products which were distilled from 0° and condensed as follows: A mixture of unreacted starting material and a white solid at −23°, an unidentified liquid which condensed at −80°, and a −80° distillate which consisted of 7.6 cc. (0.34 mmole) of difluoroethylborane. The −80° condensate had an infrared spectrum similar to chloro-(dimethylamino)-ethylborane and may have been ethyl-(dimethylamino)-fluoroborane, $C_2H_5[(CH_3)_2N]BF$.

CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA

Formation of Pentafluorosulfur Fluorosulfonate and Bispentafluorosulfur Oxide from the Direct Reaction of the Elements[1]

BY BERNARD COHEN AND ALAN G. MACDIARMID[2]

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In addition to SF_6 and S_2F_{10}, the direct reaction of sulfur with fluorine has been found to produce small quantities of pentafluorosulfur fluorosulfonate, SF_5OSO_2F, and bispentafluorosulfur oxide, $(SF_5)_2O$. The compounds S_2F_{10}, SF_5OSO_2F, and $(SF_5)_2O$ have been obtained in a high state of purity by gas chromatographic separations and a number of their physical properties have been examined.

It has been reported that the only products in addition to SF_6 resulting from the reaction of sulfur with fluorine are S_2F_{10}, SF_5OOSF_5, SF_4, S_2F_2, and SO_2.[3,4] Traces of oxygen or oxygen fluorides in the fluorine presumably account for the oxygenated compounds. In view of the presence of bispentafluorosulfur peroxide, SF_5OOSF_5, among the products it appeared possible that other species containing the interesting $-SF_5$ group also might be present. This investigation was performed in order to see if this were the case.

The higher boiling (approximately 30°) fraction remaining after the removal of SF_6 from the products of the reaction of fluorine with sulfur was separated into more than a dozen components by means of gas–liquid chromatographic columns. The three most abundant materials found were S_2F_{10} (~40%), SF_5OSO_2F (~30%), and $(SF_5)_2O$ (~10%).

Since the physical properties reported for S_2F_{10} vary widely (melting points ranging from −92 to −53° have been given[5–8]) the melting point, vapor pressure data, and infrared spectrum of the compound were re-examined.

During the course of the present investigation it was reported that the new compound SF_5OSO_2F was obtained during the irradiation of a mixture of S_2F_{10} and SO_2 by ultraviolet light.[9] It therefore is not surprising to find that SF_5OSO_2F is formed during the reaction of fluorine with sulfur since both S_2F_{10} and SO_2 also are present among the reaction products.[4]

It has been reported previously that SF_5OOSF_5 was a minor product of the reaction of fluorine with sulfur.[3] Although it may be present in the material investigated in this research, it certainly does not appear to be present in as large quantities. Slight variations in reaction conditions would undoubtedly lead to variations in the relative amounts of products obtained, especially since it appears likely that SF_5OOSF_5 is converted to $(SF_5)_2O$ in the presence of SF_5 radicals[10] which might be expected to be present in the reaction system.

The mass spectra of S_2F_{10}, SF_5OSO_2F, and $(SF_5)_2O$ are analogous to that of SF_6[11] in that no

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parent molecule ion fragment is observed and that the most abundant fragment in all four cases is the SF_5^+ ion.

Attempts to prepare S_2F_{10} from SF_6 by various electrical discharge methods and by reaction with boiling mercury and molten tin were unsuccessful.

Experimental

Apparatus.—All work was performed in a Pyrex glass vacuum system using a fluorinated grease (Kel F 90) on joints and stopcocks. Temperatures were measured by an iron–constantan thermocouple, standardized by the National Bureau of Standards. Melting points were determined by means of a magnetic plunger apparatus.[12] Pressures were measured by means of mercury manometers.

Disulfur Decafluoride. (a) From Products of the Reaction of Sulfur with Fluorine.—The colorless liquid from which this material was isolated was obtained as a high-boiling (~30°) product from the direct reaction of sulfur with fluorine.[13] No separation of the mixture into its components was possible by ordinary vacuum distillation techniques. The liquid was examined by gas chromatographic techniques by means of a Perkin-Elmer Model 154D vapor fractometer using a 0.5-in., 35-ft. column packed with either Dow Corning 200 silicone oil dispersed on 30 to 60 mesh Chromasorb P in a one to three weight ratio or a fluorocarbon oil (Kel F 3) dispersed on Chromasorb W.[14] The material was further purified by means of a low temperature distillation column similar to that described by Denbigh and Whytlaw-Gray,[5] held at approximately −96°. When the original mixture was passed through the chromatographic column containing fluorocarbon oil, thirteen components were observed whereas only eight appeared when the silicone oil column was used.

(b) From Sulfur Hexafluoride.—Sulfur hexafluoride was subjected to a glow discharge by streaming the gas at low pressures through a glass tube in contact with a standard laboratory tesla coil "leak detector." A mixture of SF_6 and chlorine was treated in a similar manner. No S_2F_{10} or SF_5Cl was obtained. Similarly, no S_2F_{10} or SF_5Cl was obtained when the materials were streamed through an H-tube between mercury electrodes having potential differences up to 15,000 volts. No S_2F_{10} was obtained when SF_6 was bubbled through mercury or molten tin under a variety of experimental conditions. When air was admixed with the SF_6 no new sulfur-containing products were observed.

Properties of Disulfur Decafluoride.—Experimental molecular weights of S_2F_{10} were within less than one mass unit of the calculated value, 254.1. A melting point of −52.7 ± 0.3° was obtained and was found to be very sensitive to traces of impurities.

The vapor pressure of S_2F_{10} was measured in an all-glass tensiometer attached to a mercury manometer. Values for a number of different temperatures are given in Table I.

TABLE I

VAPOR PRESSURE OF DISULFUR DECAFLUORIDE

T, °C.	P, mm. (obsd.)	P, mm. (calcd.)	T, °C.	P, mm. (obsd.)	P, mm. (calcd.)
−80.7	1.2	1.1	−30.1	48.3	48.0
−70.2	3.0	3.0	−18.7	87.0	87.0
−60.4	6.2	6.4	−10.8	140.6	140.2
−55.7	8.6	8.6	0.0	239.8	238.6
−45.5	18.0	17.8	−23.0	72.9[a]	72.4
−38.8	25.9	26.1	−66.1	4.3[a]	4.2
			−78.2	1.9[a]	1.4

[a] Pressure observed on decreasing temperature. No non-condensable gas was present at −196° at the conclusion of the determination. The molecular weight of the entire sample at the end of the experiment was 254.7.

The vapor pressure of the liquid in the temperature range −51 to 0° is given by the equation

$$\log P\ (\text{mm.}) = -\frac{1498.8630}{T} - \frac{5324.0740}{T^2} + 7.9361210$$

The vapor pressure of the solid in the temperature range −80 to −56° is given by the equation

$$\log P\ (\text{mm.}) = \frac{2527.6478}{T} - \frac{410684.93}{T^2} - 2.0036024$$

Additional values to those given in Table I were used to derive the above relationships. The extrapolated boiling point is 26.7°, the heat of vaporization is 7.07 kcal. mole^{-1}, and the Trouton constant is 23.6 cal. deg.$^{-1}$ mole^{-1}.

The infrared spectrum was measured over the 2–15 μ range by means of a Perkin-Elmer Model 137B Infracord spectrophotometer with sodium chloride prisms. Three spectra of disulfur decafluoride have been reported.[15–17] One of these[15] is the spectrum of impure S_2F_{10} containing oxygenated sulfur fluorine compounds. The spectra obtained in this study are in good agreement with the work of Wilmshurst and Bernstein[17] and are an exact duplication of the work of Dodd, Woodward, and Roberts.[16] The nuclear magnetic resonance spectrum was surprisingly complex and was essentially identical with that recently reported.[18]

The mass spectrum fragmentation pattern was obtained by means of a Consolidated Electrodynamics Model 21–130 mass spectrometer at an ionizing potential of 72 volts and an ionizing current of 20 μa. The principal fragments (those having an abundance greater than 3.1%) observed were: SF_5^+, 100%; SF_3^+, 36.0%; SF_2^+, 14.0%; SF^+, 5.9%; SF_3^{+2}, 5.7%; S^+, 3.7%. Examination of the material at an ionizing potential of 10 volts produced no ions larger than SF_5^+. The over-all fragmentation pattern is very similar to that of SF_6.[11]

Pentafluorosulfur Fluorosulfonate.—This material could be isolated by use of either the silicone or fluorocarbon oil gas chromatographic columns. In both cases the material

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[13] Sample kindly donated by Pennsalt Chemicals Corporation, Philadelphia, Pa.

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was contained in the last fraction to elute from the columns. Final purification was carried out by tensiometric distillation from a trap immersed in a Dry Ice bath after first removing a more volatile impurity from the material when it was held in a trap at melting toluene temperatures.

Experimental molecular weights were within less than one mass unit of the calculated value, 226.1, and the melting point observed for pure SF_5OSO_2F was −105.1 ± 0.1° (literature[9] −107 ± 0.5°). The infrared spectrum was almost identical to that previously reported,[9] except that the shoulder at 795 cm.$^{-1}$ was replaced by a weak but well defined peak at 778 cm.$^{-1}$. The nuclear magnetic resonance spectrum was identical with that previously published.[19]

The vapor pressure of the material was determined in an all-glass tensiometer attached to a mercury manometer. Values for a number of different temperatures are given in Table II.

TABLE II

VAPOR PRESSURE OF PENTAFLUOROSULFUR FLUOROSULFONATE

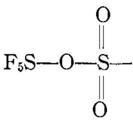
T, °C.	*P*, mm. (obsd.)	*P*, mm. (calcd.)	*T*, °C.	*P*, mm. (obsd.)	*P*, mm. (calcd.)
−45.9	8.3	8.6	−15.6	64.6	64.2
−41.0	12.5	12.4	−10.4	87.2	86.4
−35.5	17.9	18.1	− 3.5	118.6	119.0
−30.0	26.0	26.2	0.0	150.1	150.7
−25.5	35.5	35.1	−26.3	33.9[a]	33.3
−20.6	48.1	47.4	−45.2	9.0[a]	9.0

[a] Pressure observed on decreasing the temperature. No non-condensable gas was present at −196° at the conclusion of the determination. The molecular weight of the entire sample at the end of the experiment was 225.3.

Vapor pressures in the range −45.9 to 0° are represented by the equation

$$\log P\,(\text{mm.}) = -\frac{1682.35}{T} + 8.33703$$

The extrapolated boiling point is 35.1°, the heat of vaporization is 7.70 kcal. mole^{-1}, and the Trouton constant is 25.0 cal. deg.$^{-1}$ mole^{-1}.

The mass spectrum fragmentation pattern was obtained on the same instrument and under experimental conditions identical with those described for S_2F_{10}. The principal fragments (those having an abundance greater than 2.6%) observed were: SF_5^+, 100%; SF_3O^+, 13.2%; SFO_2^+, 12%; SF_3^+, 9.5%; SF_4^+, 4.0%; SFO^+, 4.0%. No evidence for ions larger than SF_5^+ could be obtained even when the material was examined at an ionizing potential of 10 volts. The mass spectrum therefore confirms the proposed fluorosulfonate structure,  $F_5S{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}F$, of the compound.

Bispentafluorosulfur Oxide.—This material was isolated by use of the fluorocarbon oil gas chromatographic column, but was slightly contaminated with S_2F_{10}, which is the next material to be eluted. Final purification was carried out by tensiometric distillation of the sample from a trap immersed in a melting toluene bath.

Experimental molecular weights were within less than one mass unit of the calculated value, 270.1. The melting point observed for SF_5OSF_5 was −118.5 ± 0.1° (literature[20] −115 ± 4°). The infrared spectrum was identical with that previously reported.[20]

The mass spectrum fragmentation pattern was measured on the instrument previously described using the same experimental conditions. The principal fragments (those having an abundance greater than 1.5%) observed were: SF_5^+, 100%; SF_3O^+, 11.6%; SF_3^+, 6.0%; SF_2^+, 2.3%; SFO^+, 1.6%. No evidence for ions larger than SF_5^+ could be obtained even when the material was examined at an ionizing potential of 10 volts.

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[20] H. L. Roberts, *ibid.*, 2774 (1960).

CONTRIBUTION NO. 766 FROM THE CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON 98, DELAWARE

Preparation and Properties of Tetracoördinate Sulfur(IV) Fluorides

BY R. M. ROSENBERG AND E. L. MUETTERTIES

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The new perfluoroalkyl derivatives of SF_4, $[(CF_3)_2CF]_2SF_2$, $(CF_3)_2CFSF_3$, and $(CF_3)_2CFSF_2CF_3$ have been prepared by the addition of SF_4 and CF_3SF_3 to $CF_3{-}CF{=}CF_2$. Investigation of their chemistry has led to the preparation of $(CF_3)_2CFSF$, $(CF_3)_2CFSOCF(CF_3)_2$, $(CF_3)_2CFS(O)OH$, and $(CF_3)_2CFS(O)OCH_2CH_3$.

Introduction

Only a limited number of tetracoördinate sulfur(IV) halides have been reported. Of these, the only well established perfluoroalkyl derivative is CF_3SF_3.[1] Reported methods for the

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