FLUOROSULFURIC ACID, ITS SALTS, AND DERIVATIVES

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I. Fluorosulfuric Acid

Fluorosulfuric (fluorosulfonic) acid has been known since 1892, when it was prepared by Thorpe and Kirman (*1*) by reacting sulfur trioxide and anhydrous hydrogen fluoride. The compound may be considered to

$$SO_3 + HF \rightarrow HSO_3F$$

be derived by the replacement of an OH group in H_2SO_4 by the isoelectronic F. It is of particular great interest since it and mixtures of it with SbF_5 and SO_3 are among the strongest acids known. Its physical and chemical properties commend it as a medium for a variety of experimental approaches. The radical formed by the oxidation of its anions as well as its anhydride is a particularly useful synthetic reagent.

The chemistry of fluorosulfuric acid and its derivatives has been previously discussed by Lange (*2*), Cady (*3*), Williamson (*4*), Nickless (*5*), and Gillespie (*6*).

A. Physical Properties

The anhydrous acid is a colorless liquid which fumes in moist air. It may be conveniently handled in glass apparatus, provided it is free of excess hydrogen fluoride. It may easily be purified by distillation. Traces of excess SO_3 result from the distillation process (ref. *d*, Table I). They can be removed by adding an equivalent amount of HF. Several of its physical properties are given in Table I.

TABLE I

PHYSICAL PROPERTIES OF FLUOROSULFURIC ACID

Property	Value	Reference
Boiling point	162.7°	*a*
Freezing point	−88.98°	*b*
Density at 25°	1.726	*c*
Viscosity at 25° (cP)	1.56	*c*
Specific conductivity at 25° (ohm^{-1} cm^{-1})	1.085×10^{-4}	*c*
Heat of formation at 25° (kcal/mole)	189.4 ± 0.06	*d*
Cryoscopic constant (deg. mole^{-1} kg)	3.93 ± 0.05	*e*

[a] Thorpe, T. F., and Kirman, W., *J. Chem. Soc.* 921 (1892).
[b] Gillespie, R. J., Milne, J. B., and Thompson, R. C., *Inorg. Chem.* **5**, 468 (1966).
[c] Barr, J., Gillespie, R. J., and Thompson, R. C., *Inorg. Chem.* **3**, 11 (1964).
[d] Richards, G. W., and Woolf, A. A., *J. Chem. Soc.*, A 1118 (1967). Woolf, A. A., *J. Inorg. Nucl. Chem.* **14**, 21 (1969). Note: the heat of formation of aqueous acid is 5.9 kcal/mole higher.
[e] Gillespie, R. J., Milne, J. B., and Thompson, R. C., *Inorg. Chem.* **5**, 468 (1966).

The rather high boiling point is a reflection of its association. The long liquid range is an asset. The relatively low freezing point makes it possible to carry out low-temperature NMR work in the solvent. Its viscosity is considerably lower than that of sulfuric acid (as is its freezing point). In this respect, it is a more suitable strongly acid medium, since experimental difficulties are less. Conductivity and cryoscopic techniques have been quite important.

Brazier and Woolf (7) investigated qualitatively the reaction of several metals in HSO_3F. They reported that Au, Mg, Zn, Cd, B, Al, Ce, Sm, Lu, Ga, V, Cr, W, Mn, Re, Fe, Co, Ni, Ru, Os, and Pt were inert to boiling acid; Cu and Bi gave white precipitates (fluorosulfates) and colorless supernatant liquids, Ag, As, and Sb gave clear solutions which were probably solutions of fluorosulfates in the acid. Nb, Ta, U, and Pb dissolved to give green solutions, while Na, K, Ca, In, Tl, and Sn all dissolved to give green supernatant liquids over white precipitates. The white precipitates were fluorosulfates or decomposition products, while the green solutions were paramagnetic. The ESR behavior and ultraviolet spectrum of the green solutions are like those of sulfur in oleum. The metals which give the green solutions are those which are good reducing agents in highly acidic solutions and reduce the sulfur to elemental form, whereas the less potent reducing metals go only as far as SO_2.

Engelbrecht has shown that HSO_3F is a good fluorinating agent. It reacts with many oxides and oxy acids as well as their salts (*8*). Usually oxyfluorides result, but sometimes complete fluorination results. Many of the reactions are carried out at room temperature. Others require heating. Table II summarizes most of these reactions.

TABLE II

REACTION PRODUCTS FROM HSO_3F

Reaction	Product
$B(OH)_3$	BF_3
$SiO_2 \cdot xH_2O$	SiF_4
As_2O_5	AsF_5, $AsF_2(SO_3F)_3$, $AsF_3(SO_3F)_2$
As_2O_3	AsF_3
$KMnO_4$	MnO_3F
K_2CrO_4	CrO_2F_2
CrO_3	CrO_2F_2
$K_2Cr_2O_7$	$Cr_2O_2F_2$
P_4O_{10}	POF_3
$BaSeO_4$	SeO_2F_2
$BaTeO_4$	$Te(OH)F_5$
BaH_4TeO_6	$TeF_5(SO_3F)$
$KClO_4$	ClO_3F
KCl	KSO_3F
KF	KSO_3F

A fluorosulfate intermediate has been proposed for some of these reactions.

$$KClO_4 + HSO_3F \rightarrow HClO_4 + K^+ + SO_3F^-$$
$$HClO_4 + 2HSO_3F \rightarrow ClO_3SO_3F + H_3O^+ + SO_3F^-$$
$$ClO_3SO_3F \rightarrow ClO_3F + SO_3$$

The reaction of alkali and alkaline earth chlorides and fluorides to form fluorosulfates is facilitated by the removal of HCl or HF which is also formed (*9*, *10*).

Nitrosyl fluoride forms when the HSO_3F reacts with the chloride (*11*) or N_2O_5, while N_2O_3 yields the nitrosyl salt (*12*, *13*).

Woolf (*14*) has made the rather interesting observation that there is a nearly linear relationship between the increase in boiling point caused by the insertion of sulfur trioxide into fluorides (yielding fluorosulfates) and the ratio of the molecular weight of the fluorides to that of the fluorosulfate. The boiling point increase effect is greatest for fluorides of low molecular weight. Deviations are found when one liquid is more (or less) associated than its parent. Deviations in melting point behavior are observed in the case of ionicity.

B. SOLVENT SYSTEM

According to the solvent systems concept, autoionization occurs via proton transfer to give $H_2SO_3F^+$ or to reduce the concentration of SO_3F^- while bases increase the concentration of SO_3F^- or reduce the concentration of $H_2SO_3F^+$.

Barr, Gillespie, and Thompson (*15*) have investigated electrical conductivity and transport numbers in the fluorosulfuric system and showed that electrical conductivity of acids and bases in the system occurs primarily via proton transfer involving the ions $H_2SO_3F^+$ and SO_3F^-. Mobilities involving this mechanism are much greater than would be predicted for ordinary diffusion mechanisms. The observation that conductivity of the various alkali metal fluorosulfates of identical concentrations is very similar is explained by the high mobility of SO_3F^-.

Although the conductivities of the alkali metal fluorosulfates are very similar at any given concentration, they decrease slightly in the order: $NH_4 > Nb \sim K > Na \sim Li$. The conductivities of $Ba(SO_3F)_2$ and $Sr(SO_3F)_2$ are also similar, that of the strontium salt being somewhat less than that of barium. The small differences were attributed to an increase in the extent of solvation of the cations in the series $NH_4 < Rb \sim K < Na \sim Li < Ba < Sr$. The cation transport numbers for the potassium and barium salts were 0.11 ± 0.63 and 0.075 ± 0.02, respectively.

Conductivity measurements showed that acetic acid, benzoic acid, nitrobenzene, and *m*-nitrotoluene are all strong bases in the fluorosulfuric acid solvent system, whereas nitromethane, *p*-nitrochlorobenzene, *m*-nitrochlorobenzene, 2,4-dinitrotoluene, 2,4-dinitrofluorobenzene, and trinitrobenzene are weak bases.

The conductivity of potassium sulfate is consistent with

$$K_2SO_4 + 2HSO_3F \rightarrow 2K^+ + 2SO_3F^- + H_2SO_4$$

in that its conductivity is slightly less than twice that of an equivalent solution of potassium fluorosulfate. This fact is attributed to an increase in viscosity. Sulfuric acid was found to be weakly conductive, insignificant compared to the total conductivity of potassium sulfate, with a basic dissociation constant of 10^{-4}. This is inconsistent with Woolf's (*16*) earlier report that sulfuric acid forms solutions comparable in conductivity with potassium fluorosulfate. The basic behavior is consistent with the finding that fluorosulfuric acid is a weak acid in the sulfuric acid solvent system.

$$H_2SO_4 + HSO_3F \rightarrow H_3SO_4^+ + SO_3F^-$$

Woolf (*16*) and Barr *et al.* (*15*) both have given evidence that HF is a base in this solvent system.

$$HF + HSO_3F \rightarrow H_2F^+ + SO_3F^-$$

Woolf found a net transport of fluorine on electrolysis of HF in the solvent. Barr *et al.* showed that potassium fluoride solutions are very slightly more conducting than solutions of potassium fluorosulfate. Woolf isolated potassium fluorosulfate from potassium fluoride solutions in HF.

$$KF + HSO_3F \rightarrow KSO_3F + HF$$

The situation with respect to perchloric acid is not quite so clear. Woolf (*16*) found a minimum conductivity in a titration with perchloric acid, suggesting basic behavior. Rather than concluding that perchloric acid is a proton acceptor, he suggested the following path yielding four

$$2HSO_3F + HClO_4 \rightarrow ClO_3^+ + H_3O^+ + 2SO_3F^-$$

ions per mole of perchloric acid. This reaction is inconsistent with the finding of Barr *et al.* (*15*). They found that the conductivities of potassium perchlorate solutions were only slightly greater than that of potassium fluorosulfate, suggesting solvolysis. Rather than attribute the slight

$$KClO_4 + HSO_3F \rightarrow K^+ + SO_3F^- + HClO_4$$

increase in conductivity to protonation of the perchloric acid, they suggested that small differences in viscosity, caused by the presence of perchloric acid, might account for differences in conductivity.

Woolf (*16*) and Barr *et al.* (*15*) have reported that arsenic trifluoride and antimony trifluoride behave as weak bases in fluorosulfuric acid solutions. Barr *et al.* (*15*) reported that the conductivity of both of these increase on standing, the conductivity and rate of increase in conductivity with time being greater for the antimony compound. They explained this by the following reactions.

Initially: $AsF_3 + HSO_3F \rightarrow HAsF_3^+ + SO_3F^-$

On standing: $AsF_3 + HSO_3F \rightarrow AsF_2SO_3F + HF$

Woolf (*16*) found that antimony pentafluoride gives conducting solutions in fluorosulfuric acid. These can be titrated with the strong base, potassium fluorosulfate. Thompson *et al.* (*17*) conducted conductometric, cryoscopic, and nuclear magnetic resonance studies on solutions of SbF_5, $SbF_4(SO_3F)$, and SbF_5–SO_3 mixtures in fluorosulfuric acid solutions. They showed that there exists a series of acids which may be considered to be derived by the substitution of one to four SO_3F groups for F^- in the acid $HSbF_6$. The strengths of these acids increase with increasing substitution. These acids dimerize through fluorosulfate bridges. There is some evidence that higher polymers exist.

The monofluorosulfate, SbF_4SO_3F, had been prepared earlier in the absence of solvents by reaction of SbF_5 and SO_3 (*18*).

Gillespie (*19*) and his students continued the work on the fluorosulfuric acid system and carried out conductivity measurements of PF_5, BiF_5, NbF_5, PF_5–SO_3, NbF_5–SO_3, and AsF_5–SO_3 solutions. All the fluorides gave smaller conductivity than does SbF_5. Niobium and phosphorus pentafluorides gave negligible conductivity increases and are considered to be nonelectrolytes in the system. AsF_5, BiF_5, and TiF_4 gave smaller increases in conductivity, that of BiF_5 being somewhat greater than that of AsF_5. The solubility of TiF_4 (about 4×10^{-2} *M* at 25°) limited the conductivity range which could be investigated. The behavior of BiF_5 and AsF_5 when titrated conductometrically with KSO_3F was consistent with the following ionization scheme (analogous to that of SbF_5).

$$AsF_5 + 2HSO_3F \rightarrow H_2SO_3F^+ + AsF_5(SO_3F)^-$$

$$BiF_5 + HSO_3F \rightarrow H_2SO_3F^+ + BiF_5(SO_3F)^-$$

A possible scheme for TiF_4 is:

$$TiF_4 + 2HSO_3F \rightarrow H_2SO_3F^+ + TiF_4(SO_3F)^-$$

The addition of sulfur trioxide had no effect on the conductivity of solutions of NbF_5 or PF_5, but it had marked effects on the conductivity of AsF_5 solutions. Solutions of SO_3 in HSO_3F–BiF_5 solutions are unstable. The investigators concluded that the order of strengths of acids is $PF_5 \sim NbF_5 < TiF_4 \sim AsF_5 < BiF_5 < AsF_4(SO_3F) < SbF_5 < AsF_2(SO_3F)_3 < SbF_2(SO_3F)_3$. Therefore, SbF_5 is the strongest acceptor of the Group V pentafluorides. When fluoride is replaced by fluorosulfates in one of the pentafluorides, an increase in strength occurs. The maximum acidity which can be obtained is limited by the stability of the compound formed.

Gillespie and Pez (*20*) investigated the behavior of N_2, O_2, Ne, Xe, H_2, NF_3, CO, CO_2, SO_2, and 1,3,5-trichlorobenzene in the system HSO_3F–SbF_5–SO_3. They made solubility and conductivity measurements and reported on observations of the infrared spectra of CO_2 and

SO_2 (also ultraviolet as well as the NMR spectra of CO_2). They found that N_2, O_2, CO_2, Ne, Xe, H_2, and NF_3 had solubilities less than 1 ml gas/100 ml of the solvent HSO_3F–SbF_5(0.36 m)–SO_3(1.06 m). These solubilities are similar to those in water. No change in conductivity was observed when the He, N_2, and O_2 were equilibrated with the solvent (1 atm). It seems clear that no significant base behavior is seen. Although the lack of basicity of NF_3 to common acids is well known, it is worthwhile to note that the substitution of fluorine for hydrogen in ammonia reduces the basicity of the lone pairs so much that they are not basic even to the extremely acidic medium.

Carbon dioxide showed a moderate solubility (0.2 *M* at 1 atm and 20.3°) in HSO_3F–SbF_5. The solubility did not change appreciably as more SbF_5 or SO_3 was added. The solubility behavior followed Henry's law from 0 to 1 atm.

Small changes in conductivity were associated with the solutions of SO_2 in HSO_3F–SbF_5 and HSO_3F–SbF_5–SO_3. These were attributed to changes in viscosity rather than protonation. Infrared and Raman data were consistent with this viewpoint.

SO_2 solubilities in HSO_3F–SbF_5 and HSO_3F–SbF_5–SO_3 systems are sizable and follow Henry's law. Conductivity behavior was like that of CO_2. Raman and ultraviolet spectra showed no evidence for protonation.

In this same paper the authors demonstrated the acidity of HSO_3F–SbF_5–SO_3 vs. HSO_3F by showing conductometrically that 1,3,5-trinitrobenzene, a weak base in HSO_3F, is completely ionized in the mixed solvent system.

Olah and McFarland (*21*) have studied the behavior of a series of fluoro- and oxyphosphorus compounds in HSO_3F and HSO_3F–SbF solutions using primarily NMR methods. H_2PO_3F is essentially completely protonated, HPO_2F_2 is largely protonated, whereas POF_3 and PF_3 are not, in excess HSO_3F. When SbF_5 is also present, POF_3 is protonated and the protonation of HPO_2F_2 goes further. Polyphosphates are cleaved to fluorophosphates and phosphoric acid. Fluorination reactions are also observed.

Arnett, Quirk, and Larson (*22*) have measured the enthalpies of transfer of 31 amines from carbon tetrachloride to fluorosulfuric acid. Since they found a linear correlation between these enthalpies and pK_a values of the corresponding conjugate acids in water, they proposed that these heats of protonation be basis for a basicity scale. They (*23*) made similar measurements of 52 carbonyl bases and compared the measured enthalpies with other criteria for base strength. They reported that cyclopropyl and α,β-unsolvated ketones are very basic compared to aliphatic or aromatic ketones. By this criterion, aliphatic ketones are more basic than previous pK_a's had suggested. These aromatic ketones for which related pK's are known fit well into the correlation of pK_a's vs. H for the amines. Benzaldehyde was found to be of low basicity.

Paul and his associates have published a series of papers (*24*) in which he investigated several nonaqueous solvents including nitromethane, ethyl acetone, molten acetamide, nitrobenzene (with anthrane), alcohols, acetic acid, and methane sulfuric acid. The following acid strength orders are shown by his work: $H_2S_2O_7 > HSO_3F > HSO_3Cl > H_2SO_4$. He demonstrated the usefulness of HSO_3F as an acid titrant in acetic acid and alcoholic solutions. He found that HCl is only slightly soluble and is a nonelectrolyte in HSO_3F solutions but that it is fairly soluble and a weak base in the super acid HSO_3F–SbF_5–SO_3^- (*25*).

Benoit *et al.* (*26*) have studied sulfolane solutions of HSO_3F, $HClO_4$, $HSbCl_6$, and $H_2S_2O_7$ and have concluded that the order of acid strength is $HClO_4$, ($K = 10^{-2.7}$), HSO_3F ($K = 10^{-3.3}$), $H_2S_2O_7$ ($K = 10^{-5}$), while $HSbCl_6$ is a strong acid. Note that is not the order found in strongly associated protonic solvents like H_2SO_4.

The solubilities of the bases, Group I and II fluorosulfates, in fluorosulfuric acid have been investigated by Seely and Jache (*27*). The solubilities have been compared with those of the corresponding fluorides in hydrogen fluoride and rationalized on the basis of lattice energy and solvation energy considerations. The data pertaining to the fluorosulfates are given in Table III.

TABLE III

SOLUBILITIES OF FLUOROSULFATES IN FLUOROSULFURIC ACID[a]

	Solubility	
Fluorosulfate	HSO_3F (gm/100 gm)	HSO_3F (mole/100 gm)
Li	33.78 ± 0.64	0.319
Na	80.21 ± 0.99	0.658
K	63.83 ± 0.51	0.461
Rb	89.48 ± 0.99	0.486
Cs	132.4 ± 1.5	0.992
Mg	0.12 ± 0.04	5.4×10^{-4}
Ca	16.39 ± 0.46	6.86×10^{-2}
Sr	14.52 ± 0.33	5.10×10^{-2}
Ba	4.67 ± 0.35	1.39×10^{-2}

[a] Reproduced from *J. Fluorine Chem.* **2**, 225. Copyright 1972 by Elsevier Scientific Publishing Company. Reprinted with permission of the copyright owner.

It is a convenient coincidence that 100 gm of HSO_3F (MW = 100.07) is very nearly a mole, while 100 gm of HF (MW = 20.01) is very nearly five moles. Therefore, the solubilities are essentially reported in a mole (or gram) per mole basis.

It is interesting to note that in Group I the smooth trend of increasing solubility with increasing atomic number is spoiled by sodium fluorosulfate (or potassium fluorosulfate) if one considers solubility on a gram basis or by sodium (or potassium or rubidium fluorosulfate) on a mole basis. One would expect that solvation energy for the Group I cations would follow the same trends as do the hydration energies, i.e., decrease with increasing atomic number. On this basis alone, one would expect that the solubility would decrease with increasing atomic number. Lattice energies should reflect the increasing size of cation with increasing atomic number and decrease. Lattice energy considerations should then lead to a prediction of increase in solubility with increasing atomic number. The solubilities suggest that a crossover of the predominance of one effect on the other occurs close to the middle of the group. The solubilities of calcium, strontium, and barium fluorosulfate drop off with increasing atomic number. Magnesium fluorosulfate is not included in the rationalization since magnesium compounds frequently show differences from similar compounds of other Group II elements. The high size/change ratio of magnesium may bring in considerable degree of covalency. The solubility in water of sulfates, nitrates, and chlorides (but not the smaller fluorides) of calcium, strontium, and barium also decrease with increasing atomic number. This is consistent with a decrease in solvation energy of the metal ions. It may also be that within the group lattice energies may be larger with larger cations than with very small cations, reflecting a more desirable radius ratio (anion, anion repulsing).

We have not been able to include the large volume of work dealing with organic molecules in super acid (magic acid) media.

II. Fluorosulfates

Various methods for the preparation of particular fluorosulfates have been reported. In general, the fluorosulfate salts are usually prepared by one of the following methods: displacement of chlorides, fluorides, and oxyfluorosulfates with fluorosulfuric acid (*9, 10, 28, 29*), addition of SO_3 to fluoride (*30, 31*); fluorination of oxy salts of sulfur or mixtures containing SO_3 with BrF_3(*11*); or reaction of $S_2O_6F_2$ with metals, oxides, or halides.[1] They are also formed in displacement reactions of acetates, sulfates, chlorides, and fluorides in fluorosulfuric acid (*7*).

The thermal decomposition of fluorosulfate salts usually follows one or both of the following paths.

$$M(SO_3F)_x \rightarrow MF_x + xSO_3$$

$$2M(SO_3F)_x \rightarrow M_2(SO_4)_x + xSO_2F_2$$

Muetterties (*31, 32*) has pointed out that differences in behavior reflect small differences in structure. The coordination number of the cations increases from six to eight as one moves from calcium to barium, whereas the polarizing power is less for barium than for calcium. $Ca(SO_3F)_2$ is pyrolyzed to CaF_2 and SO_3, whereas $Ba(SO_3F)_2$ decomposes to $BaSO_4$ and SO_2F_2.

These factors are reflected in lattice energy. Ryss (*33*) apparently considered the relative lattice energies of the fluoride and sulfate salts which may result from pyrolysis when he developed his free energy of formation approach. He used standard free energies of formation of individual compounds from the following equations

$$M(SO_3F)_2 \rightarrow MSO_4 + SO_2F_2$$

$$M(SO_3F)_2 \rightarrow MF_2 + 2SO_3$$

in the expression:

$$\frac{P_{SO_2F_2}}{P_{SO_3^2}} = Ke^{\left[\frac{\Delta F_{MF_2} - \Delta F_{MSO_4}}{RT}\right]}$$

He arbitrarily set the ratio $P_{SO_2F_2}/P_{SO_3^2}$ equal to 1 for $Ca(SO_3F)_2$ pyrolysis. Using this he arrived at the ratios for other salts as shown in tabulation below. The expression is successful in predicting the behavior on pyrolysis of the alkaline earth fluorosulfates, but is less successful for that of the alkali metals.

Salt	Mg^{2+}	Ca^{2+}	Ba^{2+}	Pb^{2+}	Na^+	K^+
$\frac{P_{SO_2F_2}}{P_{SO_3^2}}$	1×10^{-6}	1	1×18^8	6×10^5	4×10^4	1×10^6

$NaSO_3F$ is thermally decomposed to SO_2F_2 and SO_3. This is in keeping with the prediction that KSO_3F gives only SO_3.

[1] See section dealing with $S_2O_6F_2$.

In Group II the conversion to SO_2F_2 correlates favorably with the free energy of formation prediction (Table IV).

TABLE IV

CONVERSION OF GROUP II SALTS TO SO_2F_2

Salt	SO_2F_2 (%)	Conversion to SO_3
$Be(SO_3F)_2$	Trace	47
$Mg(SO_3F)_2$	Trace	50
$Ca(SO_3F)_2$	4	90
$Sr(SO_3F)_2$	65	1
$Ba(SO_3F)_2$	56	1
$Zn(SO_3F)_2$	50	Trace
$Hg(SO_3F)_2$	25	Trace

When antimony, vanadium, niobium, and tantalum pentafluorides are reacted with sulfur trioxide, salts of the type $MF_3(SO_3F)_2$ are believed to form as intermediates which decompose on further heating to give SO_2F_2 and $S_2O_5F_2$.

Woolf (*34*) was able to prepare fluorosulfates of divalent Mn, Fe, Ni, Cu, Zn, and Cd by displacement reactions in fluorosulfuric acid. The ease of replacement is in the order $CH_3CO_2^- > SO_4 > Cl^- > F^-$. Factors in addition to the relative strengths of the acids are involved. Since these are heterogeneous reactions the nature of the solid liquid interface and ease of migration through the film is probably important. Cuprous compounds become oxidized to cupric salts, whereas cobaltic salts are converted to the lower oxidation state fluorosulfates. Metallic copper is converted to $Cu(SO_3F)_2$ by the acid. Brazier and Woolf (*35*) felt that the stability of the cations in particular oxidation states could be estimated by analogy with redox potentials in aqueous solutions. Richards and Woolf (*36*) have demonstrated application of fluorosulfuric acid as a calorimetric medium and have determined the heats of formation of several fluorosulfates.

Many oxyfluorosulfates have been made using $S_2O_2F_6$ as a reactant. For example, Dev and Cady (*37*) prepared the oxidizing $MnO(SO_3F)$, $CoO(SO_3F)$, $NiO(SO_3F)$, $TlO(SO_3F)$, and $Ag_2O(SOF_3)$ from $MnCO_3$, $CoCO_3$, $NiCO_3$, Ag_2CO_3 (and Ag_2O), Tl_2CO_3, and $S_2O_6F_2$. Here $S_2O_6F_2$ reacts both as a fluorosulfating agent and as an oxidizing agent. These compounds are strong enough oxidizing agents to liberate both iodine and oxygen from potassium iodide solutions. The existence of the Ni(III), Ag(II) salts is particularly interesting. Kleinkopf and Shreeve (*38*) reacted $S_2O_6F_2$ with several transition metals, or their anhydrous chlorides, and obtained the appropriate fluorosulfates. They prepared $VO(SO_3F)_3$ (from VCl_5), $NbO(SO_3F)_3$ ($NbCl_5$ or metal), $TaO(SO_3F)_3$ ($TaCl_5$), ReO_3SO_3F (metal), and $ReO_2(SO_3F)_2$ (metal). ReO_3SO_3F, along with $S_2O_5F_2$, is a thermal decomposition product of $ReO_2(SO_3F)_2$. Previously $MnO_2SO_3F_2$ (*39*) and $CrO_2(SO_3F)_2$ (*40*) had been prepared.

Des Marteau and Cady (*41*) prepared the first compound in which a fluorosulfate is attached to a phosphorus, $PO(OSO_2F)$ by the reaction of $S_2O_5F_2$ on $POBr_3$. When Noftle and Cady (*42*) reacted $S_2O_6F_2$ with SbF_5 they obtained an unstable compound which may contain more than four SO_3F groups. With a large excess of $S_2O_6F_2$, a stable compound containing 3–3.5 SO_3F groups per cation of antimony and chlorine in a partial oxidation state results. The fluorosulfates $Sb(SO_3F)_3$ (*43*), $SbCl_4(SO_3F)$ (*44*), and $SbF_4(SO_3F)$ (*45*) are known and the compound $2AsF_3 \cdot 3SO_3$ has been reported (*46*).

Lustig (*47*) was the first to prepare compounds containing more than one *O*-fluorosulfate group attached to a single carbon. He prepared $F_2C(OSO_2F)_2$ and $F_2C(SO_3F)_3$ by the reaction of $S_2O_6F_2$ with CBr_2F_2 and CBr_3F. The first member, F_3COSO_3F, had been previously prepared by the reaction of CF_3I (*47*), CF_3Br, or CF_3Cl (*48*) with $S_2O_6F_2$. It had also been prepared in low yield by the reaction of SO_2 and CF_3OF (*49*).

When $SnCl_4$ was reacted with $S_2O_6F_2$ at temperatures below 100°, the product $SnCl(SO_3F)_3$ was reportedly formed (*40*). Excess $S_2O_6F_2$ at 120° yields (*50*) $Sn(SO_3F)_4$. The only other two known examples of neutral compounds where four fluorosulfates are coordinated, are the unstable $C(SO_3F)_4$ (*51*) and $Si(SO_3F)_4 \cdot 2MeCN$ (*52*). $Sn(SO_3F)_4$ reacts with an excess of $SnCl_4$ to give $SnCl_2(SO_3F)_2$, a true redistribution product. The investigators attempted to confirm the existence of $SnClSO_3F$ and concluded that it is a reaction intermediate between the two stable compounds $Sn(SO_3F)_4$ and $SnCl_2(SO_3F)_2$. On the basis of Mössbauer and vibrational spectroscopy, the authors suggested a polymer chain or sheet structure with bridging fluorosulfate groups. A similar polymer structure was suggested for $SnMe_2(SO_3F)_2$. They also found that solvolysis of the methyl chloride in fluorosulfuric acid was a more convenient route to $SnMe_2(SO_3F)_2$ than routes using $S_2O_6F_2$ (*53*). Attempts to prepare tin(IV) hexafluorosulfate salts by reaction of $S_2O_2F_6$ with K_2SnCl_6 were unsuccessful.

Lange (*54*) first prepared $NOSO_3F$ by the reaction of N_2O_3 and HSO_3F. Woolf (*11*) was able to prepare the substance in better purity from a solution of $(NO_2)_2S_2O_7$ in BrF_3. Roberts and Cady (*55*) in their early investigation of the nature of $S_2O_6F_2$ as SO_3F radical formerly prepared it via the methods described by the following reactions.

$$2NO + S_2O_6F_2 \rightarrow 2NOSO_3F$$
$$2NO_2 + S_2O_6F_2 \rightarrow NOSO_3F + NO_2SO_3F + \tfrac{1}{2}O_2$$

NO_2SO_3F has been obtained earlier by Goddard, Hughes, and Ingold (*56*), who prepared it by treating N_2O_5 with HSO_3F in nitromethane. Miller (*57*) showed that this compound does indeed have an ionic lattice containing NO_2^+ and SO_3F^- ions.

In their study (*55*), Roberts and Cady also showed that $S_2O_6F_2$ reacts with elemental mercury to give $Hg(SO_3F)_2$ in a manner similar to the attack of a halogen on mercury.

The chemistry of the halogen fluorosulfates is discussed in the section dealing with $S_2O_6F_2$ in order to emphasize the pseudohalogenlike behavior of $S_2O_6F_2$.

Bartlett *et al.* (*58*) have prepared two xenon derivatives, $FXeOSO_2F$ and $Xe(OSO_2F)_2$ by the reaction of XeF_2 and HSO_3F. The crystal structure of $FeXOSO_2F$ (*59*) has been determined by three-dimensional X-ray techniques. The fluorosulfate group is rather similar to that in alkali metal salts, the group being somewhat distorted as a result of an oxygen being bonded to the xenon. This oxygen has a longer bond to the sulfur than do the other oxygens.

Eisenberg and Des Marteau (*60*) have found, contrary to earlier reports (*59, 61*), that no Xe(IV) fluorosulfates are formed with XeF_4 that is reacted with HSO_3F. The only Xe(VI) fluorosulfate formed by the reaction of XeF_6 or HSO_3F is XeF_5OSO_5F, a solid which melts with decomposition at about 73°. This is the most stable of the three xenon fluorosulfates. These compounds give $S_2O_6F_2$ on decomposition.

A. HYDROLYSIS

Traube *et al.* (*10*) reported that the fluorosulfates are decomposed rapidly in strong mineral acid, but much more slowly in basic solutions.

$$SO_3F^- + H_2O \rightarrow HSO_4^- + HF$$
$$SO_3F^- + 2OH \rightarrow SO_4 + H_2O + F^-$$

Ryss and Gribanova (*62*) studied these reactions under uncontrolled conditions. Later Ryss and Drabkina (*63*) studied the second over a relatively narrow pH range. Jones and Lockhart (*64*) have more recently reported a kinetic study over a wide range of acid and base concentrations, i.e., from 4 *M* aqueous HCl to 5 *M* aqueous sodium hydroxide.

They found that for constant HCl or NaOH concentrations the decomposition rate was first order with respect to fluorosulfate ion concentration.

The experimental data were consistent with these processes over the entire range: (*a*) The attack of SO_3F^- by a proton, (*b*) the attack of SO_3F^- by an OH^-, and (*c*) the attack of SO_3F^- by a water molecule. The attack by water is a very slow process.

The empirical rate law found is

$$\frac{-d(SO_3F^-)}{d^+} = \{K[H^+] + K_{H_2O} + K_1[OH^-]\}[SO_3F^-]$$

Ryss and Drabkina (*65*) have also reported on the reaction of SO_3F^- with ammonia in aqueous solution. They report E_a and $\Delta S\pm$ for the reaction of SO_3F^- with NH_3 to be 14.68 kcal/mole and –30.43 eu, which are to be compared with 19.85 kcal/mole and 21.1 eu for the reaction with OH^-.

B. Spectra

The infrared spectra of substituted sulfuric acids, including $HSOF_3$, have been reported by Savoie and Giguere (*66*) and Chackalackal and Stafford (*67*). The latter were able to observe the spectra of the monomer by superheating the vapors within the gas cell.

Bernard *et al.* (*68*) prepared the magnesium, calcium, and barium salts and thermally decomposed the first two salts to MF_2 and SO_3, while the barium salt went to $BaSO_4$ and SO_2F_2 at higher temperatures. They pointed out that the thermal stability decreases with increasing electronegativity of the metal and S–F stretching frequency (v_2). The stretching frequency increases approximately linearly with increasing ionization energy of the metals. The symmetry of the FSO_3^- group was found to be C_{3v} for the Group I metal salts, C_s for Ca^{2+}, Mg^{2+}, and H^+ compounds, and intermediate for $BaSO_3F$. The degree of covalency is reflected in this. Ruoff *et al.* (*69*) investigated the infrared Raman spectra of the Group I metal fluorosulfates.

Aubke (*70*) interpreted his assignments of vibrational frequencies of infrared and laser Raman spectra of a number of fluorosulfate compounds and discussed the following structure and bond types: (*a*) the SO_3F ion ($NOSO_3F$, KSO_3); (*b*) the SO_3F ion in a lower symmetry site (NO_2SO_3F); (*c*) the weakly interacting ion SO_3F [$Pb(II)(SO_3F_2)$, $Sn(II)(SO_3F)_2$]; (*d*) the covalently bridging ion [$(CH_3)_2Sn(SO_3F)_2$]; (*e*) the monodentate OSO_2F group [$Br(OSO_2F)_4$], [$I(OSO_2F)_4$]; (*f*) the bridging covalent

O_2SOF group CO_2COSO_2F, $Cl_2Sn(OSO_2F)_2$; and (*g*) bridging and terminating covalent group $Sn(SO_3F)_4$, $[(SO_3F)_3$ and $Br(SO_3F)_3]$.

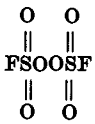
Hohorst and Shreeve (*71*) investigated the earlier statement of Lustig (*45*) that resonance of fluoride bonded to sulfur in the –50 ppm regions of NMR spectra is diagnostic of fluorine in fluorosulfate since the frequency in organic molecules seems to be relatively constant. The majority of shifts were in the –40 to –50 ppm region, but they ranged from –33.0 ($ClOSO_2F$) to –65.61 ppm ($HOSO_2F$). Although they were unable to relate the observed shifts to any single factor, the data were entirely consistent. The following observations were drawn: "(1) Introduction of CF_2 group(s) shifts resonances to lower field: $FOSO_2F > CF_3OSO_2F > C_2F_5OSO_2F$; $ClOSO_2F > ClCF_2OSO_2F$; $FO_2SOOSO_2F > FO_2SOCF_2OSO_2F > FO_2SOC_2F_4OSO_2F$; $NF_2OSO_2F > NF_2C_2F_4OSO_2F$. (2) Substitution of SO_3F for fluorine shifts to lower field: $FO_2SOSO_2F > FO_2SOSO_2OSO_2F$; $CF_2OSO_2F > FO_2SOCF_2OSO_2F$; $FOSO_2F > FO_2SOOSO_2F$. (3) Substitution of a halogen or pseudo-halogen for a fluorine may shift to lower field: $CF_3OSO_2F > ClCF_2OSO_2F$; $FOSO_2F > NF_2OSO_2F$; $FOSO_2F > BrOSO_2F$; or to higher field: $FOSO_2F < ClOSO_2F$. (4) Introduction of an oxygen atom varies: $FOSO_2F > FOOSO_2F$, while $CF_2OSO_2F < CF_2OOSO_2F$."

III. Pyrosulfuryl Fluoride and Peroxydisulfuryl Difluoride

Pyrosulfuryl fluoride, $S_2O_5F_2$, is the anhydride of fluorosulfuric acid and can indeed be made by removal of the elements of water, while peroxydisulfuryl, $S_2O_6F_2$, is a peroxide.

$$\mathrm{F}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{O}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{F}$$

Pyrosulfuryl fluoride



$$\mathrm{F}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{OO}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{F}$$

Peroxydisulfuryl difluoride

Pyrosulfuryl fluoride has been prepared by several methods, including the following: Sulfur trioxide has been heated under pressure with NaF (*72*) or CaF_2 (*73*); it has been treated at atmospheric pressure with SbF_5 (*74*), IF_5 (*75*), or VF_5 (*76*); halogen exchange on the corresponding chloride has been carried out by refluxing with benzoyl fluoride (*77*). Sulfur dioxide has been reacted with FSO_3F at 195° (*55*). Fluorosulfuric acid has been treated with As_2O_5 (*78*) or with ClCN (*79*).

Paul *et al.* (*80*) claimed, contrary to the report of Engelbrecht *et al.* (*78*), that it forms during the dehydration of HSO_3F with P_4O_{10}. The best method appears to be that described by Kongpricha *et al.* (*81*). They essentially modified the method of Appel and Eisenhauer (*82*) by reacting cyanuric chloride (instead of cyanogen chloride) with fluorosulfuric acid. Particular care must be taken to avoid forming the chlorofluoride (b.p. 100.5°). The product, whose toxicity is reported to be similar to that of phosgene, is a clear colorless liquid with a boiling point of 51°. Its vapor pressure (*74*) can be described by $\log_{10} p_{\text{mm}} = 8.015 - 1662/T$ from –28° to 43°. It decomposes rapidly to SO_3 and SO_2F_2 at 400°–5°°00. The decomposition is not significant below 200°. The presence of metal fluorides such as CsF or NaF considerably lowers the temperature of decomposition. It is not very soluble in cold concentrated sulfuric acid or fluorosulfuric acid. It is soluble in acetonitrile, ethyl ether, carbon tetrachloride, monofluorotrichloromethane, and benzene (*78*). Its hydrolysis to fluorosulfuric acid is rather slow (*74*).

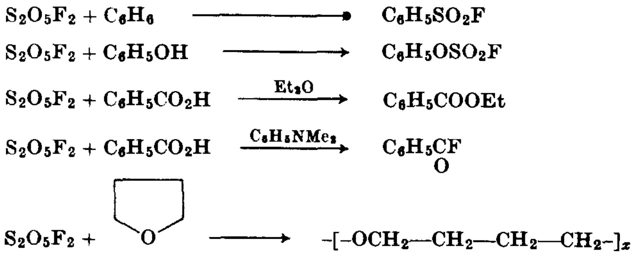
Appel and Eisenhauer (*82*) reported that the low-temperature action of ammonia on $S_2O_5F_2$ in a mole ratio of 2 : 1 in ether or acetonitrile led to no substitution of fluorine, but rather to aminolytic fission of the S–O–S bond. Kongpricha *et al.* (*81*) confirmed these results and found the following reactions with NH_3 and C_2H_5NH in the polar solvent, ether.

$$S_2O_5F_2 + 2NH_3 \rightarrow NH_2SO_2F + NH_4SO_3F$$
$$S_2O_5F_2 + 2C_2H_4NH \rightarrow C_2H_4NSO_2F + C_2H_4NH_2SO_3F$$

Apparently polar solvents are needed for this reaction to go in this way.

Ruff and Lustig (*83*, *84*) have also reported on studies of sulfur oxyfluoride chemistry involving $S_2O_5F_2$. Lustig (*85*) and Boudakian *et al.* (*86*) have reported on some organic aspects of the chemistry of $S_2O_5F_2$.

The following reactions describe some of its chemistry.



$$S_2O_5F_2 + C_6H_6 \longrightarrow C_6H_5SO_2F$$
$$S_2O_5F_2 + C_6H_5OH \longrightarrow C_6H_5OSO_2F$$
$$S_2O_5F_2 + C_6H_5CO_2H \xrightarrow{Et_2O} C_6H_5COOEt$$
$$S_2O_5F_2 + C_6H_5CO_2H \xrightarrow{C_6H_5NMe_2} C_6H_5\underset{O}{C}F$$
$$S_2O_5F_2 + \longrightarrow \text{-[-OCH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{-]}_x$$

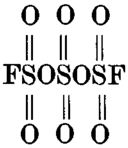
Peroxydisulfuryl difluoride (FSO_2OOSO_2F) may be considered to be a pseudohalogen in many of its reactions. Its discovery and the development of its chemistry is largely due to the efforts of G. H. Cady and those privileged to associate with him. This difluoride can be made by the action of fluorine on sulfur trioxide in the presence of silver-containing catalysts (*87–90*). This can be thermally or photochemically activated.

$$SO_3 + F_2 \rightarrow FSO_2OF$$
$$FSO_2OF + SO_3 \rightarrow FSO_2OOSO_2F$$

It can also be synthesized by the electrolysis of fluorosulfuric acid at about −20° (*91*). One can conveniently think of the formation of the compound via dimerization of the radical resulting from anodic oxidation of the acid.

$$HSO_3F \rightarrow \tfrac{1}{2}H_2 + 2OSO_2F$$

An additional preparative method involves the reacting of F_2 or FSO_3F with metal fluorosulfates (*92*). The compound is in equilibrium with the radical, the degree of dissociation increasing with increasing temperature (*93–95*). Dudley and Cady (*94*) studied the equilibrium $S_2O_6F_2 \rightleftharpoons 2SO_3F$, in nickel, and calculated equilibrium constants for this reaction from pressure-dependent measurements at temperatures between 450° and 600°K. This method gave an enthalpy change for the reaction of 22.0 kcal/mole. They also followed the absorption of the SO_3F radical at 474 nm as the function of temperature. The enthalpy change calculated from these measurements is 23.3 kcal/mole. Castellano *et al.* (*93*) followed the pressure dependence in quartz apparatus and determined $\Delta H = 21.8$ kcal/mole. Temperature dependence of the ESR signal gave $\Delta H = 22.4$ kcal/mole. The values determined from pressure dependence are probably the most reliable.

Shortly after its discovery, Roberts and Cady (*96*) showed that fluorine and $S_2O_6F_2$ diluted with nitrogen reacted at 290° to give FSO_3F. At 200° diluted $S_2O_6F_2$ and SO_2 reacted to give $S_3O_8F_2$. Earlier this compound had been prepared (*96*) by reacting liquid SO_3 with BF_3 and treating the solution with 70% sulfuric acid, and by reacting SO_3 on alkaline earth fluorides (*73*). The structure  $F\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}O\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}O\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}F$ is consistent with the NMR spectrum. The analogous bistetrafluorosulfur bisfluorosulfate $FSO_2OSF_4OSO_2F$ results from reaction of $S_2O_6F_2$ with SF_4 (*97*). Most of the reactions of $S_2O_6F_2$ are those to be expected of the radical. It can, however, oxygenate under some conditions. An interesting series of pseudointerhalogens, the halogen fluorosulfates, can be made by reacting $S_2O_2F_6$ with the halogens.

The successful preparation of fluorine fluorosulfate (FSO_3F) by Roberts and Cady (*96*) from peroxydisulfuryl difluoride and fluorine suggested the stability of other halogen fluorosulfates. Roberts and Cady (*96*) investigated this suggestion and reported the existence of $BrSO_3F$, $Br(SO_3F)_3$, and $I(SO_3F)_3$. Iodine trifluorosulfate has also been made by the oxidation of I_2 by $S_2O_6F_2$ in fluorosulfuric acid. In a later paper, Gilbreath and Cady (*97*) reported the preparation of $ClSO_3F$ by heating excess Cl_2 with $S_2O_6F_2$ under pressure for an extended time. More recently, Fox *et al.* (98) have reported a more convenient preparation involving the reaction of ClF with SO_3.

$$ClF + SO_3 \rightarrow ClSO_3F$$

Schack and Pilipovich (*99*) have found that $ClSO_3F$ is a useful reagent in that they were able to prepare the pure perchlorate $ClOClO_3$ by its metathetical reaction with $CSClO_4$ or NO_3ClO_4 at –43°. In the course of investigation of the chemistry of fluorine fluorosulfate, Cady and his co-workers showed that fluorine fluorosulfate reacts with iodine at room temperature to give the interesting iodine trifluoride bisfluorosulfate ($IF_3SO_3F_2$) (*100*). They also found that it was rather reactive toward water and aqueous solutions of base and aqueous iodide (*87*). It

$$FSO_3F + 2OH \rightarrow SO_3F^- + F^- + H_2O + \tfrac{1}{2}O_2$$
$$FSO_3F + 2I^- \rightarrow SO_3F^- + F^- + I_2$$

reacts with SO_2 to give $S_2O_5F_2$ and with SOF_2 to give SOF_4 and $S_2O_6F_2$ (*100*). They found no reaction with chlorine up to 100°.

Aubke and Cady (*101*) further investigated the iodine fluorosulfates, producing ISO_3F and I_3SO_3F by reaction of I_2 with $S_2O_6F_2$. Spectra of solutions of these compounds in fluorosulfuric acid were characteristic of I^+ and I^{3+}. When chlorine was reacted with ISO_3F, ICl_2SO_3F was produced. Gillespie and Milne (*102*, *103*) investigated the reaction of I_2 and $S_2O_5F_2$ in HSO_3F solutions using Raman, cryoscopic, and conductivity techniques. The trifluorosulfate is the highest fluorosulfate found. They found only a single Raman peak for $I(SO_3F)_3$ dissolved in $S_2O_6F_2$ down to –55.4° (freezing point of $S_2O_6F_2$). A rapid exchange of fluorosulfate groups is therefore likely. There seems to be rapid exchange between $I(SO_3F)_3$ in HSO_3F even at low temperatures. Cryoscopic and conductivity measurements in HSO_3F both indicate the number of ions to be expected by the stoichiometry ($S_2O_6F_2$ is a nonelectrolyte in HSO_3F).

$$I_2 + 3S_2O_6F_2 \rightarrow 2I(SO_3F)_3$$

The trifluorosulfate shows amphoteric behavior in the solvent. It hydrolyzes with water in the solvent as follows:

$$I(SO_3F)_3 + H_2O \rightarrow IO(SO_3F) + (HSO_3F)$$

Chung and Cady (*104*) have very recently reported the I_2–$S_2O_6F_2$ system. The melting points observed in this system showed the existence of the previously found $I(SO_3F)_3$, ISO_3F, and I_3SO_3F and previously unknown I_8SO_3F; there was no evidence for I_2SO_3F (I_2^+ has been observed in oleum). They investigated the magnetism in the mole fraction $S_2O_6F_2$ in the 0.133 to 0.664 region and found only diamagnetic behavior. The I_2^+ ion shows paramagnetism. Bromine(I) fluorosulfate has been found to be a quite useful reagent for the preparation of compounds containing the fluorosulfate group. Des Marteau (*105*) prepared and characterized the following compounds, $[C(O)SO_3F]_2$, $C(O)Sl(O)SO_3F$, $CFCl_2SO_3F$, $CFCl(SO_3F)$, $CCl(SO_3F)_3$, $C(SO_3F)_4$, $SO(OSO_2F)_2$, $POSO_3FCl_2$, and $SiCl_2(SO_3F)_2$, according to the equation:

$$MCl_x + yBrSO_3F \rightarrow MCl_{x-y}(SO_3F)_y + yBrCl$$

Woolf and Brazier (*106*) have reported that both gold and platinum are inert to boiling fluorosulfuric acid, while Cady and his associates (*107*) have found that gold, as well as tin and zinc, did not react extensively with $S_2O_6F_2$. Rhenium does react (*20*). They did, however, find reactions of $BrSO_3F$ with both gold (at 63°, slowly even at room temperature) and platinum (95°). The product of the room temperature reaction with gold is a crystalline, $Au(SO_3F)_3 \cdot 2BrSO_3F$, which decomposes when heated under reduced pressure to give the bright orange-yellow $Au(SO_3F)_3$ (m.p. ~ 94°). Platinum forms $Pt(SO_3F)_4$ (m.p. 182°) as well as two adducts, $Pt(SO_3F)_4 \cdot 4BrSO_3F$ and $Pt(SO_3F$ and $Pt(SO_3F)_4 \cdot 2BrSO_3F$.

IO_2SO_7F and oxygen result from the reaction of I_2O_5 with an excess of $S_2O_2F_6$ (*108*). KCl reacts with the compound to give Cl_2 and KSO_3F, while KBr and KF give $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$. Chung and Cady (*109*) have reported the compound $Cs[Br(SO_3F)_2]$ containing the $[Br(SO_3F)_2]^-$ ion. This reacts with $S_2O_6F_2$ to give $Cs[Br(SO_3F)_4]$. It will slowly react with a pseudohalogen N_2F_4 to give the accepted product NF_2SO_3F (*110*).

Although the organic chemistry of this compound is outside of the sphere of this chapter it is likely to become important. For example, it will add to double bonds—$C_2F_4(SO_3F)_2$ and polymer is produced from C_2F_4. It reacts with fluorinated anhydrides as follows:

$$R_f(CO)_2O + S_2O_6F_2 \rightarrow R_fOSO_2F + R_fOOSO_2F + CO_2$$

The addition of halogen fluorosulfates to double bonds in perfluorocyclic alkenes is developing further the chemistry of the compound.

Schumacher and his associates have concerned themselves with the radical chemistry of fluorine compounds. They (*111*) reported the photochemical synthesis of FSO_2OOF from OF_2 and SO_3. They proposed (*112*) a mechanism for the reaction which involves the photochemical dissociation of OF_2 to give a fluorine atom which, in turn, attacks the SO_3 to give the FSO_3 radical. The addition of an OF radical gives the end product.

They followed this work with a report of a kinetic study of the photochemical reaction of F_2 and SO_3 to form $F_2S_2O_6$ and concluded that its formation came about through the association of two FSO_3 radicals. This, of course, is consistent with earlier speculation and with the dissociation to the radical concepts (*113*).

Schumacher and associates (*114*) further investigated the thermal reaction of SO_2 with $F_2S_2O_6$ and found that the reaction was first order with respect to both SO_2 and $F_2S_2O_6$ and concluded that the mechanism involved a bimolecular collision between the two. They (*115*) also investigated the chemistry of the thermal reaction between F_2 and $F_2S_2O_6$ and found the sole primary product to be F_2SO_3 (extensive heating did give some O_2 and F_2SO_2). The rate of formation of $F_2S_2O_6$ was proportional to the concentration of FSO_3 radicals and fluorine. The mechanism proposed was

$$FSO_3\cdot + F_2 \rightarrow F_2SO_3 + F\cdot$$
$$F\cdot + FSO_3\cdot \rightarrow F_2SO_3$$

The first step is rate-determining.

Franz and Neumayr (*116*) irradiated mixtures of OF_2 with SO_3, SO_2, or $S_2O_6F_2$ and found support for radical intermediates. Neumayr and Vanderkooi (*117*) studied the radical decompositions of FSO_2OOF, FSO_2OOSO_2F, FSO_2OF, and OF_2 using NMR, IR, and EPR methods. Decomposition was induced by ultraviolet irradiation and addition of N_2O_4.

Nutkowitz and Vincour (*118*) have studied the temperature dependence of the line width of the EPR signal of SO_3F dissolved in solution. This was studied in the neat dimer, $S_2O_6F_2$, and in solutions of $S_2O_6F_2$ in perfluorodimethylcyclohexane. The line width was a nonlinear function of temperature and independent of concentration. They proposed that the most likely mechanism for line broadening is spin relaxation due to motional modulation of the spin rotational interaction. Stewart (*119*) had earlier reported that the line width of SO_3F in a mixture of $S_2O_6F_2$ and $S_2O_5F_2$ is independent of temperature. Nutkowitz and Vincour suggested that the explanation for the dissimilarity between the two sets of observations was partial decomposition of Stewart's sample. They reported similar results when they observed bubbling (of O_2).

The spectrum of $S_2O_6F_2$ has been investigated and interpreted by Dudley and Cady (*94*), Castellano *et al.* (*93*), and King *et al.* (*120*). The ^{19}F NMR spectra consist of a single line in the region where SO_3F groups are found (*88*).

The chemistry of sulfur–oxygen–fluorine combining compounds is extensive and rapidly developing. Fluorosulfate chemistry presents challenges to many areas of chemistry.

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