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 $-105.1 \pm 0.1°$ (literature[9] $-107 \pm 0.5°$). 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

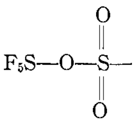
T, °C.	P, mm. (obsd.)	P, mm. (calcd.)	T, °C.	P, mm. (obsd.)	P, mm. (calcd.)
−45.9	8.3	8.6	−15.6	64.6	64.2
−41.0	12.5	12.4	−10.4	87.2	86.4
−35.5	17.9	18.1	− 3.5	118.6	119.0
−30.0	26.0	26.2	0.0	150.1	150.7
−25.5	35.5	35.1	−26.3	33.9[a]	33.3
−20.6	48.1	47.4	−45.2	9.0[a]	9.0

[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 $-118.5 \pm 0.1°$ (literature[20] $-115 \pm 4°$). 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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(19) R. K. Harris and K. J. Packer, *J. Chem. Soc.*, 4736 (1961).

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

CONTRIBUTION NO. 766 FROM THE CENTRAL RESEARCH DEPARTMENT
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Preparation and Properties of Tetracoördinate Sulfur(IV) Fluorides

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

Received March 6, 1962

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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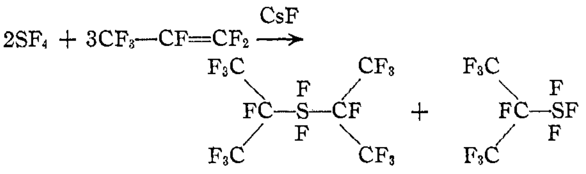
(1) E. A. Tyczkowski and L. A. Bigelow, *J. Am. Chem. Soc.*, **75**, 3523 (1953).

synthesis of alkyl or aryl derivatives of sulfur tetrafluoride include electrolytic fluorination and reactions involving elemental fluorine or metal fluorides.[2-6] Except for the latter method, complex product mixtures usually are obtained, and the yields of the desired sulfur(IV) component are generally low.

A method is herein reported for the direct synthesis of perfluoroalkyl sulfur(IV) fluorides from a fluoroölefin and sulfur tetrafluoride or a monosubstituted sulfur(IV) fluoride. The first reported examples of perfluoroalkyl sulfur(IV) difluorides, $[(CF_3)_2CF]_2SF_2$ and $(CF_3)_2CFSF_2CF_3$, have been prepared by this method.

Results and Discussion

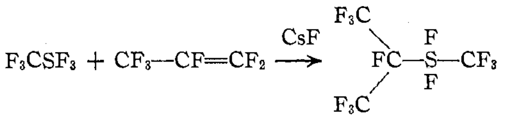
The CsF-catalyzed addition of SF_4 to perfluoropropene at 150° gives $[(CF_3)_2CF]_2SF_2$ (I) and $(CF_3)_2CFSF_3$ (II).



$$2SF_4 + 3CF_3{-}CF{=}CF_2 \xrightarrow{CsF} [(CF_3)_2CF]_2SF_2 + (CF_3)_2CFSF_3$$

I II

Formation of either I or II is simply controlled by reactant ratios. Similarly, $(CF_3)_2CFSF_2CF_3$ (III) is obtained from CF_3SF_3 and perfluoropropene.



$$F_3CSF_3 + CF_3{-}CF{=}CF_2 \xrightarrow{CsF} (CF_3)_2CFSF_2CF_3$$

III

The catalyst role of CsF is ascribed to perfluorocarbanion formation[7] and subsequent nucleophilic attack of SF_4.

Molecular models of $[(CF_3)_2CF]_2SF_2$ indicate that the sulfur atom is well shielded and that the periphery of the molecule is essentially[8] composed of fluorine atoms. This suggests a crude approximation to a fluorocarbon and, in fact, the bulk physical properties (Table I) are similar to those of the C_7 and C_8 fluorocarbons.

TABLE I

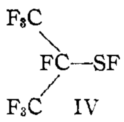
PHYSICAL PROPERTIES OF $[(CF_3)_2CF]_2SF_2$

Vapor pressure equation (0–110°)	$\log P$ (mm.) = $-(1911/T) + 7.85$
ΔH vap. (derived)	8.75 kcal.
Trouton constant	22.8
Boiling point (extrapolated)	110.8°
Freezing point	$<-78°$
Density (at 25°)	1.8662
Critical temperature	182°

Solubility properties also parallel those of fluorocarbons. This sulfur fluoride is immiscible with water, partially miscible with hydrocarbons, and readily miscible with select solvents such as ether, acetone, and chloroform. The shielding of the sulfur atom also must account for the fact that $[(CF_3)_2CF]_2SF_2$ exhibits no acceptor properties toward Lewis bases such as water and amines, whereas the less shielded sulfur atoms in SF_4[9] and CF_3SF_3 do interact with donor molecules. Hydrolysis of $[(CF_3)_2CF]_2SF_2$, a thermodynamically favored process, does not occur at 100° in the vapor phase. Again this must reflect a shielding effect since SF_4,[10] CF_3SF_3,[1] $C_6H_5SF_3$,[6] and $(CF_3)_2CFSF_3$ all hydrolyze rapidly. However, apparent anomalies in hydrolytic stability may be found in the literature. Slow decomposition of $SF_3CF_2C(O)OH$[5] reportedly occurs at 25° in neutral, aqueous solution and $SF_3CF_2SF_5$[1] is described as resistant to hydrolysis with warm aqueous alkali. In these apparently quite stable species, shielding effects cannot be invoked as the explanation.

Rather facile and drastic decomposition of $[(CF_3)_2CF]_2SF_2$ occurs with methanolic KOH. Reaction proceeds exothermically at temperatures above −78° to give SO_3^{-2}, CF_3CFHCF_3, and other, as yet unidentified, products.

In the pyrolysis of I at 200°, major products are SF_4, $[(CF_3)_2CF_2]_2$, and the sulfenyl fluoride IV.



$(CF_3)_2CFSF$

IV

This sulfenyl fluoride, believed to be the first example of a monosubstituted derivative of sulfur difluoride,[11,12] is a pale green liquid, highly reactive

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[2] F. Nesdel, *Naturwiss.*, **39**, 209 (1952).

[3] A. F. Clifford, H. K. El-Shamy, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953).

[4] D. L. Chamberlain, Jr., and N. Kharasch, *J. Am. Chem. Soc.*, **77**, 1041 (1955).

[5] R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 2684 (1956).

[6] W. A. Sheppard, *J. Am. Chem. Soc.*, **82**, 4751 (1960).

[7] W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

[8] This is qualified since it is impossible without precise structural data to assess the stereochemical impact of the non-bonding pair of electrons.

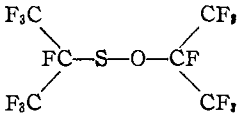
[9] E. L. Muetterties, U. S. Patent 2,897,055, July 28, 1959.

[10] C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).

[11] J. H. Simons, U. S. Patent 2,519,983, August 22, 1950, has reported a product cited as $C_8F_{17}SF$ but no data supporting the composition or structure of the compound were given.

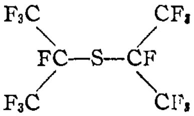
toward mercury. It does not attack glass which has been rigorously dried. In the F^{19} n.m.r. spectrum of IV, the SF resonance is shifted to high fields, +293 p.p.m. with respect to 1,1,2,2-tetrachloro-1,2-difluoroethane. This shift is unusually large since fluorine resonances, in general, are found within the limits of the F_2 and HF resonances at −492 and +133 p.p.m. The origin of this large paramagnetic shift may be a mixing of the ground state with excited states arising from promotion of the non-bonding sulfur electrons.

Boric oxide converts I to the sulfenic ester V, a



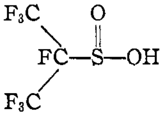
V

distillable liquid which is insoluble in and only slowly attacked by water. Reduction occurs in the reaction of I with $TiCl_4$, and the sulfide VI and chlorine are the sole volatile products.



VI

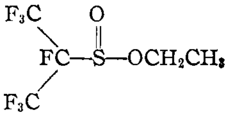
Two oxygen-containing derivatives of $(CF_3)_2CFSF_3$ have been prepared. Controlled hydrolysis of II in diethyl ether yields the sulfinic acid VII, a slightly volatile, oxygen-sensitive, viscous



VII

liquid which is unstable and undergoes detectable decomposition in an inert atmosphere within a period of several weeks. Unlike trifluoromethanesulfinic acid,[13] VII is decomposed by aqueous alkali at room temperature. Salts of the acid may be isolated from neutral solutions; a hydrated sodium salt appeared to be more stable to storage than the parent acid.

Alcoholysis of II in excess ethyl alcohol proceeds rapidly and exothermically at room temperature to give the sulfinic ester VIII, a distill-



VIII

able liquid stable toward water at room temperature.

Experimental

Materials.—Sulfur tetrafluoride was obtained from the Organic Chemicals Department, E. I. du Pont de Nemours and Co. Perfluoropropene was obtained from the Polychemicals Department, E. I. du Pont de Nemours and Co. Cesium fluoride was obtained from the American Potash and Chemical Corporation. Boric oxide was obtained from the Pacific Coast Borax Co. Titanium tetrachloride was obtained from the Fisher Scientific Co.

The pressure vessels used were stainless steel—or "Hastelloy-C"—lined shaker tubes. Either type vessel was found to be satisfactory

$[(CF_3)_2CF]_2SF_2$ (I) and $(CF_3)_2CFSF_3$ (II).—A mixture of 60 g. (0.40 mole) of perfluoropropene, 45 g. (0.42 mole) of sulfur tetrafluoride, and 3.6 g. (0.024 mole) of anhydrous cesium fluoride was heated at 100° for 2 hr. and at 150° for 10 hr. in a 240-ml. pressure vessel. Distillation of the liquid product gave three major fractions: fraction 1, b.p. 39–42° (0.95 g.); fraction 2, b.p. 46–47° (30 g.); fraction 3, b.p. 95° (473 mm.) (8.6 g.). Elemental analysis of these fractions was in agreement with the compositions $C_3F_7S(O)F$, $C_3F_7SF_3$, and $(C_3F_7)_2SF_2$, respectively.

Anal. Calcd. for $C_3F_7S(O)F$: C, 15.3; F, 64.4; S, 13.6. Found: C, 15.5; F, 64.5; S, 14.1. Calcd. for $C_3F_7SF_3$: C, 14.0; F, 73.6; S, 12.4. Found: C, 14.6; F, 73.4; S, 12.5. Calcd. for $(C_3F_7)_2SF_2$: C, 17.7; F, 74.5; S, 7.9. Found: C, 18.1; F, 74.7; S, 7.9.

$(CF_3)_2CFSF_2CF_3$ (III).—A mixture of 24 g. (0.16 mole) of perfluoropropene, 25 g. (0.16 mole) of trifluoromethylsulfur trifluoride, and 2.4 g. (0.016 mole) of anhydrous cesium fluoride was heated at 100° for 3 hr. and at 150° for 7 hr. in an 80-ml. pressure vessel. Distillation of the liquid product gave 9.8 g. of distillate, b.p. 70–71°.

Anal. Calcd. for $C_3F_7SF_2CF_3$: C, 15.6; F, 74.0; S, 10.4. Found: C, 16.0; F, 73.5; S, 10.6.

Pyrolysis of I.—A sample of 20 g. (0.050 mole) of I was heated at 200° for 10 hr. in a 145-ml. pressure vessel. Separation of the reaction products, all of which were volatile, was carried out in a vacuum system by fractional condensation through U-traps held at −78°, −112°, and −196°. The material retained at −112° was refractionated in a similar fashion. The final −112° fraction was approximately 2 ml. of a pale green, clear liquid (at 0°) which attacked mercury rapidly and slowly attacked glass. In order to remove adventitious HF, the sample was condensed onto anhydrous NaF and agitated at 0° for several minutes.

Vapor density determinations of the purified −112° fraction gave molecular weight values of 238.5 and 239.1 compared to a calculated value of 220 for C_3F_7SF. Due to the highly reactive nature of this material, the elemental

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(12) (a) D. L. Chamberlain, Jr., and N. Kharasch, *J. Am. Chem. Soc.*, **77**, 1041 (1955), have reported a product presumed to be 2-nitrobenzenesulfenyl fluoride. However, no definitive structural data were given. (b) E. Kober, *ibid.*, **81**, 4810 (1959), has reported the compounds n-C_3F_7SF and CCl_3SF. No structural data were given for the first of these. W. A. Sheppard and J. F. Harris, Jr., *ibid.*, **82**, 5106 (1960), have shown the latter compound to be CCl_2FSCl.

(13) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 2901 (1955).

analytical values are in only fair agreement with the composition of the sulfenyl fluoride.

Anal. Calcd. for C_3F_7SF: C, 16.4; F, 69.1; S, 14.6. Found: C, 20.0; F, 66.4; S, 12.1.

Definitive characterization of IV was obtained from its F^{19} n.m.r. spectrum, described in the next section, which can be explained only on the basis of a sulfenyl fluoride structure. Supporting data for this structure were obtained from mass spectrographic analysis. Some 2.5 g. of I was heated at 200° for 10 hr. in a 145-ml. pressure vessel. Mass spectrographic analysis of the products, all of which were volatile, showed the presence of $[(CF_3)_2CF]_2$, $(CF_3)_2C{=}S$, SF_4, and SOF_2. Residual fragments, the largest of which had an *m/e* of 220 ($C_3F_7SF^+$), were all consistent with a sulfenyl fluoride structure. From the mole percentages of products, assuming SOF_2 was formed by adventitious hydrolysis of SF_4, the following equation can be written.

$$3[(CF_3)_2CF]_2SF_2 \longrightarrow 2[(CF_3)_2CF]_2 + SF_4 + 2C_3F_7SF$$

Reaction of I with $TiCl_4$.—A sample of 20 g. (0.50 mole) of I was condensed onto 5.1 g. (0.027 mole) of $TiCl_4$ held at −196° in an evacuated flask. An immediate yellow color developed in the flask when the latter was warmed to −78°. The flask was held at −78° for 3 days, after which time products volatile at −78° were removed. The flask then was warmed to room temperature and the remaining volatile products were collected in a trap held at −196°. Distillation of the room temperature volatile products yielded two major fractions: fraction 1, b.p. 83–85° (5.3 g.); fraction 2, b.p. 85–86° (4.8 g.). The analysis of the second fraction was in agreement with the composition of the sulfide $(C_3F_7)_2S$.

Anal. Calcd. for $(C_3F_7)_2S$: C, 19.5; F, 71.9; S, 8.7. Found: C, 19.4; F, 71.7; S, 7.8.

The −78° volatile product was found by mass spectrographic analysis to be mainly chlorine. The solid product was a hygroscopic yellow powder which contained no sulfur.

Reaction of I with B_2O_3.—A sample of 4.0 g. (0.057 mole) of boric oxide was dried at 250° for 5 hr. under high vacuum in a 145-ml. pressure vessel. The vessel then was cooled to −78° and 41 g. (0.10 mole) of I was introduced. The reactant mixture was heated to 150° for 20 hr. Distillation of the liquid product yielded 3.5 g. of distillate, b.p. 88–89°.

Anal. Calcd. for $C_3F_7SOC_3F_7$: C, 18.7; F, 68.9; S, 8.3. Found: C, 19.4; F, 68.4; S, 8.7.

Hydrolysis of II.—Distilled water (7.0 g., 0.39 mole) was added to a stirred solution of 49 g. (0.19 mole) of II in 75 ml. of diethyl ether held at 0°. The reaction mixture then was warmed to room temperature and stirred for 2 days. Volatile products were removed to leave a yellow oil. This was molecularly distilled at 40° under high vacuum to give 8 g. of a clear, colorless, oily distillate, the analysis of which was in fair agreement with the composition of the sulfinic acid, $C_3F_7S(O)OH$.

Anal. Calcd. for $C_3F_7SO_2H$: C, 15.4; F, 56.8; S, 13.7; H, 0.43. Found: C, 16.3; F, 54.4; S, 12.7; H, 1.10.

The proton n.m.r. spectrum of the acid consisted of three peaks; a very strong peak attributed to the acidic hydrogen and two much weaker peaks, the relative intensities of which were three to two and which corresponded in chemical shift to a spectrum of diethyl ether. The presence of ether impurity would explain the high C and low F and S analytical values. Approximate pK_a values of <3 were obtained by pH measurement of a solution of known concentration of the acid at 25° and by titration of the solution to a pH of 7.

A solution of 2 g. of the acid in 15 ml. of deoxygenated distilled water was introduced into an ion-exchange column packed with Amberlite IR-120 resin (Mallinckrodt Chemical Works). (The resin had been converted into basic form by treatment with 10% NaOH followed by repeated washing with distilled water.) Evaporation of the eluate *in vacuo* yielded a white solid residue which was dried for 24 hr. under high vacuum. Analysis of the resulting 1.7 g. of solid corresponded to the composition of the hydrated sodium salt, $C_3F_7S(O)ONa{\cdot}H_2O$.

Anal. Calcd. for $C_3F_7SO_3H_2Na$: C, 13.1; F, 48.5; S, 11.7; H, 0.74. Found: C, 13.0; F, 47.2; S, 12.0; H, 0.42.

Ethanolysis of II.—Slow addition of 9.3 g. (0.036 mole) of II to 13 g. (0.28 mole) of absolute ethanol under a nitrogen atmosphere produced a vigorous, exothermic reaction. Occasional cooling with an ice bath was employed to moderate the reaction. Addition of water to the clear solution caused the separation of a heavy, pale yellow, non-aqueous liquid phase. Distillation of the latter gave 3.4 g. of colorless distillate, b.p. 131–132°.

Anal. Calcd. for $C_3F_7S(O)OC_2H_5$: C, 22.9; F, 50.7; S, 12.2; H, 1.92; mol. wt. 262. Found: C, 23.6; F, 50.6; S, 11.9; H, 2.15; mol. wt. 255, 268. (Molecular weight determined by the freezing point depression of benzene.)

F^{19} N.m.r. Spectra.—The fluorine magnetic resonance spectra were obtained with a Varian high-resolution n.m.r. spectrometer and electromagnet at a frequency of 56.4 Mc. and a field of approximately 14,100 gauss. The spectra were calibrated in terms of displacements in parts per million (p.p.m.) from the fluorine resonance of 1,1,2,2-tetrachloro-1,2-difluoroethane (capillary reference tube). All spectra are of the pure liquids. Tables II and III summarize the chemical shift and coupling constant data. The observed spectra shown in Fig. 1a–1f can be reproduced with the coupling constant values given in Table III. The enlargements of the individual resonances

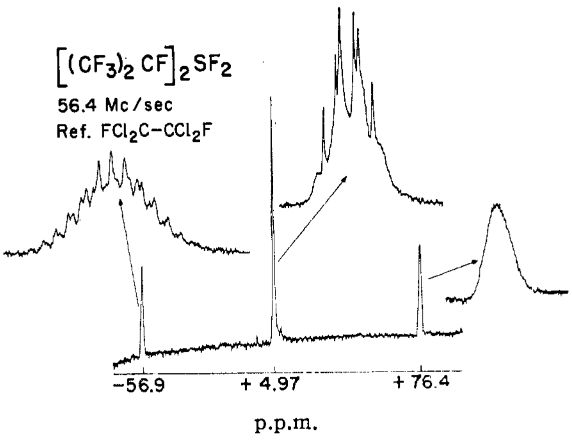

Fig. 1a.—F^{19} spectrum of $[(CF_3)_2CF]_2SF_2$ at 56.4 Mc.

Table II

F^{19} Chemical Shifts

$$\text{Chemical shift} = \frac{Hc - Hr}{Hr} \times 10^{-6} \text{ (ref.: } FCl_2C\text{–}CCl_2F)$$

Compound	SF_2	SF	CF_3	CF
$[(CF_3)_2CF]_2SF_2$	−56.9	...	+4.97	76.4
$(CF_3)_2CFSF_2CF_3$	−53.8	...	−8.25	+100
			+5.38 (i-C_3H_7)	
$(CF_3)_2CFSF_3$	−129	−13.5	+6.47	+97.4
$(CF_3)_2CFSF$	...	+293	+6.10	+91.1
$[(CF_3)_2CF]_2S$	...	...	+11.0	+99.0
$(CF_3)_2CFSOCF(CF_3)_2$	...	...	+7.87	+94.8
			+14.2	+74.8
$(CF_3)_2CFS(O)OH$	...	...	+5.33	+115
$(CF_3)_2CFS(O)OC_2H_5$	...	...	+4.76	+113

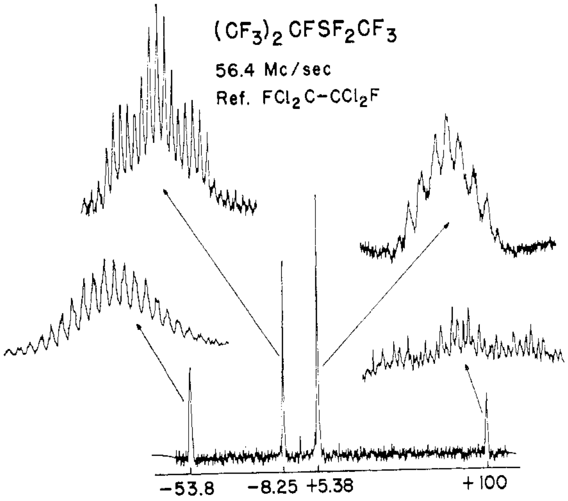

Fig. 1b.—F^{19} spectrum of $(CF_3)_2CFSF_2CF_3$ at 56.4 Mc.

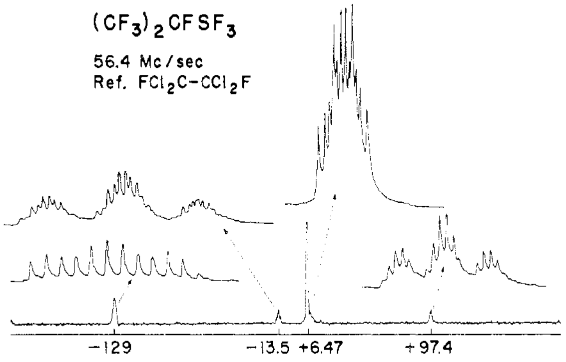

Fig. 1c.—F^{19} spectrum of $(CF_3)_2CFSF_3$ at 56.4 Mc.

were not obtained at identical sweep fields and should not be used for measurement comparison.

$[(CF_3)_2CF]_2SF_2$ (I).—There are three fluorine resonances of relative intensities two, twelve, and two assignable to SF_2, CF_3, and CF fluorine atoms (Fig. 1a). Apparent equivalence of $(CF_3)_2CF$ groups and of fluorine atoms bonded to sulfur suggests that either A or B is the structure of I (since, in all similar structures, *e.g.*, SF_4[14,15] and ClF_3,[16-18] the non-bonding electrons go into equatorial

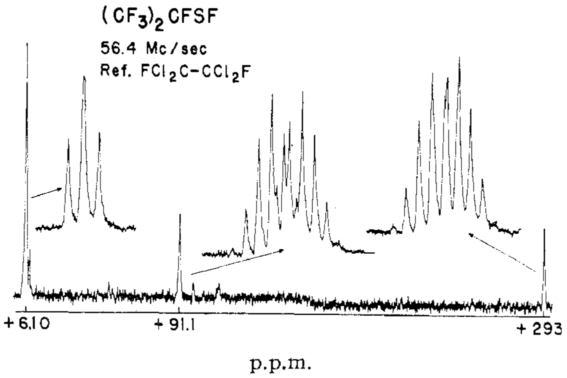

Fig. 1d.—F^{19} spectrum of $(CF_3)_2CFSF$ at 56.4 Mc.

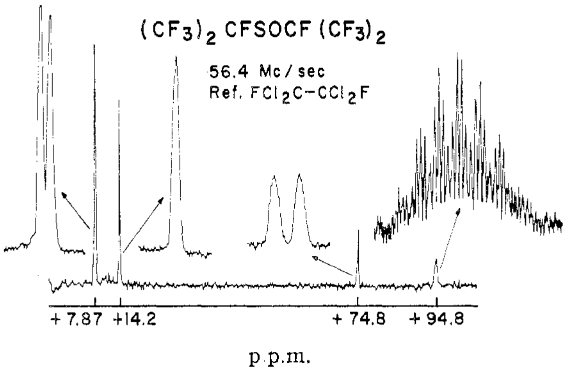

Fig. 1e.—F^{19} spectrum of $(CF_3)_2CFSOCF(CF_3)_2$ at 56.4 Mc.

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[14] F. A. Cotton, J. W. George, and J. S. Waugh, *J. Chem. Phys.*, **28**, 994 (1958).

[15] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

[16] R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, **21**, 602 (1953).

[17] D. F. Smith, *ibid.*, **21**, 609 (1953).

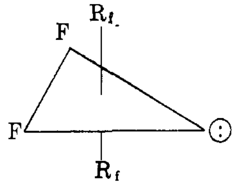
[18] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 322 (1957).

TABLE III

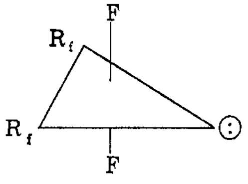
SPIN–SPIN SPLITTINGS, $A_{FF'}$, C.P.S.

Compound	SF_2–SF	SF_2–CF_3	SF_2–CF	SF–CF_3	SF–CF	CF_3–CF_3	CF_3–CF	CF–CF
$[(CF_3)_2CF]_2SF_2$	...	10	4.0	...	...	...	7.5	..
$(CF_3)_2CFSF_3$	4.8	1	2.8	0.7	0.4	...	0.4	..
$(CF_3)_2CFSF_2CF_3$	...	19 12 (i-C_3H_7)	28	...	...	4.1	7.2 4.3 (i-C_3H_7)	..
$(CF_3)_2CFSF$	...	..	...	10	22	...	9.3	..
$[(CF_3)_2CF]_2S$	...	..	...	...	...	...	...	..
$(CF_3)_2CFSOCF(CF_3)_2$	...	..	...	...	...	...	11 (CF′–CF_3′) 2 (CF′–CF_3)	20
$(CF_3)_2CFS(O)OH$	...	..	...	...	...	...	8.0	..
$(CF_3)_2CFS(O)OC_2H_5$	...	..	...	...	...	...	8.0	..

positions, other possible trigonal bipyramid models are not considered here). There is minimum crowding of the bulky $(CF_3)_2CF$ groups in structure A and this would seem



A

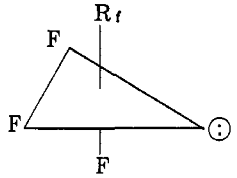


B

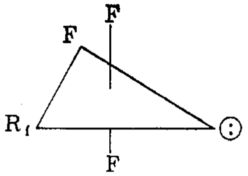
the more likely of the two possibilities. Moreover, it should be noted that in $(CF_3)_2PF_3$ the CF_3 groups occupy apical positions.[19] It should be further noted that the spectroscopic equivalence of groups could be due to a time averaging process such as some kind of intramolecular exchange; thus these n.m.r. data are not definitive.

$(CF_3)_2CFSF_2CF_3$ (III).—There are four resonances of relative intensities two, three, six, and one assignable to SF_2, CF_3, CF_3 (isopropyl), and CF fluorine atoms (Fig. 1b). Again, structure A of the preceding section is suggested to account for the apparent equivalence of the SF_2 fluorine atoms and minimize steric effects.

$(CF_3)_2CFSF_3$ (II).—There are four resonances of relative intensities two, one, six, and one assignable to SF_2, SF, CF_3, and CF fluorine atoms (Fig. 1c). Non-equivalence of S–F fluorine atoms indicates C or D to be the geometry of the molecule.



C



D

$(CF_3)_2CFSF$ (IV).—There are three resonances of relative intensities six, one, and one assignable to CF_3, CF, and SF fluorine atoms (Fig. 1d). The CF_3 resonance consists of two overlapping doublet structures. Each of the remaining resonances consists of two overlapping septuplet structures. This is in complete agreement with the fine structure expected from spin–spin splitting in the sulfenyl fluoride structure IV. Assignment of the +91.1 p.p.m. resonance to the CF fluorine atom was made on the basis that the chemical shift value falls within the expected range for this group.

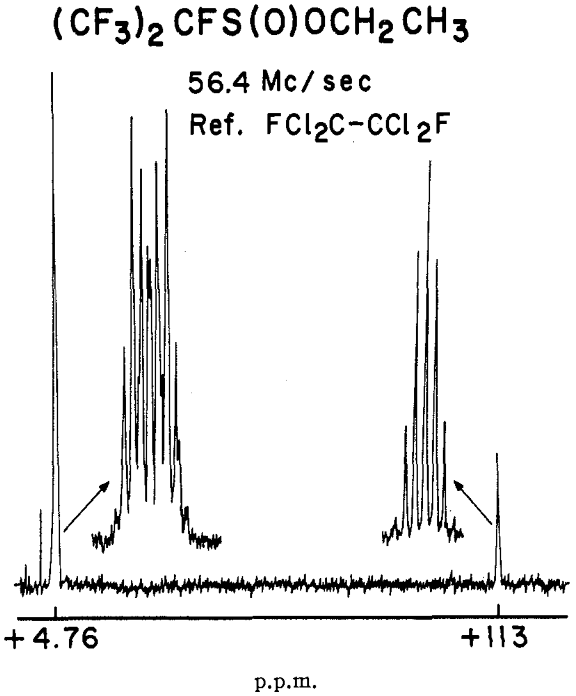


Fig. 1f.—F^{19} spectrum of $(CF_3)_2CFS(O)OCH_2CH_3$ at 56.4 Mc.

$(CF_3)_2CFSOCF(CF_3)_2$ (V).—The temperature independent spectrum shows two sets of resonances each of which consists of a pair of resonances of relative intensities six and one assignable to CF_3 and CF fluorine atoms (Fig. 1e). Spin–spin coupling values establish that the CF_3 and CF groups with chemical shifts of +7.87 and +94.8 p.p.m. belong to the same perfluoroisopropyl group. These groups are denoted by superscript "primes" in Table III.

$[(CF_3)_2CF]_2S$ (VI).—There are two resonances of relative intensities six and one assignable to CF_3 and CF fluorine atoms. No fine structure was observed.

$(CF_3)_2CFS(O)OH$ (VII).—There are two resonances of relative intensities six and one assignable to CF_3 and CF fluorine atoms. The resonances appear as doublet and septuplet structures, respectively.

$(CF_3)_2CFS(O)OCH_2CH_3$ (VIII).—The spectrum is temperature dependent and indicates that the molecule

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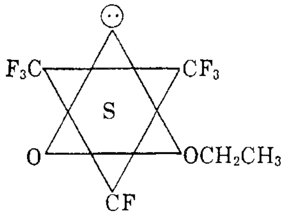
[19] R. Schmutzler, W. Mahler, and E. L. Muetterties, to be published.

contains stereochemically non-equivalent CF_3 groups. This may be explained by assuming a substituted ethane-type structure[20] in which the non-equivalence arises from a time averaging process of energetically different rotational isomers.



At room temperature there are two resonances of approximate relative intensities six and one assignable to CF_3 and CF fluorine atoms (Fig. 1f). At −20°, the CF_3 resonance is resolved into two separate resonances. Divergence of these resonances continues to −100°, at which temperature the sample begins to form a glass. Each CF_3 resonance consists of a quintuplet structure. Although eight-line patterns are expected, quintuplet structures are observed as a result of overlap of peaks arising from nearly equivalent CF_3–CF_3 and CF_3–CF spin coupling.

(20) J. A. Pople, *Mol. Phys.*, **1**, 1 (1958).

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Amine–Sulfur Dioxide Complexes. Solid–Liquid–Gas Equilibria and Infrared Spectra of Complexes with N,N-Dimethylanilines

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Received September 7, 1961

Sulfur dioxide has been found to form 1:1 addition compounds with N,N-dimethyl-*o*-toluidine, N,N-dimethyl-*m*-toluidine, and N,N-dimethyl-*p*-toluidine. In contrast to the *meta* and *para* derivatives and the previously reported complex of SO_2 with N,N-dimethylaniline, the *ortho* complex is highly unstable. Solid–liquid–gas equilibrium pressures have been measured at several temperatures for the *meta* and *para* compounds and for N,N-dimethylaniline–SO_2. From the resulting data ΔH^0, ΔF^0, and ΔS^0 for the decomposition of the solid complexes have been computed. The infrared spectra of all four complexes have been obtained in the liquid state and may be interpreted as providing evidence for the charge-transfer nature of these materials. The infrared data, together with the generally high stability of the complexes, are consistent with binding of SO_2 at the amine nitrogen. This idea is supported by the 1:2 mole ratio found for the previously unreported N,N,N′,N′-tetramethyl-*p*-phenylenediamine–SO_2. It is suggested that the low stability of N,N-dimethyl-*o*-toluidine–SO_2 may be due primarily to shielding of the nitrogen by the *ortho* methyl group.

Introduction

Complexes of amines with sulfur dioxide have long been known[1]; however, there are important gaps in information on the general properties of these materials, and almost no attention has been given to their structures. A study of properties and structures of such complexes therefore has been initiated in this Laboratory. Of particular interest is the possible application of the Mulliken charge-transfer theory.[2–4]

Although the SO_2 complexes of aniline,[5] and *o*-, *m*-, and *p*-toluidine[6] are known, the only known SO_2 complexes with the N-substituted aromatic amines include those with N-methylaniline, N-ethylaniline,[7] and N,N-dimethylaniline.[6,8] In the current study the SO_2 complexes of N,N-dimethylaniline and N,N-dimethyl-*o*-, -*m*-, and -*p*-toluidines have been examined along with the SO_2 complex of N,N,N′,N′-tetramethyl-*p*-phenylenediamine.

An important question relative to these SO_2 addition compounds is the site of the base–SO_2 linkage. It is not clear as yet whether the SO_2 is bound to the amine nitrogen or to the π-electron system of the ring. The related question of steric hindrance is likewise of interest. Tsubomura[9] found evi-

(1) A critical review of much of the early work has been given by A. E. Hill, *J. Am. Chem. Soc.*, **53**, 2598 (1931). The earliest reference on these materials is A. W. Hoffman, *Ann. Chem. Pharm.*, **47**, 64 (1843).

(2) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

(3) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

(4) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(5) A. E. Hill, *J. Am. Chem. Soc.*, **53**, 2598 (1931).

(6) A. E. Hill and T. B. Fitzgerald, *ibid.*, **57**, 250 (1935).

(7) H. W. Foote and J. Fleischer, *ibid.*, **56**, 870 (1934).

(8) J. R. Bright and W. C. Fernelius, *ibid.*, **65**, 637 (1943).

(9) H. Tsubomura, *ibid.*, **82**, 40 (1960).