The effect of pressure on the rate of this reaction is a composite quantity, since the activation volumes for the normal and base-catalyzed paths will be different. It is easily possible to make the latter predominant by using high pH, but it would be impossible to interpret the activation volume since it would include a term of unknown magnitude for the hydrolysis preequilibrium. We therefore concentrated our efforts on the suppression of the base-catalyzed path by using only data from the experiments with pH near zero. Even so, this path contributes 18% and it will be reflected to a corresponding extent in the activation volume.

At 1360 atm with the conditions of expt 5, the relative retardation of rate was 1.35, and at 1080 atm the factor was 1.32. The corresponding activation volumes are +6 and +5 ml according to (4). The activation volume

$$-RT(\partial \ln k/\partial P)_T = \Delta V^* \qquad (4)$$

in this case does not provide a critical test of mechanism, since the measured value is consistent with either a direct bimolecular substitution reaction

$$\mathrm{Fe(H_2O)_6^{3+} + SCN^- \longrightarrow activated\ complex} \qquad (a)$$

or a two-step process involving slow dissocation and rapid combination

$$\mathrm{Fe(H_2O)_6^{3+} \longrightarrow Fe(H_2O)_5^{3+} + H_2O}$$
$$\mathrm{Fe(H_2O)_5^{3+} + SCN^- \longrightarrow Fe(H_2O)_5SCN^{2+}} \qquad (b)$$

A model for eq a is the reaction of N,N,N-trimethylanilinium ion with phenoxide ion ($\Delta V^* = +7$ ml),[6] and models for eq b are the unimolecular decomposition of diazonium ions,[7] *t*-alkylsulfonium ions,[8] alkylmercuric ions,[9] and carboxylate ions[8] ($\Delta V^* = +2$ to $+14$ ml). In the first case the increase of volume results from the neutralization of charge and the release of electrostricted solvent, and in the second case it results from the breakage of a bond.

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Some Perfluoroalkylsulfinyl Halides, R$_f$S(O)X. New Preparations of Trifluoromethylsulfur Trifluoride[1]

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Abstract: The reaction of CF_3SCl with CF_3OF is the superior of four new methods for the preparation of CF_3SF_3. Trifluoromethylsulfinyl fluoride, which is prepared in good yield by the controlled hydrolysis of CF_3SF_3, undergoes metathetical reactions with HX to give new compounds, $CF_3S(O)X$. Trifluoromethylsulfinyl chloride and trifluoromethylsulfinyl bromide are prepared by reactions of $CF_3S(O)F$ with HCl and HBr, respectively. These tend to disproportionate to the respective sulfonyl and sulfenyl halides (R_fSO_2X and R_fSX). The new compound trifluoromethylsulfonyl bromide results from this disproportionation. In the presence of CsF, SOF_2 adds to C_2F_4 and C_3F_6 to give the higher perfluoroalkylsulfinyl analogs, $C_2F_5S(O)F$ and *i*-$C_3F_7S(O)F$.

Trifluoromethylsulfur trifluoride (CF_3SF_3), which was first reported as one of many products resulting from the direct fluorination of CS_2,[2a] more recently has been synthesized in better yield (40–50%) *via* the fluorination of CS_2 or $(CF_3S)_2CS$ with AgF_2.[2b] We wish to report four new methods for the preparation of CF_3SF_3 which involve the fluorination of CF_3SCl or CF_3SSCF_3 with CF_3OF, KF, or F_2. Trifluoromethylsulfur trifluoride is obtained in essentially quantitative amounts from the action of trifluoromethyl hypofluorite on trifluoromethylsulfenyl chloride

$$3CF_3OF + 2CF_3SCl \xrightarrow{-78^\circ} 2CF_3SF_3 + Cl_2 + 3COF_2$$

Potassium fluoride, particularly if present as its carbonyl fluoride or hexafluoroacetone adduct, also fluorinates CF_3SCl to CF_3SF_3 but two-thirds of the CF_3SCl is consumed in the formation of CF_3SSCF_3. Bis(trifluoromethyl) disulfide with CF_3OF or F_2 produces CF_3SF_3 in lower yields accompanied by a variety of other fluorinated compounds.

The perfluoroalkylsulfinyl halides ($R_fS(O)X$) are a new type of compound which have been observed previously only as trace impurities, *e.g.*, $CF_3S(O)F$ in the preparation of CF_3SF_3[2b] and *i*-$C_3F_7S(O)F$ in the preparation of *i*-$C_3F_7SF_3$.[3] The present work deals with the preparation, properties, and some of the reaction chemistry of five perfluoroalkylsulfinyl halides. Trifluoromethylsulfinyl fluoride ($CF_3S(O)F$) is prepared quantitatively *via* the mild hydrolysis of CF_3SF_3

$$CF_3SF_3 + H_2O \longrightarrow CF_3S(O)F + 2HF$$

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[1] Presented in part at the Northwest Regional American Chemical Society Meeting, Richland, Wash., June 1967.

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The reaction of $CF_3S(O)F$ with gaseous HX leads to the preparation of $CF_3S(O)X$.

$$CF_3S(O)F + HX \longrightarrow CF_3S(O)X + HF$$
$$X = Cl, Br$$

While pure $CF_3S(O)Cl$ is relatively stable at 25°, $CF_3S(O)Br$ tends to disproportionate rapidly to CF_3SBr and the new sulfonyl compound, CF_3SO_2Br.

The CsF-catalyzed addition of SF_4 to perfluoropropene has been used in the preparation of $((CF_3)_2CF)_2SF_2$ and $(CF_3)_2CFSF_3$.[3] In our laboratory, reactions of SOF_2 with C_2F_4 and C_3F_6 in the presence of CsF require moderate temperatures and pressures to yield $C_2F_5S(O)F$ and *i*-$C_3F_7S(O)F$, respectively. Disproportionation products are also observed.

Experimental Section

Starting Materials. The preparation and purification of CF_3OF and COF_2 were carried out by the method described by Cady.[4] Sulfinyl fluoride was prepared from sulfinyl chloride by room-temperature fluorination with either cesium or potassium fluoride in a Hoke metal pressure vessel. Anhydrous CsF was obtained from American Potash Co. and was dried at 500° immediately prior to use. Anhydrous KF was prepared from $KF \cdot 2H_2O$ by dehydrating the salt at 450° for 6 hr and powdering the resulting cake. Tetrafluoroethylene was a product of the pyrolysis of Teflon shavings at 600°. Hexafluoroacetone (Pierce Chemical Co.), hexafluoropropene (Penninsular Chem Research Inc.), anhydrous hydrogen chloride (Matheson Co.), anhydrous hydrogen bromide (Matheson Co.), and trifluoromethylsulfenyl chloride and bis(trifluoromethyl) disulfide (Columbia Organic Chemicals) were used without further purification.

General Procedures. Gases and volatile liquids were handled in a conventional glass vacuum apparatus. A stainless-steel vacuum line fitted with Hoke M327 valves and a Wallace and Tiernan mechanical gauge was used to handle gases corrosive to glass or mercury. Gaseous starting materials and purified products were measured quantitatively by PVT techniques. Separation of gaseous product mixtures was carried out either by trap-to-trap distillation techniques or by a modified codistillation apparatus[5] with vapor phase chromatographic columns. The columns were constructed of 0.25-in. aluminum tubing with Kel-F No. 3 polymer oil, FS-1265 or SF-96, on either Chromosorb P or Chromosorb W.

Physical Methods. Molecular weight measurements were carried out by vapor density techniques with a nickel or Pyrex glass weighing vessel. Infrared spectra were obtained in gas cells constructed of Pyrex glass with NaCl windows or Monel with AgCl windows with either a Beckman IR5A or a Perkin-Elmer Model 137. ^{19}F nmr spectra were measured with a Varian DP-60 at 56.4 mHz, a Varian 4311 at 40 mHz, or a Varian HA-100 at 94.1 mHz. Trichlorofluoromethane (Matheson Co.) was used as an external standard in all cases.

Preparation of CF_3SF_3. (a) $CF_3OF + CF_3Cl$. Explosions have occurred when equimolar quantities (20 mmoles) of the two reactants were warmed to −85°. A thoroughly dry system is necessary to prepare and maintain CF_3SF_3. In a typical run, 10 mmoles of CF_3SCl was condensed into a vessel maintained at −78°. Trifluoromethyl hypofluorite (15 mmoles) was added to the vessel in small portions as described below. The yields of CF_3SF_3 varied from 9.5 to 10 mmoles. CF_3OF (5 mmoles) was allowed to enter the vacuum line and was added slowly to the vessel until the system was in equilibrium. The remainder of the CF_3OF in the line was condensed into the vessel. After the reaction mixture was at −78° for about 0.5 hr, it was opened to the vacuum line and a trap at −183° until the pressure was reduced to about 5 mm. The volatile COF_2 and Cl_2 condensed in the colder trap while CF_3SF_3 and unreacted CF_3SCl remained behind. This procedure was repeated until a stoichiometric amount of CF_3OF (15 mmoles) had been added. Final purification of CF_3SF_3 was carried out by trap-to-trap fractionation.

(b) $CF_3SCl + KF$. CH_3CN (5 ml) and COF_2 (2 mmoles) (or $(CF_3)_2CO$) were transferred into a vessel which contained about 2 g of KF and were allowed to remain until all of the COF_2 ($(CF_3)_2CO$) had been consumed by the KF.[6] CF_3SCl (2 mmoles) was then condensed into the vessel and was allowed to remain at room temperature until the yellow color of CF_3SCl had disappeared. An infrared spectrum of a volatile sample from the colorless mixture showed only CF_3SF_3, CF_3SSCF_3, COF_2 ($(CF_3)_2CO$), and CH_3CN. Trap-to-trap distillation was found to be effective for the removal of COF_2 ($(CF_3)_2CO$) and CH_3CN from the mixture, but CF_3SF_3 could not be freed completely of CF_3SSCF_3. Yields were approximated to be 0.6 mmole each of CF_3SF_3 and CF_3SSCF_3. Although a longer reaction time was required, excess anhydrous KF with CF_3SCl in acetonitrile was observed to proceed to give essentially the same results.

(c) $CF_3SSCF_3 + F_2$. The CF_3SSCF_3 obtained as a byproduct in the previous reaction was effectively used to prepare CF_3SF_3 by reacting the former with a fluorine–nitrogen mixture. A 50-ml glass vessel which contained 20 ml of CH_3CN, 3 g of KF, and 5 mmoles of CF_3SSCF_3 was connected through a vacuum line to a 500-ml nickel vessel which contained 100 mm of F_2 and 500 mm of N_2. The diluted fluorine was allowed to enter the 10-ml glass line and was slowly admitted to the reaction vessel at room temperature until the system was at equilibrium. The reaction vessel was then cooled to −100° and the nitrogen pumped off. This procedure was repeated until all the fluorine had been consumed. The product mixture was subjected to trap-to-trap distillation. The CF_3SF_3 and some unreacted CF_3SSCF_3 were held in a trap at −183° while the CH_3CN and the majority of unreacted CF_3SSCF_3 were retained at −65°. Contents of the latter trap were returned to the reaction vessel for reuse with more CF_3SSCF_3 and F_2. The trap at −183° was found to contain about 90% of the CF_3SF_3 contaminated with minor amounts of CF_4, SF_6, and some unreacted CF_3SSCF_3. The conversion of CF_3SSCF_3 to CF_3SF_3 was nearly quantitative with no unreacted fluorine remaining. The yield of CF_3SF_3 was about 90% under the above conditions; however, if the nitrogen dilution was decreased, CF_4 and SF_6 were observed as the major products.

(d) $CF_3OF + CF_3SSCF_3$. An equimolar mixture of CF_3OF and CF_3SSCF_3 (1.0 mmole) was condensed into a 150-ml nickel vessel which had been prefluorinated. After 24 hr at room temperature, an infrared spectrum of the mixture showed that all of the CF_3OF had been consumed. Three major components present were COF_2, CF_3SF_3, and unreacted CF_3SSCF_3. Minor amounts of SOF_2, CF_4, CO_2, C_2F_6, and CF_3SCF_3 (identified by infrared[7]) were also found. The yield of CF_3SF_3 was estimated at about 70%.

Properties of CF_3SF_3. The boiling and melting points (−7, −110°) have been reported.[2a] The compound reacts rapidly with H_2O to give $CF_3S(O)F$ and HF. Although it is stable in glass at −183° for indefinite periods or for a few days at −78°, it decomposes in glass at room temperature to give a white solid. Its reactivity with mercury precludes the use of mercury manometers. The average molecular weight and infrared and ^{19}F nmr spectra are given in Table I.

Preparation of $CF_3S(O)F$. Trifluoromethylsulfinyl fluoride was prepared by the mild hydrolysis of CF_3SF_3. CF_3SF_3 (5 mmoles), prepared *via* method a above, was condensed into a 1-l. Pyrex glass vessel fitted with a high-vacuum stopcock. About 100 mm of air was allowed to enter the vessel to give a total pressure of 200 mm at room temperature. While the vessel was held at room temperature, a white coating formed on the glass surface which was due apparently to attack on glass by HF. After 5 hr an infrared spectrum of the two contents of the vessel indicated absorption bands which were associated only with $CF_3S(O)F$ and SiF_4. The condensable contents of the reaction vessel were trapped in a "U" trap held at −183° and the air was pumped away. The $CF_3S(O)F$ (5 mmoles) was purified by pumping away the volatile SiF_4 at −85° or by passing the gaseous mixture through a tube filled with dry NaF. For use in the measurement of physical data, the product was further purified by vapor-phase chromatography with a 12-ft FS-1265–Chromosorb P column at 25°.

Properties of $CF_3S(O)F$. Trifluoromethylsulfinyl fluoride exists as a colorless gas at room temperature and condenses to a colorless liquid. When pure, the compound is stable in glass and toward mercury and is not hydrolyzed by the moisture in the air. It has an irritating odor similar to that of SOF_2. The boiling point was found to be −1.6° from a Clausius–Clapeyron curve which is described by the equation $\log P_{\mathrm{mm}} = 7.140 - 1153/T°\mathrm{K}$. Vapor

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Table I

	CF_3- SF_3	CF_3- S(O)F	CF_3- S(O)Cl	CF_3- S(O)Br	C_2F_5- S(O)F	i-C_3F_7- S(O)F	CF_3- SBr	CF_3- S(O)(O)Br	$(C_2F_5)_2S_2$	$(i\text{-}C_3F_7)_2S$
Mol wt[a]	156 (158)	136 (136)	153 (153)	...	187 (186)	239 (236)	181 (181)	214 (213)	299 (302)	365 (370)
Anal[a]										
C	...	...	8.03 (7.87)	...	...	15.39 (15.25)	...	...	16.16 (15.90)	...
F	...	...	37.26 (37.40)	...	57.99 (61.21)	64.19 (64.40)	...	...	62.74 (62.93)	...
S	...	22.4 (23.5)	21.22 (20.98)	...	16.81 (17.19)	13.31 (13.55)	...	...	21.03 (21.20)	...
Br or Cl	...	...	23.51 (23.29)	...	...	...	45.96 (44.15)	...	...	...
Infrared	1260 s	1268 s	1238 vs	1235 s	1350 s	1300 vs		1424 s	1330 s	1290 vs
	1237 s	1227 (sh)	1216 vs	1205 s	1260 vs	1258 vs		1236 s	1227 vs	1245 vs
	1130 s	1212 s			1221 (sh)	1177 m	1180 vs	1116 s	1166 m	1185 w
		1147 s	1123 vs	1116 s	1135 s	1136 w	1116 vs		1121 s	1165 m
	848 m				990 w	980 s				1125 w
	704 vs	751 s	749 m		960 m	748 s	760 w		948 vs	960 s
					746 s	717 m			749 m	885 s
					640 w					757 m
										715 s
Nmr (ppm)										
CF_3	72.8 (3)[b] d	84.1 (3) d	81.8 s	76.4 s	81.2 (3) d	70.4 (6) d	47.0 s	78.5 s	85.4 (3) s	77.6 (6) s
CF_2					126.9 (2) s				97.2 (2) s	
CF						180.4 (1)				165.6 (1) s
SF	49.6 (1) t	21.6 (1) q			20.5 (1) q	10.2 (1)				
SF_2	−47.4 (2) d of q									

[a] Calculated value in parentheses. [b] Relative peak area.

pressure data are as follows (T, °K; P, mm): 205.0, 25; 215.8, 60; 225.5, 105; 232.3, 146; 214.5, 221; 248.0, 305; 248.8, 310; 251.3, 341; 252.0, 351; 253.5, 374; 257.5, 435; 261.0, 535; 265.5, 620; 270.2, 751; 271.0, 770. The molar heat of vaporization is 5.28 kcal and the Trouton constant is 19.5. When $CF_3S(O)F$ is cooled it forms a glass; a melting point was not obtained. The average molecular weight, elemental analysis, and infrared and ^{19}F nmr data are included in Table I.

Reactions of $CF_3S(O)F$. (a) With F_2 and CsF. In a 75-ml Hoke vessel were placed CsF (2 g) and $CF_3S(O)F$ (0.36 mmole). One atmosphere of F_2 was added to the vessel at −183°. After 24 hr at 25°, the contents were examined and found to consist of two major products, CF_4 and SF_5OF. Sulfonyl fluoride and SF_6 were present in minute amounts.

(b). With N_2F_4. An equimolar mixture (3 mmoles) of $CF_3S(O)F$ and N_2F_4 were condensed into a nickel vessel and heated at 300° for 48 hr. The mixture was separated by vpc (FS-1265–Chromosorb P) and found to contain $CF_3NF_2SOF_2$, a small amount of CF_4, and about 50% of unreacted starting materials.

Preparation of $CF_3S(O)Cl$. In a typical run, HCl (1.53 mmoles) and $CF_3S(O)F$ (1.50 mmoles) were condensed into a cylindrical glass vessel and the mixture was allowed to warm from −183 to 25° over a period of 1 hr. After separation *via* vpc (20% Kel-F–80% Chromosorb P, 3-ft column), one major product was identified as $CF_3S(O)Cl$ (1.43 mmoles). Two minor products, identified as CF_3SCl[8] and CF_3SO_2Cl,[9] were eluted and comprised about 5% of the mixture.

Properties of $CF_3S(O)Cl$. Trifluoromethylsulfinyl chloride is a colorless gas at room temperature and condenses to a colorless liquid. The reaction of $CF_3S(O)Cl$ with mercury is very rapid. The compound is stable in glass but disproportionates in the presence of water or in its preparation mixture to give CF_3SO_2Cl and CF_3SCl. After 24 hr at 25°, trifluoromethylsulfinyl chloride had reacted quantitatively with excess NaF to give $CF_3S(O)F$ as the only volatile product. Molecular weight, elemental analysis, infrared, and ^{19}F nmr data are given in Table I.

Preparation of $CF_3S(O)Br$. In a typical reaction, HBr (2.35 mmoles) and $CF_3S(O)F$ (2.0 mmoles) were allowed to remain at −78° for 1 hr. Part of the red-yellow product mixture was separated by vapor phase chromatography (20% Kel-F–80% Chromosorb P, 4-ft column) and found to contain CF_3SBr, Br_2, $CF_3S(O)Br$, and SiF_4. After 15 min at 25°, the remainder of the mixture was separated. In this portion, CF_3SBr was the major product with $CF_3S(O)Br$ and CF_3SO_2Br present in lesser amounts. Reactions carried out in nickel vessels gave similar results. The yield of $CF_3S(O)Br$ was increased somewhat by condensing HBr (2.35 mmoles) and $CF_3S(O)F$ (2.1 mmoles) onto KBr (5 g) at −183°. After 10 min at 25°, the volatile products were removed (HF, H_2O, SiF_4, and some Br_2 remained on the KBr), and separation indicated about a 60% yield of $CF_3S(O)Br$ in addition to CF_3SBr and Br_2. Complete separation of the products was not possible. Chromatographic columns brought about partial disproportionation of $CF_3S(O)Br$ to CF_3SO_2Br and CF_3SBr before it could be eluted. The Kel-F–Chromosorb P column caused the least disproportionation during separation; however, CF_3SO_2Br and $CF_3S(O)Br$ could not be completely resolved.

Properties of $CF_3S(O)Br$, CF_3SBr, and CF_3SO_2Br. Trifluoromethylsulfinyl bromide ($CF_3S(O)Br$) is a colorless liquid at 25° which attacks mercury but does not affect glass. At 25°, it undergoes rapid disproportionation to CF_3SBr and CF_3SO_2Br which made full characterization impossible. The infrared and the ^{19}F spectra are given in Table I. After 24 hr, in contact with excess NaF, a sample of $CF_3S(O)Br$ (contaminated with CF_3SBr and CF_3SO_2Br) was converted to $CF_3S(O)F$ and $CF_3SO_2SCF_3$.

Trifluoromethylsulfenyl bromide (CF_3SBr) was obtained pure by separation from CF_3SO_2Br after $CF_3S(O)Br$ had completely disproportionated. It has a reported boiling point of 36° and index of refraction, $n^{16}D$ 1.3855.[10,11] The orange-red liquid is stable to 25° in a sealed glass tube, but decomposes quantitatively in sunlight to CF_3SSCF_3 and Br_2. The molecular weight, elemental analysis, and infrared and ^{19}F nmr data are given in Table I.

Trifluoromethylsulfonyl bromide (CF_3SO_2Br) exists as a colorless liquid at room temperature. It is stable toward glass, does not hydrolyze readily, and does not react with NaF at room temperature. Molecular weight and infrared and ^{19}F nmr spectra are in Table I.

Preparation of $C_2F_5S(O)F$. Caution. Uninhibited C_2F_4 has been observed to be susceptible to spontaneous explosion when under a pressure greater than 49 psi.[12] In a typical run, CsF (1g) was placed in a 30-ml Hoke vessel or a thick-walled glass vessel fitted with a pressure valve assembly. After an equimolar quantity

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of SOF_2 and C_2F_4 (9.4 mmoles) was condensed into the vessel, it was shielded and placed in an oven at 150° for 24 hr. The product mixture was first separated by trap-to-trap distillation with unreacted SOF_2 (3.5 mmoles) and a small amount of $c\text{-}C_4F_8$ contained at −183°. The contents of the trap at −110° (5.9 mmoles) were further separated by vpc (FS-1265–Chromosorb W) and were shown to contain $C_2F_5S(O)F$ (56%), SOF_2 (30%), $C_2F_5SO_2F$ (7%), and $C_2F_5SSC_2F_4$ (7%) (quantity based on recorder peak areas). The $C_2F_5S(O)F$ (3.2 mmoles) collected from the vpc column represents a yield of 80% based on conversion of 44% for the SOF_2 consumed. Best results are obtained at 150–180° at a calculated pressure of 18–23 atm. The yield of the product was affected markedly by the dryness and state of subdivision of the CsF.

Properties of $C_2F_5S(O)F$ and $C_2F_5SSC_2F_5$. Pentafluoroethylsulfinyl fluoride ($C_2F_5S(O)F$) is a colorless liquid at 25° which is inert toward mercury and glass but readily absorbs moisture to give a cloudy liquid. The compound has a boiling point of 20° as determined from a vapor pressure curve described by the following equation: $\log P_{mm} = 7.952 - 1486/T$°K. Vapor pressure data are as follows (T, °K; P, mm): 235.0, 42.5; 245.9, 80; 253.5, 122; 263.0, 198; 270.8, 273; 273.6, 334; 277.8, 395; 285.1, 540; 289.6, 644; 291.6, 676.5. The molar heat of vaporization is 6.8 kcal and the Trouton constant is 23.0. When $C_2F_5S(O)F$ (0.1 mmole) and N_2F_4 (0.5 mmole) were heated in a nickel vessel at 300° for 2 hr, $C_2F_5NF_2$[13] and SOF_2 were collected as the two major products with C_2F_6 and unreacted N_2F_4 also present. Average molecular weight, elemental analysis, and infrared and ^{19}F nmr spectra are in Table I.

Bis(pentafluoroethyl) disulfide ($C_2F_5SSC_2F_5$) is mentioned in the patent literature;[14] however, no information was available to help identify the compound. Molecular weight, elemental analysis, and infrared and ^{19}F nmr spectra are given in Table I.

Preparation of $i\text{-}C_3F_7S(O)F$. In a typical run, SOF_2 (14.2 mmoles) and C_3F_6 (15.5 mmoles) were condensed into a 75-ml Hoke vessel containing CsF (2 g). The volatile product mixture was separated by trap-to-trap distillation after the vessel was held in an oven at 150° for 2 days. At −183°, SOF_2 and C_3F_6 along with a small amount of SO_2F_2 were found (13.4 mmoles). The mixture (5.3 mmoles) retained at −78° was comprised of four components as indicated by vpc separation. The first two components could not be separated completely from each other and accounted for 10 and 4% of the mixture, while the last two components, identified as $i\text{-}C_3F_7S(O)F$ and $(i\text{-}C_3F_7)_2S$, accounted for 71 and 15% of the product mixture. The conversion of SOF_2 was usually about 33% and the yield of $i\text{-}C_3F_7S(O)F$ was 60–80% as measured from the chromatographic peak areas.

Properties of $i\text{-}C_3F_7S(O)F$ and $(i\text{-}C_3F_7)_2S$. Heptafluoroisopropylsulfinyl fluoride is a colorless liquid at 25° and is nonreactive toward glass and mercury. Molecular weight, elemental analysis, and infrared and ^{19}F nmr spectra are in Table I.

Bis(heptafluoroisopropyl) sulfide ($(i\text{-}C_3F_7)_2S$) was partially identified from the nuclear magnetic resonance data of Rosenberg and Muetterties.[3] Molecular weight and infrared and ^{19}F nmr spectra are given in Table I.

Results and Discussion

Trifluoromethyl hypofluorite behaves as a fluorinating agent in its reactions with CF_3SSCF_3 and CF_3SCl. The main reaction with the former is

$$3CF_3OF + CF_3SSCF_3 \xrightarrow[24\text{ hr}]{25°} 2CF_3SF_3 + 3COF_2$$

No other trifluoromethylsulfur fluorides were identified although CF_3SF_5 might reasonably be expected to form. However, small amounts (about 10% of reaction mixture) of C_2F_6, SOF_2, CF_3SCF_3, CO_2, and CF_4 were observed upon gas chromatographic separation. Because of reactivity toward glass, water, and silicon-based column materials, the yield of CF_3SF_3 was often reduced owing to the *in situ* generation of $CF_3S(O)F$ and SiF_4. In the reaction of CF_3OF and CF_3SCl at −78°, the conversion of CF_3SF_3 is between 95 and 100%. This provides an easily separable product mixture, a high yield, and mole for mole return of CF_3SF_3 from CF_3SCl.

The interaction of $KOCF_3$, KOC_3F_7, or anhydrous KF with CF_3SCl in an acetonitrile solution give identical equimolar mixtures of CF_3SSCF_3 and CF_3SF_3. The existence of CF_3SF[15] as an unstable intermediate species which subsequently disproportionates is helpful in explaining the volatile products. It is unlikely that CF_3SSCF_3 results from CF_3SCl under the experimental conditions since no Cl_2 is detected. Although the reaction

$$3CF_3SCl + 3KF\cdot X \xrightarrow[CH_3CN]{25°} (3CF_3SF) \longrightarrow CF_3SSCF_3 + CF_3SF_3 + 3KCl + X$$

$$X = COF_2,\ (CF_3)_2O,\text{ or nothing}$$

goes to completion in a few hours with no apparent side reactions, it does not efficiently utilize CF_3SCl. When the reaction mixture was separated with a FS-1265–Chromosorb P column, no CF_3SF_3 was observed, but owing to reaction with the column packing equal quantities of CF_3SSCF_3 and $CF_3S(O)F$ were eluted from the column. Complete separation of CF_3SF_3 from CF_3SSCF_3 was not realized, although partial separation was obtained by trap-to-trap distillation.

While the hydrolysis of CF_3SF_3 by the moisture in the air occurs essentially quantitatively to give $CF_3S(O)F$ in a few hours at 25°, if an aqueous solution is used to hydrolyze CF_3SF_3, a more complicated series of reactions occur probably due to attack on the $CF_3S(O)F$. This process was not studied. Trifluoromethylsulfinyl fluoride reacted readily with fluorine in the presence of CsF to give CF_4 and SF_5OF which suggests that the CS bond was severed to yield CF_4 and SOF_2 which was subsequently catalytically fluorinated to SF_5OF.[16] The thermal stability of $CF_3S(O)F$ is demonstrated in its reaction with N_2F_4 which after 48 hr at 300° gave rise to CF_3NF_2 and SOF_2 and 50% of the starting materials. These products are again good evidence for the $CF_3S(O)F$ species and are formed owing to the expected reaction mode of N_2F_4 as a difluoraminating and fluorinating agent with sulfur-containing molecules.[17]

Aluminum chloride has no effect on $CF_3S(O)F$, although it has been useful in other systems for replacing S–F groups by S–Cl.[18] However, hydrogen chloride rapidly converts $CF_3S(O)F$ to $CF_3S(O)Cl$. On the 1.5-mmole scale this reaction is complete within 1 hr and $CF_3S(O)Cl$ must be removed promptly in order to prevent disproportionation. The latter is apparently catalyzed by water formed by HF attack on glass, *i.e.*

$$CF_3S(O)F + HCl \longrightarrow CF_3S(O)Cl + HF$$

$$4HF + SiO_2 \longrightarrow 2H_2O + SiF_4$$

$$CF_3S(O)Cl \xrightarrow[H_2O]{} CF_3SO_2Cl + CF_3SCl$$

When the product mixture was held at 25° for 12 hr, very little $CF_3S(O)Cl$ was found and the $CF_3S(O)Cl$ had been essentially quantitatively converted to CF_3SCl[8] and CF_3SO_2Cl.[9] In order to maximize the yield of $CF_3S(O)Cl$, about a 5% molar excess of HCl was added.

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The reaction of $CF_3S(O)F$ with HBr gives rise to a more complex system since it appears to occur by two routes when the reactants are held at −78°. $CF_3S(O)Br$ is unstable with respect to disproportionation at 25° in the reaction mixture as well as when pure. If it does disproportionate at −78°, the reaction is conveniently much slower. The reactions may proceed

$$CF_3S(O)F + HBr \xrightarrow{-78°} CF_3S(O)Br + HF\ (SiF_4 + H_2O)$$

$$CF_3S(O)F + 3HBr \xrightarrow{-78°} CF_3SBr + Br_2 + H_2O + HF\ (SiF_4 + H_2O)$$

$$2CF_3S(O)Br \xrightarrow{25°} CF_3SBr + CF_3SO_2Br$$

The presence of CF_3SBr as the only sulfur-containing product in addition to $CF_3S(O)Br$ at −78° requires a concomitant oxidation product. The fact that bromine is formed and CF_3SO_2Br is not suggests that CF_3SBr does not result from disproportionation but is rather a product of a simultaneous reaction. Also, since a slight molar excess of HBr is required to consume completely the $CF_3S(O)F$ is suggestive of a second reaction route. When the reaction mixture is allowed to stand briefly at room temperature and is then separated, CF_3SBr is the major sulfur product with lesser amounts of $CF_3S(O)Br$ and CF_3SO_2Br now observed. This indicates that the increase in the amount of CF_3SBr and the presence of CF_3SO_2Br arise from disproportionation of $CF_3S(O)Br$. In every case, CF_3SBr was present in larger amounts than CF_3SO_2Br. It may be that the system is even more complex than indicated here but, because of our inability to adequately purify $CF_3S(O)Br$ and because of its rapid disproportionation, a quantitative study of the reaction system was not carried out.

The disproportionation of $CF_3S(O)Br$ can be readily followed by infrared. After 8 hr at 25°, an equimolar mixture of CF_3SO_2Br and CF_3SBr remains. The infrared band at 1205 cm^{-1} (characteristic of $CF_3S(O)Br$) decreases in intensity and bands at 1423 and 1180 cm^{-1} (characteristic of CF_3SBr and CF_3SO_2Br) increase.

When a mixture of CF_3SO_2Br, CF_3SBr, and $CF_3S(O)Br$ remained in contact with NaF for 24 hr, CF_3SO_2Br and CF_3SBr were not affected and $CF_3S(O)F$ was the only new product. Thus, as with $CF_3S(O)Cl$, $CF_3S(O)Br$ is converted to its more stable fluoro analog. In some cases, $CF_3SO_2SCF_3$ was observed and is thought to arise from the hydrolysis of CF_3SBr brought about by inadequately dried NaF.[19] Trifluoromethylsulfonyl bromide did not react with NaF even at 135°

That the reaction of SOF_2 with C_2F_4 will proceed in the presence of CsF under moderate conditions to give $C_2F_5S(O)F$ as the major product indicates an intermediate of the type CsC_2F_5, which subsequently undergoes nucleophilic attack by SOF_2. Under no conditions which were tried was the symmetrical bis(pentafluoroethyl) sulfoxide identified as a product. Polymerized C_2F_4 was invariably a product and increasing the amount of C_2F_4 to attain a larger conversion of SOF_2 did not affect the yield of $C_2F_5S(O)F$ but resulted in additional polymer formation. The presence of $C_2F_5SSC_2F_5$ and $C_2F_5SO_2F$ as minor volatile products suggests the partial disproportionation of $C_2F_5S(O)F$.

$$2C_2F_5S(O)F \longrightarrow C_2F_5SO_2F + (C_2F_5SF)$$

$$(3C_2F_5SF) \longrightarrow (C_2F_5SF_3) + C_2F_5SSC_2F_5$$

$$(2C_2F_5SF_3) \xrightarrow{SiO_2} C_2F_5S(O)F + SiF_4$$

We do not have proof for either C_2F_5SF or $C_2F_5SF_3$. The reaction between SOF_2 and C_3F_6 apparently occurs *via* a route similar to the above. The formation of larger quantities of $(i\text{-}C_3F_7)_2S$ than of SO_2F_2 has not been explained. No evidence is found for the formation of a symmetric sulfoxide.

The nuclear magnetic spectrum of CF_3SF_3 is in essential agreement with that of Muetterties.[20] Our assignments of a broadened triplet at 49.6 ppm to SF and two overlapping quartets at −47.4 ppm to SF_2 were based on relative peak areas (1:2) ($J_{SF-SF_2} = 70$ cps). A resonance at 72.8 ppm is a doublet assigned to CF_3. Resonances observed for $CF_3S(O)F$ occur as a quartet at +21.6 ppm (SF) and a doublet at +84.1 ppm (CF_3) with a coupling constant $J_{CF-SF} = 8$ cps. The ^{19}F nmr spectrum of $CF_3S(O)Br$ was obtained on a mixture which contained CF_3SBr, $CF_3S(O)Br$, and CF_3SO_2Br. Two intense resonances were observed at +47.0 and 78.5 ppm (equal area) and one at +76.4 ppm. The former two were assigned to CF_3SBr and CF_3SO_2Br, respectively, based on values obtained when pure samples of these compounds were examined which led to the assignment of the resonance at +76.4 ppm to $CF_3S(O)Br$. This fits into the trend of shifts, since, as the sulfinyl halide changes from F to Cl to Br, the chemical shift of the CF_3 group decreases from +84.1 to 81.8 to 76.4 ppm. A chemical shift of +47.0 ppm for CF_3SBr seems to be in agreement with that expected since the CF_3 chemical shift for CF_3SF and CF_3SCl are reported to be +58 and 51 ppm, respectively.[15]

No hyperfine interaction is observed for the methyl and methylene groups in $(C_2F_5)_2S_2$. Such is the case for other perfluoroethyl compounds.[21] Singlets at +85.4 (CF_3) and at 97.3 ppm (CF_2) have an area ratio of 3:2. In $C_2F_5S(O)F$ with a singlet (CF_2, +126.9), a doublet (CF_3, +81.2), and a quartet (SF, +20.5), spin coupling occurs only between CF_3 and SF to give $J_{SF-CF_3} = 12$ cps. The SF resonance in $i\text{-}C_3F_7S(O)F$ occurs as a septet of doublets centered at +10.2 ppm as does the CF resonance at 180.4 ppm. The CF_3 resonance is a doublet at 70.4 ppm. Hyperfine interactions give $J_{CF-SF} = 5$; $J_{CF-CF_3} = 8.5$; $J_{SF-CF_3} = 9.2$ cps. It is not clear why the CF_3 resonance is only a doublet arising from interaction of CF and CF_3 ($J = 8.5$ cps) since CF_3–SF interaction should also be observed. For $(i\text{-}C_3F_7)_2S$, our data are consistent with that reported earlier.[3] No fine structure was observed. Chemical shifts for the S–F fluorine in $R_fS(O)F$ decrease from +21.6 to 20.5 to 10.2 as the R_f group changes from CF_3 to C_2F_5 to $i\text{-}C_3F_7$.

Although the infrared spectra of the perfluoroalkylsulfinyl halides contain comparatively few absorption bands, the close proximity of the C–F asymmetric stretch and the S–O stretching frequency causes difficulty in the assignment of either. While a characteristic strong absorption band in the 1055-cm^{-1} region is assigned to the S–O stretch in some alkyl sulfoxides, the

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(19) Hydrolysis of CF_3SCl has been shown to give $CF_3SO_2SCF_3$. Dr. A. Haas, Göttingen supplied the infrared spectrum.

(20) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 3, 1298 (1964) (SF and SF_2 at 51.6 and −48.4 ppm; $J_{SF-SF_2} = 70$ cps). In $i\text{-}C_3F_7SF_3$, SF and SF_2 at 54.3 and −61.3 ppm.[3]

(21) J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, 87, 230 (1965).

S–O stretches in SOF_2 and $SOCl_2$ occur at 1312 and 1229 cm^{-1}, respectively.[22] Kagarise[23] was able to demonstrate a linear relationship between carbonyl stretching frequency and the sum of the electronegativity values (Gordy scale[24]) of atoms X and Y in molecules of the type XCOY. However, when this was applied to structurally similar sulfinyl compounds,[25] the points fell on a smooth curve and it was noted that changes in electronegativities of substituents in XSOY had smaller effects on S–O stretching frequency than on C–O analogs. This is in agreement with Moffitt[26] who showed that there is a relatively small variation in bond order in many XSOY compounds. When the electronegativities[22,23] of the trifluoromethylsulfinyl halides are superimposed on this curve, the absorption bands at 1268, 1238, and 1235 cm^{-1} for $CF_3S(O)F$, $CF_3S(O)Cl$, and $CF_3S(O)Br$, respectively, correspond to the S–O stretching frequency. By the same process, bands at 1260 and 1258 cm^{-1} in the spectra of $C_2F_5S(O)F$ and i-$C_3F_7S(O)F$ are attributable to S–O stretch. Based on the above, CF asymmetric stretching frequencies are assigned to 1227, 1216, and 1205 cm^{-1} and symmetric bands to 1147, 1123, and 1116 cm^{-1} in $CF_3S(O)F$, $CF_3S(O)Cl$, and $CF_3S(O)Br$, respectively. As the size and electronegativity of the substituent halide increase, there is a concomitant decrease in the S–O and asymmetric and symmetric C–F stretching frequencies. This decrease is observed for asymmetric and symmetric S–O stretch in CF_3SO_2F and CF_3SO_2Cl[9] at 1463 and 1239 cm^{-1} and 1439 and 1239 cm^{-1}, respectively, and, from this work, for CF_3SO_2Br at 1424 and 1236 cm^{-1}. For CF_3SBr, by comparison with CF_3SCl,[8] bands at 1180 and 1116 are asymmetric and symmetric C–F stretches and the band at 760 is a CF_3 deformation. The characteristic broad band centered at approximately 748 cm^{-1} in $CF_3S(O)F$, $C_2F_5S(O)F$ and i-$C_3F_7S(O)F$ is probably due to S–F stretch; however, CF_3 deformation occurs in this region.

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Additional Studies Concerning the Existence of "O_3F_2"

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Abstract: Additional O^{17} and F^{19} data on the oxygen fluorides have been obtained. The reactions of the oxygen fluorides with boron trifluoride are also described. All of the evidence obtained supports the conclusion that "O_3F_2" is actually a mixture of O_2F_2 and $(OOF)_n$.

Several oxygen fluorides have been reported, namely OF_2,[1] O_2F_2,[2] O_3F_2,[3] O_4F_2,[4] and recently O_5F_2[5] and O_6F_2.[5] The structures of OF_2 and O_2F_2 are well known, but very little is known about the higher oxygen fluorides. Recently, the structure and even the existence of "O_3F_2" have been subjects of considerable concern.

Malone and McGee[6] applied cryogenic mass spectrometry to the problem and concluded that "O_3F_2" consists of loosely bonded O_2F and OF radicals. Nebgen, *et al.*,[7] studied the F^{19} nmr spectrum of "O_3F_2" and postulated an "O_3F_2" model consisting of O_2F_2 and interstitial oxygen. Previous work in our laboratories[8] on both F^{19} and O^{17} nmr spectroscopy of "O_3F_2" led us to conclude that the system is best explained as

$$\begin{tikzcd}
(O_2F_2,\ O_4F_2) \arrow[d, shift left] & & \\
2OOF \arrow[u, shift left] \arrow[r] & O_2F_2 + O_2 & (1)
\end{tikzcd}$$

We wish to report recent results that we believe further substantiate this conclusion.

Experimental Section

OF_2 was obtained from the Allied Chemical Corp. The other oxygen fluorides were prepared by using previously reported procedures.[2-4] The O^{17}-enriched OF_2 was obtained from the Texaco Research Center.

The nmr spectrometer used was the conventional Varian DP-60 equipped with a low-temperature wide-line dewar coil; the cooling system was altered slightly to obtain better temperature control and to allow rapid insertion of the sample. Cooling was achieved with gaseous nitrogen previously cooled by passage through a copper coil immersed in liquid nitrogen. The temperature was controlled by varying the flow of the nitrogen.

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