely divided molybdenum metal was weighed into the bulb and the stopcock and break seals were then attached. The bulb was evacuated and, while pumping was continued, was heated strongly to remove any trace of moisture. Peroxydisulfuryl difluoride was distilled onto the metal until present in at least a three-fold excess. The stopcock was pulled off and the bulb was maintained at 75° until all visible reaction had ceased (no metal left). Through use of one break seal, the excess $S_2O_6F_2$ and other volatile materials (largely $S_2O_5F_2$) were removed. The white solid was still moist with an orange liquid. The bulb was wrapped with uniformly spaced nichrome resistance wire and covered with asbestos tape. When a small electric current was passed through the wire to warm the bulb, the more volatile orange liquid was distilled under good vacuum into the side arm to which the second break seal was attached. Heating was continued until the solid became white or cream colored, and the side arm was pulled off. The bulb was opened in a dry box and portions of the solid were placed in a weighed bulb and in a melting point tube. A sample of the solid (1.3419 g.) was hydrolyzed and analyzed for molybdenum, sulfur and fluorine. Oxygen was determined by difference. The ratio, in terms of atoms, found for Mo:S:F:O was 1.0:2.0:2.1:8.0 compared to 1.0:2.0:2.0:8.0 theoretical for $MoO_2(SO_3F)_2$. The experimentally obtained percentage composition for dioxobis-(fluorosulfonato)-molybdenum(VI) was Mo, 29.13%; S, 19.76%; F, 12.22%; and O, 38.89%. Calcd.: Mo, 29.42%; S, 19.66%; F, 11.65% and O, 39.24%. In an attempt to determine the melting point the tube was placed in a furnace and the temperature was allowed to increase slowly. At about 230° decomposition to a blue solid occurred and the Pyrex tube was badly etched.

The very viscous orange liquid (collected in the side arm as stated above) was transferred under anhydrous conditions and 0.2067 g. was subjected to basic hydrolysis. The experimental ratio of Mo:SO₃F:O was 1:2:3:0.7. This suggests the formula $MoO(SO_3F)_2$. It is very unlikely, however, that this compound would: (1) exist under such highly oxidizing conditions, (2) show a definite but somewhat broadened n.m.r. spectrum (the two unpaired electrons in a Mo(IV) compound could prevent one from obtaining a n.m.r. spectrum) and (3) be a liquid which melts sharply at approximately $-65°$ when the analogous oxyfluoride is a high melting solid. Further work is indicated.