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Sulfur Oxyfluoride Derivatives. III[1]

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The reaction of $S_2O_6F_2$ with the anions CF_3O^-, SF_5O^-, $^-N(SO_2F)_2$, and $(NO_2)_2CCN^-$ produced the corresponding covalent fluorosulfate derivatives: CF_3OOSO_2F, SF_5OOSO_2F, $FSO_2ON(SO_2F)_2$, and $FSO_2OC(NO_2)_2CN$. Several reactions of these and related materials are discussed.

Peroxydisulfuryl difluoride,[2] $S_2O_6F_2$, has proven to be a versatile reagent for the preparation of new sulfur oxyfluoride derivatives. It is a strong oxidizing agent capable of oxidizing the halide ions (except fluoride) to Cl_2, $Br(SO_3F)_4^-$, and $I(SO_3F)_4^-$, respectively.[3,4] This investigation extends the oxidation reaction to include the anions CF_3O^-, $(CF_3)_2CFO^-$, SF_5O^-, $N(SO_2F)_2^-$, CF_3COO^-, and $C(NO_2)_2CN^-$. Several reactions of the products and related compounds are discussed.

Experimental Section

Preparation of $S_2O_6F_2$.—A 6.6-g sample of SO_3[5] was condensed into a 300-ml Monel cylinder equipped with a needle valve. Fluorine, 0.042 mol, was condensed into the reactor. The cylinder was heated to 170° for 3 hr. The reactor was cooled to $-196°$ and the noncondensable gases were pumped off. Fractionation of the remaining mixture through a $-78°$ cold trap gave 7.1 g of crude $S_2O_5F_2$ (95% $S_2O_6F_2$ and 5% $S_2O_5F_2$ by F^{19} nmr analysis). Slow refractionation through a $-78°$ cold trap served to remove the $S_2O_5F_2$ from the product.

Preparation of CF_3OOSO_2F.—Carbonyl fluoride, 1.64 mmol, and $S_2O_6F_2$, 1.11 mmol, were condensed into a metal cylinder containing 5 g of dried and powdered KF. The reactor was allowed to stand for 2 hr at ambient temperature before fractionation through -78, -126, and $-196°$ cold traps. The first trap contained a small amount (0.21 mmol) of unreacted $S_2O_6F_2$; the second contained 0.87 mmol of pure CF_3OOSO_2F (vapor density molecular weight: calcd, 184; found, 182) while the liquid nitrogen trap contained 0.14 mmol of SO_2F_2 and 0.77 mmol of COF_2.

The reaction of 2.01 mmol of $(CF_3)_2C{=}O$ with 2.07 mmol of $S_2O_6F_2$ was carried out in the presence of 5 g of KF as described above. After standing for 1 hr at 0° the mixture was fractionated through -78 and $-196°$ cold traps. The coldest trap contained 0.70 mmol of CF_3COF, 0.12 mmol of CO_2, 0.12 mmol of SO_2F_2, and 0.20 mmol of $(CF_3)_2C{=}O$. The mixture of $S_2O_6F_2$ and $(CF_3)_2CFOOSO_2F$ contained in the $-78°$ trap was passed several times through a U tube containing NaCl (to remove the $S_2O_6F_2$). The product, 0.65 mmol, was obtained by refractionation. It decomposed on standing at 25° and was consequently only characterized by infrared and F^{19} nmr spectroscopy.

Preparation of SF_5OOSO_2F.—A 3.37-mmol sample of $S_2O_6F_2$ and 5.16 mmol of SF_4O were condensed into a Monel reactor containing KF and several stainless steel balls. The reactor was shaken for 6 hr at 25°. Fractionation of the reaction mixture yielded 2.04 mmol of SF_5OOSO_2F (vapor density molecular weight: calcd, 242; found, 239, 238) in the $-78°$ trap and a mixture of 1.28 mmol of SO_2F_2 and 1.59 mmol of SF_4O in the $-196°$ trap.

Preparation of $FSO_2ON(SO_2F)_2$.—A 9.6-mmol (3.02-g) sample of $CsN(SO_2F)_2$[6] was allowed to react with 14.9 mmol of $S_2O_6F_2$ for 12 hr at 25° in the absence of any solvents. The mixture was then fractionated through -35, -78, and $-196°$ cold traps. The product, 2.6 g, was obtained in 98% purity (by F^{19} nmr analysis) in the $-35°$ trap. It was further purified by vapor-phase chromatography using an 8-ft Kel-F–Chromosorb P column operating at 91°. Several passes of the compound were necessary to condition the column. *Anal.* Calcd for $FSO_2ON(SO_2F)_2$: N, 5.02; F, 20.4; S, 34.4. Found: N, 5.16; F, 20.1; S, 33.9.

Preparation of $(NO_2)_2C(CN)OSO_2F$.—A 0.588-g (3.48-mmol) sample of $K(NO_2)_2CCN$[7] was placed in a glass reactor and 3.80 mmol of $S_2O_6F_2$ was condensed into the reactor. The mixture was stirred overnight at 0° before being fractionated through -45, -78, and $-196°$ cold traps. The crude product, 0.355 g (1.55 mmol or 54% yield), was retained in the $-45°$ cold trap. Further purification was achieved by gas chromatography using a 4-ft Kel-F–Chromosorb P column operating at 50°. The material slowly decomposed on standing at 25°. Small amounts of N_2O, NO, NO_2, and SO_2F_2 were found in the colder traps, but no quantitative measurements were made. *Anal.* Calcd for $(NO_2)_2C(CN)OSO_2F$: F, 8.3; N, 18.34; C, 10.49. Found: F, 8.1; N, 18.30; C, 10.55.

Preparation of CF_3OSO_2F.—A 0.52-g (3.82-mmol) sample of CF_3COONa and 0.824 mmol of $S_2O_6F_2$ were loaded into a glass bulb equipped with a Teflon needle valve and allowed to stand for 1 hr at 25°. The mixture was fractionated through -78 and $-196°$ cold traps. The former trap contained 0.44 mmol of $S_2O_6F_2$, and the latter trap contained a mixture of CO_2 (0.35 mmol) and CF_3OSO_2F (0.36 mmol). The latter compound was identified by infrared and mass spectrometry.

Reactions of CF_3OOSO_2F. (A) With CsF.—A 0.315-mmol sample of CF_3OOSO_2F was shaken with 5.0 g of CsF and approximately 30 $^3/_8$-in. stainless steel balls for 2 hr. The total volatile phase (0.39 mmol) consisted of 31% oxygen and 69% SO_2F_2. The volatiles were removed, and fluorine, 0.4 mmol, was expanded into the reactor and allowed to stand at $-78°$ for 2 hr. This produced 0.24 mmol of CF_3OF.

(B) **With CF_3OF.**—A 0.507-mmol sample of CF_3OOSO_2F and 1.10 mmol of CF_3OF were condensed into a metal reactor which contained 5.0 g of dried CsF. After standing for 3 hr at 25°, the product mixture was fractionated through -126, -145, and $-196°$ cold baths. Some noncondensables were present. The $-196°$ trap contained 9.91 mmol of unreacted CF_3OF and a trace of SO_2F_2. Sulfuryl fluoride, 0.49 mmol, was retained in the $-145°$ trap and CF_3OOOCF_3, 0.11 mmol, was present in the $-126°$ trap. This compound was identified by a comparison of its infrared and F^{19} nmr spectra with the known spectra[8,9] and by vapor density molecular weight (calcd, 186; found, 184).

Reaction of SF_5OOSO_2F with CsF.—A 0.57-mmol sample of SF_5OOSO_2F was condensed into a metal reactor containing 5.0

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[1] Part II: J. K. Ruff, *Inorg. Chem.*, **4**, 567 (1965).

[2] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 513 (1957).

[3] J. M. Shreeve and G. H. Cady, *ibid.*, **83**, 4521 (1961).

[4] M. Lustig and G. H. Cady, *Inorg. Chem.*, **1**, 714 (1962).

[5] Sulfan B®, General Chemical Co.

[6] J. K. Ruff, *Inorg. Chem.*, **4**, 1446 (1965).

[7] C. O. Parker, *et al.*, *Tetrahedron*, **17**, 79 (1962).

[8] P. G. Thompson, *J. Am. Chem. Soc.*, **89**, 4316 (1967).

[9] W. B. Fox, *et al.*, *ibid.*, **89**, 4313 (1967).

g of CsF and several stainless steel balls. The mixture was shaken for 2 hr at 25°. Mass spectral analysis of the total volatile fraction indicated 34% O_2 and 66% SO_2F_2. The latter compound was isolated (0.55 mmol) in a pure state by pumping through a −196° trap. Fluorine, 0.65 mmol, was expanded into the reactor, and it was allowed to stand overnight at ambient temperature. The volatile products consisted of 0.45 mmol of SF_5OF in 98% purity after removal of the excess fluorine.

Reaction of $(FSO_2)_2NOSO_2F$ with NaF.—A 0.671-g (2.40-mmol) sample of $(FSO_2)_2NOSO_2F$ and 0.32 g of NaF were stirred together in 5 ml of CH_3CN for 12 hr at 25°. Mass spectral analysis of the vapor phase indicated the presence of nitrogen in addition to SO_2, SO_2F_2, and CH_3CN. The amount of nitrogen formed was determined by means of a Toepler pump and a calibrated bulb system: found, 1.11 mmol. Fractionation of the mixture through −78 and −196° cold traps resulted in the separation of 3.67 mmol of SO_2F_2 and 1.14 mmol of SO_2 in the latter trap. The infrared spectrum of the solid residue indicated the presence of $NaSO_3F$.

Reaction of $FN(SO_2F)_2$ with NaF.—A 0.746-mmol sample of $FN(SO_2F)_2$ was allowed to stand in contact with NaF at 25° for 3 days. The reactor was cooled to −196°, and the amount of noncondensable gas was determined by means of a Toepler pump and a calibrated bulb system. Nitrogen, 0.364 mmol, was obtained. The condensable fraction consisted of 1.025 mmol of SO_2F_2, 0.254 mmol of SO_2, and a trace of unreacted $FN(SO_2F)_2$. When the reaction was repeated in the presence of an equivalent of chlorine, low yields (5–10%) of $FNCl_2$ were produced in addition to the above products.

Analysis of Gas Mixtures.—The analysis of mixtures of the product gases was performed by mass spectrometry. The instrument was calibrated with pure samples of each of the products so that accurate cracking patterns could be obtained. Some difficulty was experienced in obtaining a reproducible cracking pattern for $S_2O_6F_2$. Therefore its quantitative estimation was not possible.

Nmr Spectra.—The F^{19} nmr spectra of the compounds were taken with a Varian Model 4300B spectrometer operating at 40 Mc. The chemical shifts were measured from the internal standard CCl_3F and are reported in ppm. The compound, chemical shift (assignment), and coupling constants (where appropriate) are: CF_3OOSO_2F, $\delta_{CF_3} = +68.3$, $\delta_{SF} = -37.9$; $(CF_3)_2CFOOSO_2F$, $\delta_{CF_3} = 76.2$, $\delta_{CF} = 137.5$, $\delta_{SF} = -38.2$, $J_{SFCF} = 8$ cps; CF_3OSO_2F, $\delta_{CF_3} = 57.8$, $\delta_{SF} = -46.8$, $J_{SFCF_3} = 6.5$ cps; $(NO_2)_2C(CN)OSO_2F$, $\delta_{SF} = -52.5$; and $(FSO_2)_2NOSO_2F$, $\delta_{SO_2F} = -52.7$, $\delta_{OSO_2F} = -45.9$, $J_{FF} = 2$ cps.

Infrared Spectra.—The infrared spectra of the new compounds were obtained with a Perkin-Elmer 521 spectrometer. The bands observed are: $(FSO_2)_2NOSO_2F$: 1499 (s), 1247 (s), 897 (m), 848 (vs), 767 (s), and 686 (s) cm^{-1}; $(NO_2)_2C(CN)OSO_2F$: 2262 (m), 1632 (vs), 1486 (s), 1321 (mw), 1282 (s), 1247 (s), 1080 (sh), 1053 (s), 855 (vs), 826 (m), and 794 (s) cm^{-1}; $(CF_3)_2CFOOSO_2F$: 1492 (ms), 1312 (s), 1258 (s), 1196 (mw), 1162 (m), 1106 (ms), 1016 (ms), 860 (vs), 806 (mw), 776 (ms), and 735 (m) cm^{-1}. The infrared spectra of CF_3OOSO_2F,[10] CF_3OSO_2F,[11] SF_5OOSO_2F,[11] and CF_3OOCF_3[8,9] were identical with those in the literature.

Results and Discussion

Peroxydisulfuryl difluoride has proven to be one of the most versatile reagents in the derivative chemistry of the sulfur oxyfluorides. It was initially prepared from SO_3 and F_2 by Cady and co-workers using a high-temperature catalytic-flow reactor,[2] although it is also available from the low-temperature electrolysis of fluorosulfuric acid.[12] Small amounts of peroxydisulfuryl difluoride may conveniently be prepared by the fluorination of SO_3 in a static and presumably noncatalytic system. No reaction between 2 equiv of SO_3 and 1 equiv of fluorine is observed at temperatures up to 120° in a closed system. However, heating to 170° produces a high yield of $S_2O_6F_2$. Pyrosulfuryl fluoride is the major impurity formed, and only trace amounts of FSO_3F were observed.

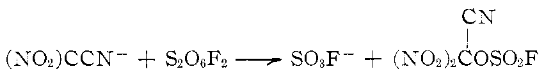
The oxidation of anions by $S_2O_6F_2$ has only been attempted using the halide anions (except fluoride), and only ionic fluorosulfate derivatives were formed.[3,4] However other anions are capable of being oxidized to form covalent fluorosulfate derivatives. For example the reaction of the CF_3O^- anion with $S_2O_6F_2$ produces CF_3OOSO_2F in high yield. It is not necessary however to prepare the pure salt since COF_2 and $S_2O_6F_2$ react in the presence of KF to produce the same product

$$COF_2 + S_2O_6F_2 + CsF \longrightarrow CF_3OOSO_2F + CsSO_3F$$

The yield is lower however due to a side reaction of the excess fluoride with the product (see discussion later). In a similar fashion $(CF_3)_2C{=}O$ may be converted to $(CF_3)_2CFOOSO_2F$. This material is not very stable and decomposes in glass at ambient temperature. This made a complete characterization impossible. However its F^{19} nmr and infrared spectra were in agreement with its formulation as the peroxide. In a similar fashion thionyl tetrafluoride could be oxidized with $S_2O_6F_2$ in the presence of excess KF to SF_5OOSO_2F. The product was identical with that obtained by the reaction of SF_5OOSF_5 and $S_2O_6F_2$.[11] The yields were moderate due to a side reaction of the excess fluoride ion with the product.

Other anions were also found to be oxidized by $S_2O_6F_2$ to produce covalent sulfur oxyfluoride derivatives. These reactions were generally carried out between the neat reagents using a slight excess of $S_2O_6F_2$. The three salts used were CF_3COOCs, $CsN(SO_2F)_2$, and $KC(NO_2)_2CN$. The reaction was found to proceed readily at ambient temperature, and the expected products were formed in good yield when $CsN(SO_2F)$ and $KC(NO_2)_2CN$ were used

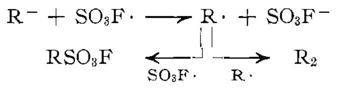
$$N(SO_2F)_2^- + S_2O_6F_2 \longrightarrow SO_3F^- + FSO_2ON(SO_2F)_2$$



$$(NO_2)CCN^- + S_2O_6F_2 \longrightarrow SO_3F^- + (NO_2)_2\overset{\displaystyle CN}{\overset{|}{C}}OSO_2F$$

However the acyl fluorosulfate presumably obtained from trifluoroacetate ion could not be isolated, and CF_3OSO_2F and CO_2 were found instead. The intermediate acyl fluorosulfate is believed to be unstable and to undergo decarboxylation to the observed product readily under the experimental conditions.

The oxidation of these anions is believed to involve a radical oxidation followed by radical recombination reactions



Thus, when an excess of $CsN(SO_2F)_2$ was employed in the above reaction, moderate yields of $N_2(SO_2F)_4$[13] were

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[10] W. P. Van Meter and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 6005 (1960).

[11] C. I. Merrill and G. H. Cady, *ibid.*, **85**, 909 (1963).

[12] F. B. Dudley, *J. Chem. Soc.*, 3407 (1963).

[13] J. K. Ruff, *Inorg. Chem.*, **5**, 732 (1966).

obtained in addition to $FSO_2ON(SO_2)F_2$. Since no reaction was observed between $N_2(SO_2F)_4$ and $S_2O_6F_2$ under the same conditions, $N_2(SO_2F)_4$ cannot be an intermediate in the formation of $FSO_2ON(SO_2F)_2$ and probably represents a simple coupling reaction of the R· radicals in the above scheme.

The reaction of covalent fluorosulfate derivatives with fluoride ion has been shown to follow the generalized equation[1,14,15]

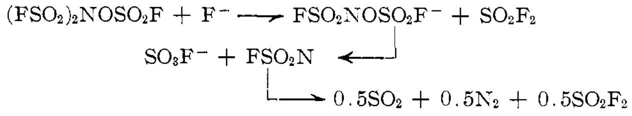
$$ROSO_2F + F^- \longrightarrow RO^- + SO_2F_2$$

The fate of the new anion (RO^-) was found to be dependent on its nature. This reaction was extended to the fluorosulfate derivatives prepared in this study. Both peroxyfluorosulfates, CF_3OOSO_2F and SF_5OOSO_2F, underwent reaction with fluoride ion at ambient temperature in a similar manner

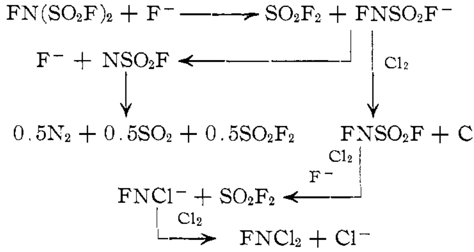
$$ROOSO_2F + F^- \longrightarrow RO^- + 0.5O_2 + SO_2F_2 \quad (R = CF_3 \text{ or } SF_5)$$

Evidence for the nature of the anion formed in this reaction was obtained by fluorination of the residue after the volatiles produced in the reaction had been removed. High yields of either SF_5OF or CF_3OF were produced. It is not known whether the peroxy anion ROO^- is an important species in the reaction scheme. However, when the reaction of CF_3OOSO_2F and KF was carried out in the presence of excess CF_3OF, moderate yields of the trioxide, CF_3OOOCF_3,[8,9] were isolated. This may indicate the existence of CF_3OO^- anions in the system although conclusive evidence is lacking. No reaction was observed when SF_5OOSO_2F and CF_3OF were allowed to interact in the presence of an alkali metal fluoride. Only the decomposition of SF_5OOSO_2F occurred under these experimental conditions as discussed above.

The reaction of $FSO_2ON(SO_2F)_2$ with NaF was also investigated. In this case there are two types of SO_2F groups, and it was of interest to see which type would be the most reactive toward fluoride ion. The reaction was found to follow the scheme (see the Experimental Section)



The reaction of $FN(SO_2F)_2$[16] with the fluoride ion appeared to follow a similar course. Thus, when $FN(SO_2F)_2$ was allowed to contact cesium fluoride in the absence of a solvent, only nitrogen, sulfur dioxide, and sulfuryl fluoride were obtained. When the reaction was carried out in the presence of an equimolar amount of chlorine, a low yield (about 10%) of dichlorofluoramine was produced



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(14) J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).
(15) M. Lustig and J. K. Ruff, *ibid.*, **3**, 287 (1964).
(16) M. Lustig, *et al.*, *ibid.*, **3**, 1165 (1964).

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The Reaction of Dioxygen Difluoride and Sulfur Dioxide. Transfer of the OOF Group

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The reaction of dioxygen difluoride with sulfur dioxide produces mainly sulfuryl fluoride and lesser amounts of pyrosulfuryl fluoride and fluorosulfuryl hypofluorite. The mechanism of this reaction was studied using O^{17}-tracer techniques and O^{17} nmr measurements. It was concluded that the sulfuryl fluoride is formed by a simple fluorination reaction. The pyrosulfuryl fluoride is formed *via* an FSO_3· intermediate, which results in scrambling. It was concluded that fluorosulfuryl hypofluorite results *via* an OOF intermediate.

Introduction

The chemistry of dioxygen difluoride (O_2F_2) is quite unique in that O_2F_2 reacts with most substances at temperatures of −160° or below.[1] Even at these low temperatures, a violent reaction or an explosion occurs when O_2F_2 reacts with most organic or inorganic materials containing hydrogen. Many other reactions of O_2F_2 are so violent that cleavage of most bonds occurs and results in simple degradation products.

We found that the reaction of O_2F_2 with sulfur dioxide can be controlled and is particularly useful in

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(1) A. G. Streng, *J. Am. Chem. Soc.*, **85**, 1380 (1963).