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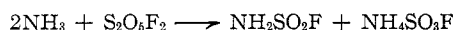
Sulfur Oxyfluoride Derivatives. II¹

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The reaction of nucleophiles with pyrosulfuryl fluoride, pyrosulfuryl chloride, and trisulfuryl fluoride has been studied. Two basic types of reactions were observed: S-O cleavage and chlorination of the nucleophile. The new compounds FSO_2N_3 and $\text{CF}_3\text{SO}_2\text{N}_3$ were prepared and characterized.

A number of inorganic compounds containing the fluorosulfuryl group (FSO_2-) appear to be susceptible to attack by nucleophilic reagents. For example, hydrolysis of pyrosulfuryl fluoride yielded fluorosulfuric acid,² while hydrolysis of trisulfuryl fluoride produced two equivalents of fluorosulfuric acid and one equivalent of sulfuric acid.³ The reaction of ammonia with pyrosulfuryl fluoride⁴ has been reported to give aminosulfuryl fluoride.



Furthermore, it has recently been shown that treatment of a variety of compounds containing the fluorosulfuryl group with an alkali metal fluoride resulted in the liberation of sulfuryl fluoride.^{1,5} This study was initiated to explore further the action of anionic nucleophiles on related fluoro and chloro sulfuryl derivatives.

Experimental

Materials.—The sodium salts were obtained from commercial sources and used after vacuum drying. Pyrosulfuryl fluoride,² trisulfuryl fluoride,³ tetrasulfuryl fluoride,⁶ pyrosulfuryl chloride,⁷ sulfuryl bromide fluoride,⁸ and the anhydride of trifluoromethyl sulfonic acid⁹ were prepared by literature methods. Sulfuryl chloride fluoride was prepared by reaction of sulfuryl chloride with excess sodium fluoride in acetonitrile. It was purified by low-temperature distillation. Acetonitrile, tetramethylene sulfone (TMS), nitromethane, and sulfur dioxide were obtained from commercial sources. The first three were dried over Linde 5A Molecular Sieves several days before use. Sulfur dioxide was passed through concentrated sulfuric acid, condensed, and stored in a 250-ml. stainless steel bomb.

The reactions of the sulfuryl derivatives with the various nucleophiles are summarized in Table I. More explicit details are given below.

Reaction of $\text{S}_2\text{O}_5\text{F}_2$ and $(\text{CF}_3)_2\text{S}_2\text{O}_5$ with the Anions.—The reactions of $\text{S}_2\text{O}_5\text{F}_2$ and $(\text{CF}_3)_2\text{S}_2\text{O}_5$ with the anionic nucleophiles were performed in a similar manner. For example, a 12.5-mmole sample of $\text{S}_2\text{O}_5\text{F}_2$ was condensed into a heavy wall reactor bulb (fitted with a Teflon needle valve) containing 17.5 mmoles of NaN_3 and 2 ml. of nitromethane. The mixture was stirred for 14 hr. and then fractionated through -35 , -78 , and -196° cold baths on the vacuum line. The contents of the -196° trap consisted of 1.10 mmoles of SO_2 and 1.28 mmoles of SO_2F_2 as

determined by mass spectral analysis. The product contaminated with a small amount of nitromethane was found in the -78° trap. Several runs were made and the combined crude products were distilled through a Holtzman column; b.p. $38-39^\circ$ (215 mm.).

Anal. Calcd. for FSO_2N_3 : F, 15.2; N, 33.6; mol. wt., 125. Found: F, 14.9; N, 33.3; mol. wt., 127 (vapor density), 124 (mass spectrometer).

The reaction of $(\text{CF}_3)_2\text{S}_2\text{O}_5$ with NaN_3 was performed in an identical manner using TMS as solvent. The product could be purified by vacuum line fractionation.

Anal. Calcd. for $\text{CF}_3\text{SO}_2\text{N}_3$: C, 6.86; N, 24.0; F, 43.4; mol. wt., 175. Found: C, 6.60; N, 24.2; F, 41.8; mol. wt., 178 (vapor density).

The reactions of FSO_2Cl with NaCN , $\text{FS}_2\text{O}_5\text{Cl}$ with NaCN , and $\text{FS}_2\text{O}_5\text{Cl}$ with NaF were also performed in an analogous fashion.

The vapor pressure of $\text{CF}_3\text{SO}_2\text{N}_3$ as a function of temperature, determined by the method of Kellog and Cady,¹⁰ is (given as t ($^\circ\text{C}$.), p (mm.): (12.9, 55.0), (14.7, 63.2), (17.1, 73.3), (18.8, 80.9), (21.5, 94.1), (22.7, 101.9), (25.8, 123.7), (30.7, 155.1), (33.4, 178.8), (36.6, 209.0), (40.4, 256.0), (44.6, 307.5), (47.2, 352.5), (49.2, 386.7), and (52.3, 444.3).

Reaction of $\text{S}_2\text{O}_5\text{F}_2$, FSO_2Br , and $\text{S}_4\text{O}_{11}\text{F}_2$ with the Anions.—These reactions were carried out in a manner similar to that described above. A typical example is given below: a 27.1-mmole sample of $\text{S}_2\text{O}_5\text{F}_2$ was loaded into a pressure reactor equipped with a Teflon needle valve. Approximately 20 ml. of sulfur dioxide was condensed into the reactor. Then under an atmosphere of dry nitrogen 24.7 mmoles of sodium chloride was added. The mixture was stirred overnight at ambient temperature. It was then cooled to 0° and the sulfur dioxide was allowed to escape slowly. The reactor was attached to the vacuum line and the remaining volatile materials were collected in a -78° trap. The crude product from several runs was distilled in a Holtzman column, b.p. 100° .

Anal. Calcd. for $\text{FS}_2\text{O}_5\text{Cl}$: Cl, 17.9. Found: Cl, 17.4.

The reaction of $\text{S}_4\text{O}_{11}\text{F}_2$ with NaCl to produce $\text{FS}_3\text{O}_8\text{Cl}$ was performed in an identical manner, b.p. $52-53^\circ$ (20 mm.).

Anal. Calcd. for $\text{FS}_3\text{O}_8\text{Cl}$: F, 6.8; Cl, 12.7. Found: F, 6.1; Cl, 12.3.

Reactions of $\text{S}_2\text{O}_5\text{Cl}_2$ with the Anions.—These reactions were carried out in an open system which was connected to a -196° cold trap, since the solvent (TMS) and the starting materials were relatively nonvolatile. A typical example is: a U-tube, equipped with a side-arm dropper, containing 8.32 mmoles of $\text{S}_2\text{O}_5\text{Cl}_2$ and 2 ml. of TMS was attached to a fractionation train on the vacuum line. Sodium chloride (9.42 mmoles) was placed in the side-arm dropper, and the system was cooled to 0° and evacuated briefly. The U-tube was opened to a -196° cold bath and both traps were pressurized to 20 mm. with dry nitrogen. Then the sodium chloride was added and the mixture stirred for 1 hr. After stirring the reactor was pumped on through the -196° cold bath. The contents of the -196° trap were fractionated through -78 and -196° cold baths. A mixture of Cl_2 and SO_2 , 7.44 and 7.43 mmoles, respectively, was found

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(4) R. Appel and G. Eisenhauer, *ibid.*, **310**, 90 (1960).

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TABLE I
 SUMMARY OF REACTIONS OF THE SULFURYL DERIVATIVES

Substrate ^a	Nucleophile ^a	Solvent (time) ^b	Products ^a
S ₂ O ₅ F ₂ (4.42)	NaF (5.17)	CH ₃ CN (3 hr.)	SO ₂ F ₂ (4.10), S ₂ O ₅ F ₂ (0.21)
S ₂ O ₅ F ₂ (4.48)	NaCl (5.34)	CH ₃ CN (5 hr.)	FSO ₂ Cl (4.28), S ₂ O ₅ F ₂ (0.15)
S ₂ O ₅ F ₂ (12.6)	NaN ₃ (17.5)	CH ₃ NO ₂ (14 hr.)	^c FSO ₂ N ₃ (8.16), SO ₂ (1.10), FSO ₂ F (1.28)
(CF ₃) ₂ S ₂ O ₅ (2.88)	NaF (3.19)	TMS (2 hr.)	CF ₃ SO ₂ F (2.69) mol. wt. 151, 148; calcd. 152)
(CF ₃) ₂ S ₂ O ₅ (2.67)	NaCl (2.82)	TMS (3 hr.)	CF ₃ SO ₂ Cl (2.49) (mol. wt. 167, 166; calcd. 168.5)
(CF ₃) ₂ S ₂ O ₅ (1.79)	NaN ₃ (2.04)	TMS (2 hr.)	^c CF ₃ SO ₂ N ₃ (1.51)
S ₂ O ₅ F ₂ (3.49)	NaF (3.38)	SO ₂ (16 hr.)	S ₂ O ₅ F ₂ (2.97), SO ₂ F ₂ (0.21)
S ₂ O ₅ F ₂ (27.08)	NaCl (24.7)	SO ₂ (16 hr.)	^c FS ₂ O ₅ Cl (15.16), F ₂ S ₂ O ₅ (1.79)
S ₂ O ₁₁ F ₂ (24.8)	NaF (20.6)	SO ₂ (36 hr.)	F ₂ S ₂ O ₅ (16.2), F ₂ S ₂ O ₅ (3.86)
S ₂ O ₁₁ F ₂ (32.1)	NaCl (27.4)	SO ₂ (36 hr.)	^c FS ₂ O ₅ Cl (6.52), F ₂ S ₂ O ₅ (trace), FS ₂ O ₅ Cl (1.52)
S ₂ O ₂ F ₃ (2.16)	NaBr (2.18)	CH ₃ CN (6 hr.)	^c Br ₂ (1.02), SO ₂ (1.11), SO ₂ F ₂ (1.12)
S ₂ O ₅ F ₂ (4.24)	NaCN (4.61)	CH ₃ CN (12 hr.)	SO ₂ (1.98), S ₂ O ₅ F ₂ (0.10), SO ₂ F ₂ (1.92), (CN) ₂ (2.10)
FSO ₂ Br (4.11)	NaBr (5.75)	SO ₂ (12 hr.)	Br ₂ (3.81)
FSO ₂ Cl (4.19)	NaCN (2.97)	CH ₃ CN (16 hr.)	ClCN (2.79), (CN) ₂ (0.03), FSO ₂ Cl (0.98), SO ₂ (2.64), SO ₂ F ₂ (0.10)
S ₂ O ₅ F ₂ (4.67)	NaBr (3.87)	SO ₂ (3 hr.)	S ₂ O ₅ F ₂ (0.49), Br ₂ (3.46)
S ₂ O ₅ F ₂ (4.58)	NaCN (4.45)	CH ₃ CN (2 hr.) 0°	(CN) ₂ (3.11), SO ₂ (3.07), SO ₂ F ₂ (0.21), S ₂ O ₅ F ₂ (0.38)
FS ₂ O ₅ Cl (3.60)	NaCl (4.15)	TMS (1 hr.)	Cl ₂ (2.78), SO ₂ (2.69), SO ₂ Cl ₂ (0.55), FSO ₂ Cl (0.12)
FS ₂ O ₅ Cl (3.15)	NaCN (3.68)	CH ₃ CN (4 hr.)	ClCN (2.97), SO ₂ (2.89), (CN) ₂ (0.04)
S ₂ O ₅ Cl ₂ (8.32)	NaCl (9.42)	TMS (1 hr.)	Cl ₂ (7.44), SO ₂ (7.43), SO ₂ Cl ₂ (0.62)
S ₂ O ₅ Cl ₂ (8.56)	NaCN (9.27)	TMS (1 hr.)	ClCN (7.94), SO ₂ (8.34), (CN) ₂ (0.16), SO ₂ Cl ₂ (0.22)
S ₂ O ₅ Cl ₂ (8.72)	NaBr (8.89)	TMS (1 hr.)	SO ₂ (8.41), ^c total chloride (8.04), ^c total bromide (8.12)
S ₂ O ₅ Cl ₂ (8.60)	NaN ₃ (9.01)	TMS (1 hr.)	SO ₂ (8.47), ^c ClN ₃ (8.32)
S ₂ O ₅ Cl ₂ (7.98)	NaNO ₂ (8.22)	TMS (1 hr.)	SO ₂ (7.72), ^c ClNO ₂ , ClNO, NO ₂ , Cl ₂
FS ₂ O ₅ Cl (1.69)	NaF (2.27)	CH ₃ CN (4 hr.)	FSO ₂ Cl (1.67), SO ₂ F ₂ (0.01)
S ₂ O ₅ Cl ₂ (7.28)	NaF (8.45)	TMS (1 hr.)	FSO ₂ Cl (7.04)

^a Numbers in parentheses are millimoles. ^b All reactions were performed at ambient temperature unless otherwise noted. ^c See Experimental section for further details.

in the -196° trap. Sulfuryl chloride, 0.62 mmole, was retained in the -78° trap. The reaction of FS₂O₅Cl with NaCl was performed the same way, except the reactor and -196° trap were pressurized to 100 mm. with nitrogen.

Analysis of Products.—Analyses of the volatile products from all the reactions which produced known materials were performed as described previously¹ with several exceptions. Those reactions in sulfur dioxide in which bromine was formed were worked up by vacuum line fractionation and the bromine was identified by vapor density molecular weight. However, the reactions in which bromine or bromine monochloride was formed in acetonitrile or TMS were analyzed by addition of mercury to the reaction mixture. After stirring overnight the mercuric halides formed were analyzed for bromide and chloride. Qualitative analysis of the reaction mixture consisting of sulfur dioxide and chlorine azide was accomplished by infrared spectroscopy. Irradiation of this mixture in a Pyrex bulb with a high-pressure mercury lamp decomposed the chlorine azide into chloride and nitrogen. The amount of nitrogen formed was determined with a Toepler pump and a calibrated storage bulb system. No evidence for any other nitrogen-containing species was found by infrared or mass spectral analysis of the mixture after irradiation. The amount of nitrogen found was taken as a measure of the amount of chlorine azide originally present. No quantitative analysis was made on the reaction mixture consisting of nitryl chloride, nitrosyl chloride, nitrogen dioxide, etc., although a good estimate of the amount of sulfur dioxide present was obtained by mass spectral means.

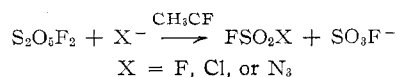
Spectra.—The infrared spectra were taken in the gas phase or as capillary layers on silver chloride plates with a Perkin-Elmer Model 21 spectrometer. A Consolidated Engineering Corp. Model 21-620 spectrometer was used to obtain the mass spectra of the reaction products. The mass number, species, and relative abundance for some of the more prominent peaks for FSO₂N₃ are as follows: 83, FSO₂⁺, 100%; 42, N₃⁺, 86%; 125, FSO₂N₃⁺, 63%; 67, FSO⁺, 53%; 77, FSO₂N⁺, 49%; 28, N₂⁺, 44%; 14, N⁺, 36%; 30, NO⁺, 33%; 48, SO⁺, 30%; and for CF₃SO₂N₃: 69, CF₃⁺, 100%; 48, SO⁺, 6.7%; 28, N₂⁺ (CO⁺),

5.4%; 14, N⁺, 4.4%; 42, N₃⁺, 3.9%; 64, SO₂⁺, 3.9%; 106, SO₂N₃⁺, 3.3%.

Results and Discussion

The reaction of various nucleophiles such as fluoride, chloride, bromide, azide, and cyanide ions with compounds containing a -SO₂Cl or a -SO₂F group was found to occur readily in polar solvents at ambient temperatures. The majority of the sulfur oxyhalides used contained a S-O-S linkage such as found in pyrosulfuryl fluoride.¹¹ A great difference in the mode of reaction was noted in comparing the chloro and fluoro derivatives, and the nucleophile employed also had an effect on the nature of the products isolated. Table I summarizes the experimental results.

A simple cleavage of the S-O bond was observed when pyrosulfuryl fluoride was allowed to react with either sodium fluoride, sodium chloride, or sodium azide.

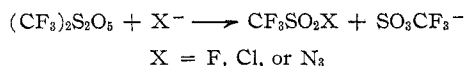


The yield of the substituted sulfuryl fluoride was good in each case, although some difficulty was experienced in separating sulfuryl azide fluoride from the solvent, acetonitrile. Therefore it was found advantageous to use nitromethane. The above reaction employing sodium fluoride is analogous to the reported preparation of fluorosulfate salts by the interaction of ammonium fluoride with a potassium pyrosulfate.¹²

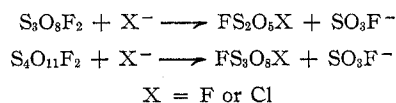
(11) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2179 (1961).

(12) W. Traube, *Ber.*, **46**, 2513 (1913).

Treatment of the anhydride of trifluoromethyl sulfonic acid with the same anions resulted in a similar cleavage reaction



and isolation of the substituted trifluoromethylsulfonyl derivatives was accomplished in high yield. This reaction was extended to include trisulfuryl fluoride, which is believed to be structurally related to pyrosulfuryl fluoride¹¹ and to tetrasulfuryl fluoride.⁶ Cleavage of the sulfur-oxygen bond by the nucleophile produced the substituted sulfuryl fluoride derivatives, although the yield of FSO_2Cl was quite low.



It was necessary to employ sulfur dioxide as a solvent since some decomposition of trisulfuryl fluoride and tetrasulfuryl fluoride occurred in acetonitrile or TMS. The presence of the fluorosulfate ion or trifluoromethyl sulfonate ion in the residue from the above reactions was confirmed by infrared spectroscopy,^{13,14} although no quantitative estimate was obtained.

The two new azide derivatives¹⁵ are colorless distillable liquids and they were characterized by analyses and infrared, ultraviolet, and mass spectroscopy (see Table II). The two bands at 2155 and 1181 cm^{-1} observed in the infrared spectrum of FSO_2N_3 are assigned to the asymmetric and symmetric stretching frequencies of the azide group. A similar assignment can be made for the bands found at 2155 and 1167 cm^{-1} in the spectrum of $\text{CF}_3\text{SO}_2\text{N}_3$. The assignment of the symmetrical stretching frequency may be in some doubt due to the presence of another band at 1231 and 1236 cm^{-1} in the spectra of FSO_2N_3 and $\text{CF}_3\text{SO}_2\text{N}_3$, respectively. This band is believed to be due to the symmetric $\text{S}=\text{O}$ stretching mode which also occurs in this region. The choice between the two possible assignments was made by analogy with the corresponding chloro-substituted sulfuryl derivatives, FSO_2Cl and $\text{CF}_3\text{SO}_2\text{Cl}$, which contained bands attributable to the symmetric $\text{S}=\text{O}$ stretching mode at 1233 and 1239 cm^{-1} , respectively.^{14,16} The agreement between the position of the bands assigned to the $\text{S}=\text{O}$ asymmetric stretching mode in the azido and chloro derivatives also supports the above argument: FSO_2N_3 , 1468 cm^{-1} ; FSO_2Cl , 1470 cm^{-1} ; $\text{CF}_3\text{SO}_2\text{N}_3$, 1437 cm^{-1} ; and $\text{CF}_3\text{SO}_2\text{Cl}$, 1437 cm^{-1} . The presence of the two stretching modes for the azide group demonstrates the covalent nature of these azides as do their ultraviolet spectra. The latter also consist of two bands similar to the ultraviolet spectra of typical alkyl

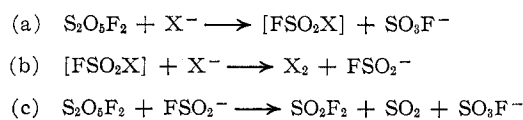
azides.¹⁷ However, the bands in these azides occur at much higher energy than those of the alkyl azides. This is probably due to the strong electron-withdrawing

TABLE II
INFRARED AND ULTRAVIOLET SPECTRA OF THE SUBSTITUTED
SULFURYL AZIDES

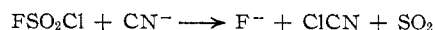
FSO_2N_3	$\text{CF}_3\text{SO}_2\text{N}_3$
Infrared, cm^{-1}	
2155 s	2155 s
1468 s	1437 s
1231 s	1236 vs
1181 s	1167 ms
826 vs	1133 s
775 m	784 m
	752 m
Ultraviolet: λ_{max} , $m\mu$ (ϵ , l./mole cm^{-1})	
199 (710)	195 (750)
249 (24)	238 (10)

power *via* an inductive effect of the substituted sulfuryl group since both bands undergo appreciable shifts.^{17,18} There is the possibility of some π -bonding between sulfur and nitrogen and this may also contribute to the shift of the low-energy band to higher energies.¹⁸

Since the cleavage reaction of pyrosulfuryl fluoride with chloride and azide ions provided a simple synthesis of the substituted sulfuryl fluoride derivatives, an attempt was made to extend this reaction to other ions. However none of the desired product, FSO_2X , was formed when either cyanide or bromide ions were employed. Instead a more complicated spectrum of products was observed. Their formation could be explained by the following reaction scheme.



The ratio of X_2 to SO_2 to SO_2F_2 was close to 1:1:1 when either an equivalent amount or an excess of pyrosulfuryl fluoride was used. Excess cyanide or bromide, on the other hand, depressed the formation of sulfuryl fluoride as would be expected if F^- (or FSO_2^-) and X^- ions were in competition for the pyrosulfuryl fluoride. Reaction step (c) was independently confirmed since the reaction of pyrosulfuryl fluoride and sodium sulfinate gave SO_2 and SO_2F_2 in the expected amounts. However, sodium fluorosulfinate does not appear to be stable in polar solvents so that evolution of sulfur dioxide could have resulted in step (b). Reaction step (b) could also be checked when $\text{X} = \text{Br}$. A good yield of bromine was formed, but the amount of SO_2 obtained could not be determined since SO_2 was used as the solvent. Although sulfuryl chloride fluoride did not react with either fluoride or chloride ions at ambient temperature, reaction with cyanide ion did occur.



(13) D. W. A. Sharp, *J. Chem. Soc.*, 3761 (1957).

(14) T. Gramstad and R. N. Haszeldine, *ibid.*, 173 (1957).

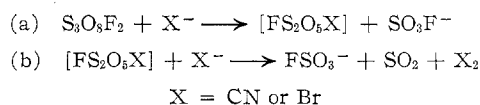
(15) Caution should be exercised in handling these materials since frequent explosions occurred when FSO_2N_3 was frozen with liquid nitrogen. The explosions, however, could be avoided by use of a Dry Ice-acetone bath.

(16) R. J. Gillespie and E. A. Robinson, *Spectrochim. Acta*, **18**, 1473 (1962).

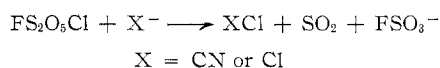
(17) W. D. Closson and H. B. Gray, *J. Am. Chem. Soc.*, **85**, 290 (1963).

(18) J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 889 (1964).

The reaction of trisulfuryl fluoride with cyanide or bromide ions was similar to that of pyrosulfuryl fluoride in that none of the substituted pyrosulfuryl fluoride derivative was isolated. The products obtained can be explained on the basis of the reaction scheme



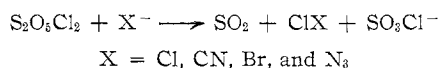
The reaction between sodium cyanide and trisulfuryl fluoride was performed in cold acetonitrile, but since the latter undergoes decomposition in the media the yield was not as good as in some of the other systems. Step (b) of the above reaction scheme could not be directly confirmed since the requisite pyrosulfuryl fluoride derivatives are unknown. However, chloride or cyanide ions were found to react with pyrosulfuryl chloride fluoride in a manner analogous to (b), which perhaps supports the above scheme.



The isolation of pyrosulfuryl chloride fluoride from the reaction between sodium chloride and trisulfuryl fluoride indicates that the latter sulfuryl derivative successfully competes with pyrosulfuryl chloride fluoride for the chloride ion.

The products obtained from the reaction of chloride or cyanide ions with pyrosulfuryl chloride fluoride suggest a direct nucleophilic attack on the chlorine atom by the anion. Although this assumes an $\text{S}_\text{N}2$ mechanism, prior dissociation of the pyrosulfuryl chloride fluoride into the reactive ions FS_2O_5^- and Cl^+ cannot be ruled out. Direct attack of the nucleophile on sulfur followed by decomposition of the unstable sulfuryl derivative can be ruled out when chloride ion is employed since the sulfuryl chloride formed would be stable.

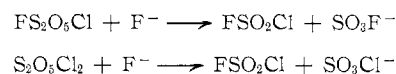
It was not surprising to find that pyrosulfuryl chloride acted primarily as a chlorinating agent toward numerous anions. The general reaction observed is



High yields of sulfur dioxide and ClX were obtained in

most cases. Treatment of pyrosulfuryl chloride with sodium nitrite produced nitryl chloride and sulfur dioxide, although no quantitative estimate of the yield was made. In addition to the nitryl chloride small amounts of nitrogen dioxide, chlorine, and nitrosyl chloride were formed. A similar observation was reported in the reaction of nitrogen dioxide with peroxydisulfuryl difluoride.¹⁹ However, when pyrosulfuryl fluoride was treated with sodium nitrite in nitromethane, no volatile sulfuryl species were formed. Instead the residue consisted of approximately an equimolar mixture of sodium fluorosulfonate and nitrosyl fluorosulfonate. This again contrasts the behavior of the fluoro and chloro sulfuryl derivatives toward nucleophiles.

The nature of the nucleophile apparently does play an important role. For example, fluoride ion behaved differently toward pyrosulfuryl chloride fluoride and pyrosulfuryl chloride than the other nucleophiles. The reactions are summarized below.



Sulfuryl chloride fluoride was obtained in high yield essentially free from sulfuryl fluoride in both reactions. The site of attack by the fluoride ion is not known, although it is believed to be on the sulfur and not on the chlorine. If it did attack the latter, chlorine monofluoride and sulfur dioxide would be formed. These two species could then combine to form the observed product. However, the formation of this very reactive interhalogen in solution might be expected to result in side reactions so that a mixture of products would be obtained. Since the reactions gave only sulfuryl chloride fluoride in high yield this latter course is not as likely. A difference in site of attack of a nucleophile on a sulfonate ester has been reported²⁰ and was found to depend on the polarizability of the nucleophile.

Acknowledgment.—This work was performed under Contract No. DA-01-021 ORD-11878.

(19) J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 353 (1960).

(20) J. F. Bunnett and J. Y. Bassett, *ibid.*, **81**, 2104 (1959).