

## Chapter 9

# RECENT ADVANCES IN MAIN GROUP FLUORIDE CHEMISTRY

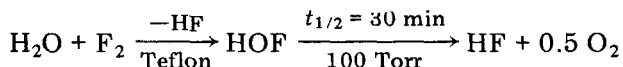
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### Introduction

The simple fluorides of several of the nonmetals were among the compounds which Moissan prepared for the first time in the years following his isolation of fluorine, although calcium fluoride, of course, had long been known [1]. Thus, one may recall the first synthesis of carbon tetrafluoride and of sulfur hexafluoride by the reaction of fluorine with the elements. It is virtually certain that he made the first known compounds with N—F bonds in his experiments on the fluorination of cyanides, although he was unable to characterize them at the time. It is appropriate, therefore, in commemorating the discovery of the element, to recall some of the recent advances in the field of nonmetal fluorine chemistry which he pioneered. It is only possible to mention just a very few highlights of this field, but it is hoped to sensitize the reader not only to the beauty of fluorine chemistry but also to the untrapped opportunities in this field.

Although hydrofluoric acid was first recognized by Scheele in 1771, it was Davy and Ampère in 1813 who concluded that hydrofluoric acid was a compound of hydrogen and a new element, fluorine. Nearly 160 years later in 1971, the next most simple fluorine-containing acid, hypofluorous acid (HOF), was observed in a time-of-flight mass spectrometer after a drop of water in a poly(chlorofluoroethylene) polymer tube was exposed to ~100 Torr of fluorine gas [2].

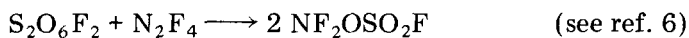
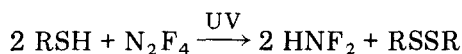


Hypofluorous acid has the distinction of having the smallest known oxygen bond angle (97°), which results from the electrostatic attraction between the ends of the molecule  $\text{H}^{\delta+}\text{OF}^{\delta-}$ . Although its chemistry has not been studied exhaustively, HOF has been shown to act only as an oxygenating or as a hydroxylating agent, *i.e.* as a donor of atomic oxygen or of its conjugate acid,  $\text{OH}^+$ .

### Nitrogen fluorides

After a quarter of a century of experimentation, Ruff was able to make nitrogen trifluoride by the electrolysis of molten anhydrous ammonium

hydrogen fluoride in a copper cell [3]. The two binary fluorides of nitrogen which have generated the most interest are tetrafluorohydrazine,  $N_2F_4$ , and the tetrafluoroammonium cation,  $NF_4^+$ . Colburn *et al.* [4] synthesized  $N_2F_4$  by the thermolysis of  $NF_3$  in a copper-packed flow reactor at 375 °C. The nitrogen–nitrogen bond energy is only about 84 kJ mol<sup>-1</sup> and as a result, even at room temperature, the molecule is in dynamic equilibrium with its radical monomer. Thus, many of its reactions are free radical which are enhanced by UV irradiation to increase the  $\cdot NF_2$  concentration.  $NF_2\cdot$  exhibits pseudohalogen behavior, *i.e.* it abstracts hydrogen and halogen atoms, and it combines with other radicals, *e.g.*,



While it reacts with aldehydes to form  $\text{RC}(\text{O})\text{NF}_2$ , because of the instability of the  $\text{R}_f\text{C}(\text{O})\cdot$ ,  $\text{R}_f\text{C}(\text{O})\text{NF}_2$  must be prepared via an ionic pathway utilizing the sometimes explosive  $\text{HNF}_2$  with  $\text{R}_f\text{C}(\text{O})\text{F}$ . Tetrafluorohydrazine behaves as a fluoride-ion donor with  $\text{SbF}_5$  to form  $\text{N}_2\text{F}_3^+\text{SbF}_6^-$  in HF solution. This salt is useful in metathesis reactions. Unfortunately this is not true for Lewis acid compounds of  $\text{N}_2\text{F}_2$ . The latter is easily formed by photolysis of a mixture of  $\text{N}_2\text{F}_4$  and  $\text{Br}_2$ , and readily reacts with  $\text{SbF}_5$  to give  $\text{N}_2\text{F}^+\text{SbF}_6^-$ . However, the cation is decomposed under all metathetical conditions tried to date. Tetrafluorohydrazine may also be used to introduce  $\text{NF}_2$  and  $\text{NF}$  groups into olefins, *e.g.*  $\text{N}_2\text{F}_4 + \text{CF}_2=\text{CHF} \xrightarrow{\Delta} \text{NF}_2\text{CF}_2\text{CF}=\text{NF}$  or with  $\text{CF}_2=\text{CH}_2 \rightarrow \text{NF}_2\text{CF}_2\text{C}\equiv\text{N}$ .

Advantage is taken of the reaction of a lower fluoride,  $\text{NF}_3$ , with fluorine and a Lewis acid in the presence of UV photolysis to form  $\text{NF}_4^+\text{MF}_6^-$ . A direct route to  $\text{NF}_4^+$  is not possible since the parent species,  $\text{NF}_5$ , is not known. Christe and Schack and their coworkers have synthesized a large number of  $\text{NF}_4^+\text{MF}_x^-$  salts, including  $\text{NF}_4\text{XeF}_7$  and  $(\text{NF}_4)_2\text{XeF}_8$  [7], to be used as the major ingredients in solid-propellant  $\text{NF}_3/\text{F}_2$  gas generator compositions for chemical lasers. These xenon derivatives were obtained by first reacting  $\text{NF}_4\text{SbF}_6$  with  $\text{CsHF}_2$  to give  $\text{NF}_4\text{HF}_2$ , which when subsequently reacted in anhydrous hydrogen fluoride with an excess of  $\text{XeF}_6$  formed  $\text{NF}_4\text{XeF}_7$ .

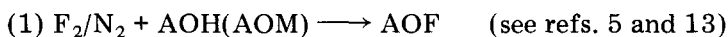
Trifluoramine oxide,  $\text{F}_3\text{N}\rightarrow\text{O}$ , is a surprisingly stable species which can be made by reacting  $\text{NF}_3$  and  $\text{O}_2$  in an electric discharge. It forms salts with Lewis acids of which  $\text{NF}_2\text{O}^+\text{SbF}_6^-$  is stable above 25 °C. The easily formed  $\text{NF}_2\text{O}^+\text{AsF}_6^-$  is effective in introducing the  $\text{NF}_2\text{O}^+$  moiety into fluorocarbon olefins. In addition, the reaction of  $\text{F}_3\text{NO}$  with  $\text{NO}$  in a 1:2 stoichiometry provides a quantitative yield of  $\text{ONF}$ . The latter can be easily generated and reacted *in situ* in Pyrex glass by contacting  $\text{KF}$  with  $\text{ONCl}$  or  $\text{KF}$  with  $\text{NO}_2$ , both in the presence of acetonitrile. Nitrosyl fluoride adds easily to olefinic

double bonds to prepare blue nitroso compounds in high yield. Moissan was the first to observe  $O_2NF$  [8]. It can be synthesized by the direct fluorination of  $NO_2$ . In a similar manner to  $ONF$ , it behaves as a fluoride-ion donor with fluoride-ion acceptors which include a large number of metal fluorides. Interestingly, neither  $ONF$  nor  $O_2NF$  is able to convert  $BrF_5$  to  $[BrF_6]^-$  [9].

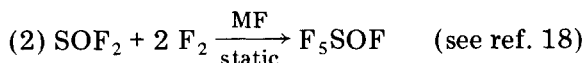
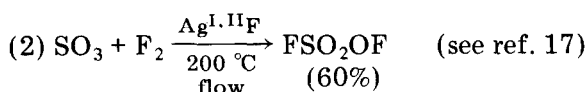
### Fluoroxo compounds and hypofluorites/hypochlorites

Much earlier, Lebeau and Damiens [10] had demonstrated that fluorine produces oxygen difluoride ( $OF_2$ ) from either neutral, acidic or basic aqueous media, although the latter is preferred. This molecule, the first  $OF$ -containing compound was soon followed by nitryl hypofluorite (fluorine nitrate,  $O_2NOF$ ) [11] which was to be the first of many such compounds to be prepared by Professor George H. Cady and his coworkers. This compound was very likely the gas that Moissan observed much earlier when he reported explosions resulting from the passage of bubbles of fluorine through concentrated nitric acid [12].

Until the 1960s the syntheses and characterization of new  $-OF$ -containing molecules were carried out exclusively, with the exception of the higher oxygen fluorides, in Cady's laboratories at the University of Washington. The usual procedure was either (1) the fluorination of aqueous acids or their anhydrous salts or (2) the catalytic fluorination of nonmetal oxides or nonmetal oxide fluorides, *viz.*



where  $A = NO_2$  [11],  $ClO_3$  [14] and  $F_5SeO$  [15];  $M =$  alkali metal and  $Hg$  [16].

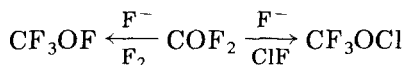


where  $M =$  alkali metal.

The last of these reactions was a clever extension by Lustig and Ruff [19] of their synthetic route to fluoroxo compounds, which entailed the addition of fluorine across the carbon-oxygen double bond in perfluoro-carbonyl compounds through an alkali-metal alkoxide intermediate. The perfluoroalkoxides, e.g.  $CF_3O^-$ ,  $C_2F_5O^-$ ,  $n-C_3F_7O^-$ ,  $i-C_3F_7O^-$ ,  $n-C_4F_9O^-$ , were demonstrated to be stable entities by Redwood and Willis [20].

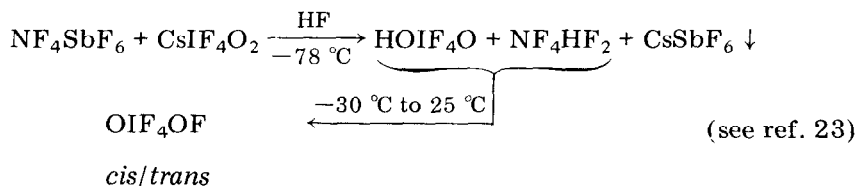
Prager and Thompson at the 3M Company had fluorinated salts of perfluorinated acids, hexafluoroacetone hydrate, polyacrylate and other compounds in a flow system to obtain very low yields of materials with one or more fluoroxo groups [5]. For example, direct fluorination of

sodium trifluoroacetate or sodium oxalate was first used to synthesize the stable  $\text{FOCF}_2\text{OF}$  (2 - 15%), whereas fluorination of  $\text{CO}_2$  at  $0^\circ\text{C}$  in the presence of  $\text{CsF}$  gave bis(fluoroxy)methane in quantitative yields [5, 21]. Thus, it was the pioneering application of alkali-metal catalysis by Ruff and Lustig which in reality opened the doors to a treasure trove of fluoroxy compounds and hypofluorites. In addition, this led to the entire field of hypochlorite chemistry when Fox and coworkers replaced fluorine with chlorine fluoride as the oxidizing reagent under analogous conditions [13]. For example,

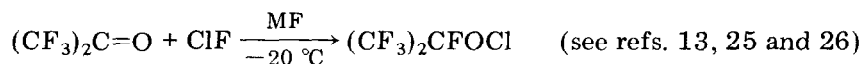


Although each research school appears to have its own technique for preparing the alkali-metal fluorides for their catalytic roles, the three commonly employed methods are thermal dehydration accompanied by mechanical powdering, heating under vacuum, and the formation of a salt which is subsequently decomposed, e.g. by the reaction with hexafluoroacetone in acetonitrile. Winfield *et al.* [22] employed  $^{85}\text{Kr}$  to study the surface areas of  $\text{RbF}$ ,  $\text{CsF}$  and  $\text{TlF}$  after each of the three pretreatment methods, and found that the surface areas of both  $\text{TlF}$  and  $\text{CsF}$  are increased markedly. The surface of  $\text{CsF}$  is enhanced particularly by the hexafluoroacetone treatment. Since  $\text{TlF}$  shows very little or no catalytic activity in spite of its improved surface area, surface area cannot be the sole factor involved.

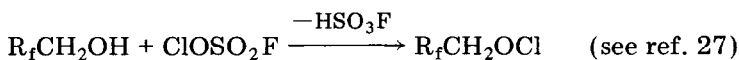
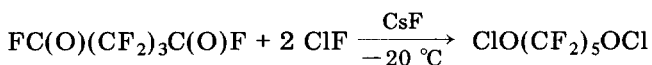
Other variations on routes to hypofluorites/hypochlorites are known, including the use of  $\text{FNO}$  as an effective catalyst or of other fluorinating or chlorinating reagents, for example,



The preparative chemistry of hypochlorites is essentially identical with that used for the analogous fluoroxy compounds and hypofluorites, except that chlorine monofluoride or another positive chlorine-containing species is used in lieu of elemental fluorine, for example,



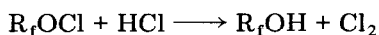
where  $\text{MF} = \text{CsF}$  or  $\text{AsF}_5$ .



where  $\text{R}_f = \text{H(CF}_2)_2, \text{H(CF}_2)_4, \text{H(CF}_2)_6, \text{or O}_2\text{NCF}_2$ .

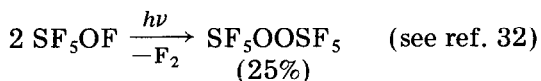
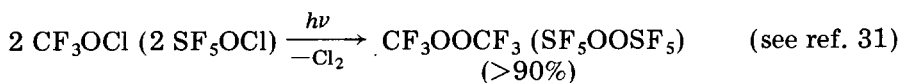
For the preparative chemist, when a good source of  $\text{R}_f\text{O}$  is required, fluorinated hypochlorites are often the reagents of choice compared to fluoroxy compounds or hypofluorites, because of higher product yields with concomitantly fewer side-products under milder conditions and with shorter reaction times. However, hypochlorites tend to be less stable both thermally and hydrolytically. Fluoroxy compounds have received much attention as fluorinating agents [13].

Advantage was taken of either the hydrolytic instability of  $\text{SF}_5\text{OCl}$  or the positive character of the chlorine in  $\text{CF}_3\text{OCl}$  and  $\text{SF}_5\text{OCl}$  to prepare the first perfluorinated alcohol,  $\text{CF}_3\text{OH}$ , or pentafluoroorthosulfuric acid,  $\text{HOSF}_5$ ,



where  $\text{R}_f = \text{CF}_3$  [28] or  $\text{SF}_5$  [29] at reaction temperatures of  $-120^\circ\text{C}$  or  $-95^\circ\text{C}$ , respectively. Fluoroxy compounds react very slowly with water or acid solution [30]. Hypochlorites/hypofluorites undergo oxidative displacement and oxidative addition reactions as well as addition to unsaturated systems.

Photolysis of either  $-\text{OF}$  or  $-\text{OCl}$ -containing compounds can provide a useful route to peroxides with typical differences in the size of the yields obtained.



This method provides a powerful route to fluorinated peroxides which is particularly useful in situations where elemental fluorine is not readily available.

### Fluorinated peroxides

Fluorinated peroxides may be regarded as derivatives of hydrogen peroxide with one or more, usually both, of the hydrogen atoms replaced by fluorine or a fluorine-rich group. The simplest of these compounds is dioxygen difluoride,  $\text{O}_2\text{F}_2$ , which was first prepared in 1933 by Ruff and

Menzel [33] by passing an electrical discharge through a gaseous mixture of fluorine and oxygen held at liquid air temperature. Subsequently, the existence of a series of other polyoxygen fluorides of the type  $O_nF_2$  ( $n = 3 - 6$ ) was proposed, using a similar technique, though only  $O_4F_2$  has been fully characterized. The chemistry of  $O_2F_2$  is not that of a peroxide, *i.e.* of the  $\cdot OF$  radical, but rather of  $F\cdot$  and  $\cdot OOF$  radicals since the O—O bond dissociation energy is approximately six times that of the O—F bond energy ( $414 v. 72 \text{ kJ mol}^{-1}$ ) [34]. In  $CF_3Cl$  at  $-183^\circ C$ , dioxygen difluoride was reacted with  $SO_2$  to give the fluoroperoxide  $FSO_2OOF$  via an  $\cdot OOF$  intermediate.

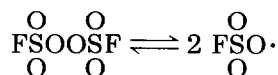
Synthesis of fluorinated peroxides has prospered and large numbers of these interesting and highly reactive compounds are described in the literature. To a considerable degree the pioneering work was carried out by Cady and his students, but researchers such as DesMarteau, Fox, Pass, Prager, Roberts, Talbott and Thompson have made important contributions to the field [6, 35]. Examples of such compounds are shown in Table 9.1. It appears that highly electronegative groups are able to stabilize the peroxy group. The simple fluoroalkyl peroxides,  $R_fOOR_f$ , are analogous in type to the well-known alkyl peroxides, but differ greatly both in their methods of preparation and in their properties. It will be seen from Table 9.1 that polyoxides, e.g.  $R_fOOOR_f$ , are also known and are, in fact, quite stable. No alkyl analogues exist.

TABLE 9.1

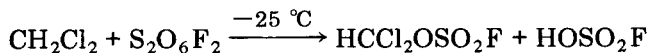
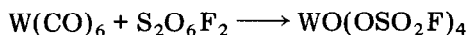
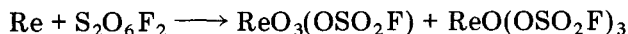
Some fluorinated peroxides

$FSO_2OOSO_2F$	$R_fOOX$ ( $R_f = \text{fluoroalkyl}; X = R_f, H, Cl, F$ )
$SF_5OOC(O)F$	$TeF_5OOTeF_5$
$SF_5OOSF_5$	$R_fC(O)OOC(O)R_f$
$SF_5OOH$	$FC(OF)OOC(OF)F$
$SeF_5OOSeF_5$	$R_fOOOR_f$
$SF_5OSF_4OOSF_4OSF_5$	$CF_3OOCF_2OOOCF_3$
$F_2P(O)OOCF_3$	$NO_2OOCF_3$

Bis(fluorosulfonyl)peroxide (peroxydisulfonyl difluoride),  $S_2O_6F_2$ , is probably the World's most studied peroxide! While its large-scale synthesis involves the  $Ag^I, II F$ -catalyzed fluorination of sulfur trioxide in a flow reactor at  $160^\circ C$ , a very useful smaller-scale route is the photolysis of  $CISO_2F$  which can be prepared quantitatively from  $ClF$  with  $SO_3$  [6]. It is a colorless liquid (b.p.,  $67.1^\circ C$ ) and its vapor, when heated to about  $100^\circ C$ , turns brown because of the reversible cleavage of the O—O bond ( $D_{O-O} < 100 \text{ kJ mol}^{-1}$ ) to form the fluorosulfate radical, paralleling the well-known  $N_2O_4$  or  $N_2F_4$  equilibrium.



Because of this ready dissociation, the chemistry of this peroxide is entirely that of the fluorosulfate radical. In its reaction modes, which include oxidation, oxygenation and/or fluorosulfation as well as hydrogen abstraction, its behavior is that of a pseudohalogen. Although a few elements, e.g. N<sub>2</sub>, Ar, Xe, and compounds are inert toward this remarkably reactive compound, a very large number of both elements and compounds can be caused to react in an orderly fashion by varying the reaction conditions, for example,



By using S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> in fluorosulfuric acid as a solvent, many nonmetals are oxidized to highly colored, polyatomic cations [36] (see Table 9.2).

TABLE 9.2

Homopolyatomic cations of Groups VI and VII

S <sub>16</sub> <sup>2+</sup> (red)			Br <sub>5</sub> <sup>+</sup> (brown)	I <sub>5</sub> <sup>+</sup> (dark brown)
S <sub>8</sub> <sup>2+</sup> (blue)	Se <sub>8</sub> <sup>2+</sup> (green)	Te <sub>4</sub> <sup>2+</sup> (red)	Br <sub>3</sub> <sup>+</sup> (brown)	I <sub>3</sub> <sup>+</sup> (red-brown)
S <sub>4</sub> <sup>2+</sup> (yellow)	Se <sub>4</sub> <sup>2+</sup> (yellow)	Te <sub>n</sub> <sup>n+</sup> (yellow)	Br <sub>2</sub> <sup>+</sup> (red)	I <sub>2</sub> <sup>+</sup> (blue)

This represents the very tip of the iceberg with respect to the chemistry associated with these novel compounds. There is still much to be done.

## Sulfur fluorides

The fluorine chemistry of sulfur and its congeners is particularly rich and, although the area has been well studied, it continues to be exciting and eventful [37]. Sulfur hexafluoride was first produced by Moissan [38] in 1891, and prepared and studied by Moissan and Lebeau [39] in 1900 by burning sulfur in fluorine. This original method continues to be used industrially. The remarkable kinetic stability of SF<sub>6</sub> is in sharp contrast with the stability of the lower sulfur fluorides, as well as with the reactivity of SeF<sub>6</sub> and TeF<sub>6</sub>. In a similar vein, SO<sub>2</sub>F<sub>2</sub> is much more inert chemically than is SeO<sub>2</sub>F<sub>2</sub>, and TeO<sub>2</sub>F<sub>2</sub> apparently does not exist. The lower fluorides of selenium have been identified only in matrix isolation, and the analogous tellurium compounds have not been reported.

Due largely to the work of Seel and his coworkers [40], suitable routes to, and the characterization of, the lower sulfur fluorides have been carried out. Disulfur difluoride, S<sub>2</sub>F<sub>2</sub>, exists in two isomeric forms — either as

a disulfane, *i.e.* with an  $\text{H}_2\text{O}_2$ -type structure, or as thio-thionyl, *i.e.* as an analogue of  $\text{OSF}_2$ , which is the more stable isomer (stable to  $250^\circ\text{C}$  in metal when pure). At  $-100^\circ\text{C}$ ,  $\text{SSF}_2$  behaves as a Lewis base. While  $\text{SF}_2$  is only stable as a highly dilute gas,  $\text{S}_2\text{F}_4$  ( $\text{SF}_3\text{SF}$ ) exists as a solid or liquid or in solution up to  $-75^\circ\text{C}$ . Higher difluoropolysulfanes,  $\text{FS}_x\text{F}$  ( $x = 3, 4$ ) have been identified using  $^{19}\text{F}$  NMR spectroscopy at  $-50^\circ\text{C}$ . The stabilizing effect of a trifluoromethyl group(s) replacing a fluorine atom(s) is interesting and typical, e.g. in order of increasing stability,  $\text{FSF} < \text{CF}_3\text{SF} \ll \text{CF}_3\text{SCF}_3$  or  $\text{FSSF} < \text{CF}_3\text{SSF} \ll \text{CF}_3\text{SSCF}_3$ . This increase in stability is not limited to these materials but is also nicely demonstrated by the relative hydrolytic stabilities in the series  $\text{SF}_4 < \text{CF}_3\text{SF}_3 \ll (\text{CF}_3)_2\text{SF}_2$ .

The sulfenyl fluorides,  $\text{R}_f\text{SF}$ , are rather novel compounds because of the large upfield chemical shifts in  $^{19}\text{F}$  NMR spectra, e.g. whereas usual S-F chemical shifts occur between *ca.*  $-11$  [ $(\text{CF}_3)_2\text{SF}_2$ ] to  $+145.2$  ppm ( $\text{SF}_5\text{Br}$ ) downfield relative to  $\text{CCl}_3\text{F}$ , compounds with the -SF group show  $^{19}\text{F}$  NMR resonances at  $-361$  [ $(\text{CF}_3)_2\text{CFSF}$ ],  $-200$  (FSSSF) and  $-163$  [ $(\text{CH}_3)_2\text{NSF}$ ] ppm, respectively. These extreme upfield shifts are very useful in facilitating identification of the compounds.

Sulfur tetrafluoride is a remarkably stable molecule in that it can be easily synthesized from  $\text{NaF}$  and  $\text{SCl}_2$ , and stored indefinitely in a metal vessel at  $25^\circ\text{C}$ , while  $\text{SH}_4$  is nonexistent and  $\text{SCL}_4$  decomposes at its melting point,  $-30^\circ\text{C}$ . Its major role has been as a fluorinating reagent for organics usually at high temperatures [37], but its monodialkylamino derivatives ( $\text{R}_2\text{NSF}_3$ ) react at least as effectively under milder conditions. Sulfur tetrafluoride has amphoteric properties reacting either with Lewis acids or bases to give cations or anions:



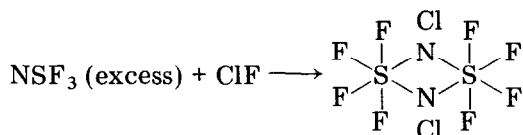
Trifluorosulfuranes behave only as fluoride-ion donors with Lewis acids to form  $\text{R}_f\text{SF}_2^+$ . Difluorosulfuranes,  $(\text{R}_f)_2\text{SF}_2$ , do not react with either Lewis acids or bases. In sharp contrast, replacement of  $\text{R}_f$  by  $\text{R}_2\text{N}$  to give  $(\text{R}_2\text{N})_2\text{SF}_2$  not only has a marked effect on the chemical reactivity but also on the bond angles at sulfur, *i.e.* although the overall geometry is still trigonal bipyramidal, the  $\angle \text{F}_a\text{SF}_a$  has changed from  $173.9^\circ$  bent away from the lone pair to  $174.7^\circ$  bent toward the electron pair. Cowley *et al.* [41] demonstrated that the bis(dialkylamino)difluorosulfuranes can be reacted with either one or two equivalents of a Lewis acid in sulfur dioxide to form either  $[(\text{R}_2\text{N})_2\text{SF}]^+[\text{MF}_6]^-$  or  $[(\text{R}_2\text{N})_2\text{S}]^{2+}[\text{MF}_6]_2^-$ .

Of the sulfur(VI) fluorides,  $\text{SF}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{CF}_3\text{SF}_4\text{Cl}$  have the richest chemistry. Addition to olefins and electrochemical fluorination are two routes to a large family of  $\text{SF}_5^-$  or  $\text{CF}_3\text{SF}_4^-$ -substituted alkanes. The reactive nucleophile  $(\text{CF}_3)_2\text{C}=\text{N}^-$  interacts with  $\text{SF}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) or  $\text{CF}_3\text{SF}_4\text{Cl}$  to form  $\text{SF}_3\text{X}=\text{NCF}(\text{CF}_3)_2$  or  $\text{CF}_3\text{SF}_2\text{Cl}(\text{NCF}(\text{CF}_3)_2)$ , respectively [37]. Lithiation of  $\text{SF}_5\text{CH}_2\text{Br}$  at  $-110^\circ\text{C}$  followed by loss of  $\text{LiF}$  at  $-70^\circ\text{C}$  gives rise to the very stable  $\text{H}_2\text{C}=\text{SF}_4$  which can be reacted further



with polar reagents, such as HCl or ICl, to form hydrolytically stable products [42]. A multistep synthesis beginning with the photolysis of  $\text{ROC}\equiv\text{CH}$  with  $\text{SF}_5\text{Cl}$  leads to the remarkable colorless gas,  $\text{F}_3\text{CC}\equiv\text{SF}_3$ , which oligomerizes rapidly at its boiling point ( $-15^\circ\text{C}$  to  $-10^\circ\text{C}$ ) [43]. Photolysis of elemental fluorine with  $\text{R}_f\text{N}=\text{SF}_2$  gives  $\text{R}_f\text{N}=\text{SF}_4$  with no concomitant addition of fluorine to the polar  $\text{N}=\text{S}$  bond.

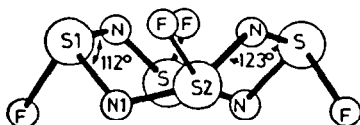
Chlorine fluoride is a particularly useful reagent for the oxidative fluorination of lower valent sulfur compounds to give sulfur(IV) or -(VI). However, occasionally it behaves as a chlorofluorinating reagent which in this case gave a novel sulfur-nitrogen heterocycle [44],



while  $\text{NSF}_3 + \text{F}_2 \rightarrow \text{F}_5\text{SN}=\text{SF}_4$ .

Essentially the entire field of nitrogen-sulfur-fluorine chemistry is based on thiazyl fluoride ( $\text{NSF}$ ) and thiazyl trifluoride which were reported in 1955 by the Glemser school in Göttingen [44]. The preferred syntheses of these two molecules are based on a common precursor,  $\text{FC(O)NSF}_2$ , which at  $20^\circ\text{C}$  with  $\text{CsF}$  gives  $\text{NSF}$  and at  $20 - 110^\circ\text{C}$  with  $\text{AgF}_2$  gives  $\text{NSF}_3$ . Both species behave as coordinating ligands forming  $\text{N}-\text{M}$  bonds, e.g. in  $\text{SO}_2$  with  $\text{Co}^{2+}$ , the stable species are  $[\text{Co}(\text{NSF})_6]^{2+}$  and  $[\text{Co}(\text{NSF}_3)_4]^{2+}$  formed from  $[\text{Co}(\text{SO}_2)_2][\text{AsF}_6]_2$  and the respective thiazyl compound. Thiazyl fluoride forms  $\text{NS}^+$  with strong Lewis acids while  $\text{NSF}_3$  only forms adducts,  $\text{NSF}_3 \cdot \text{MF}_5$  [45]. Fluoroalkenes in the presence of  $\text{F}^-$  give  $\text{NSF}_2\text{R}_f$  with  $\text{NSF}_3$ . However, fluoroalkenes with  $\text{NSF}$  under the same conditions give sulfenyl aziridines, and with fluoro 1,3-dienes cycloaddition occurs to form sulfur-nitrogen six-membered heterocycles.

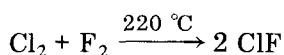
Although formally a tetramer and trimer of  $\text{NSF}$ ,  $(\text{NSF})_4$  and  $(\text{NSF})_3$  can be best obtained from  $\text{S}_4\text{N}_4$  with  $\text{AgF}_2$  in  $\text{CCl}_4$  and  $(\text{NSCl})_3$  with  $\text{AgF}_2$ . The  $(\text{NSF})_4$  molecule has a puckered eight-membered ring with two fluorine atoms axial and two equatorial.



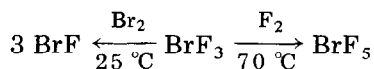
The six-membered ring has a chair configuration with axial (*cis*) fluorine atoms. The repulsive effect of the lone pairs appears to be minimized by the chair arrangement in  $(\text{NSF})_3$ , and thus it is no surprise that with Lewis acids,  $\text{N}_3\text{S}_3\text{F}_3$  gives the stable  $\text{N}_3\text{S}_3\text{F}_2^+\text{MF}_6^-$ , while  $\text{N}_4\text{S}_4\text{F}_4$  loses  $\text{NSF}$  to form  $\text{N}_3\text{S}_3\text{F}_2^+\text{MF}_6^-$  and  $\text{NS}^+\text{MF}_6^-$ , probably through an unstable intermediate,  $[\text{N}_4\text{S}_4\text{F}_3^+]$ . The nitrogen-sulfur-fluorine field has been deeply tilled, but much exciting work is still waiting to be done.

## Halogen fluorides and halogen oxofluorides

Familiar names such as Emeléus, Ruff, Menzel, Moissan, Lebeau, Simons, Schmeisser and Sukhoverkov figure prominently in the literature reporting syntheses and the characterization of the halogen fluorides [46]. As early as 1891, Moissan had discovered that  $\text{IF}_5$  could be prepared by direct combination of the elements at room temperature [12]. With the exception of  $\text{ClF}_7$ ,  $\text{BrF}_7$  and  $\text{IF}$  (which has a fleeting existence), all possible combinations of  $\text{XF}$ ,  $\text{XF}_3$ ,  $\text{XF}_5$  and  $\text{XF}_7$  are known, although all are not equally stable. The stability of the compounds with the larger number of fluorine atoms increases as X becomes larger. The preparation of these highly reactive substances is most frequently achieved either by direct combination of the elements at the appropriate temperature,



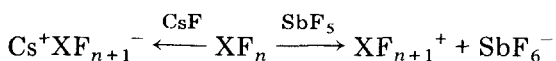
or by reaction of a higher fluoride with either fluorine, to prepare yet a higher fluoride, or with the central halogen to reduce the extent of fluorination,



These compounds are powerful fluorinating reagents for both inorganic and organic compounds, especially  $\text{ClF}$ ,  $\text{ClF}_3$  and  $\text{BrF}_3$ . Much of the pioneering work was accomplished in Emeléus' Cambridge laboratory.

With a specific conductivity of  $>8.0 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ , it is not surprising to find that  $\text{BrF}_3$  undergoes self-dissociation, *i.e.*  $2\text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^-$ . Thus, for example, when an acid  $(\text{BrF}_2)_2\text{PtF}_6$  or a base  $\text{NOBrF}_4$  dissolves in  $\text{BrF}_3$ , the solution becomes highly conducting [47]. Therefore,  $\text{BrF}_3$  is a good solvent system, as is  $\text{IF}_5$ .

One of the most interesting and useful characteristics of nearly all halogen fluorides is their amphoteric nature, which promotes the syntheses of fluorohalogen cations and anions in the presence of strong acids or strong bases:

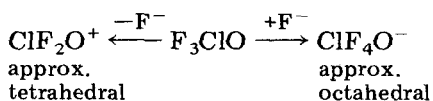


Thus, it is possible to generate nearly every cation from  $\text{Cl}_2\text{F}^+$  to  $\text{IF}_6^+$  and anion from  $\text{ClF}_2^-$  to  $\text{IF}_8^-$ . It should be noted that although  $\text{ClF}_6^+$  and  $\text{BrF}_6^+$  are known, they cannot be obtained by simple fluoride-ion extraction because their formal heptafluoro parents are nonexistent. A more powerful oxidizer,  $\text{Kr}_2\text{F}_3^+\text{SbF}_6^-$ , was employed to oxidatively fluorinate  $\text{BrF}_5$  to  $\text{BrF}_6^+$  [48].  $\text{PtF}_6$  can be used to convert  $\text{ClF}_5$  to  $\text{ClF}_6^+$  [49]. Disappointingly, to date there are no ternary halogen fluorides or fluorohalogen ions.

The geometries exhibited by these halogen fluorides range from a planar bent-T for  $\text{XF}_3$  to a square pyramid for  $\text{XF}_5$  to a distorted pentagonal

bipyramid for  $\text{IF}_7$ . Molecular shape is very easily predicted using simple VSEPR. Since these compounds are rather low melting and boiling, with the exception of  $\text{BrF}_3$ , the extent of bridging must be small.

There is a marked similarity between the halogen fluorides and the halogen oxofluorides [50, 51]. This is not surprising since formally  $\text{F}_3\text{XO}$ ,  $\text{FXO}_2$ ,  $\text{F}_5\text{XO}$ ,  $\text{F}_3\text{XO}_2$  and  $\text{FXO}_3$  are the oxo and dioxo analogues of  $\text{XF}_5$  and the oxo, dioxo, and trioxo derivatives of  $\text{XF}_7$ , respectively. Unfortunately, the oxo derivatives of  $\text{XF}_3$  ( $\text{OXF}$ ) have extremely low stability ( $\text{OCIF}$ ) or do not exist at all. Therefore, they would be expected to be reactive oxidizing and fluorinating agents, and to behave as  $\text{F}^-$  donors and acceptors. This seems to be true if the resulting anion or cation assumes tetrahedral or octahedral geometry. Thus  $\text{F}_3\text{ClO}$ , which is trigonal bipyramidal, readily undergoes reactions with Lewis acids or Lewis bases,



whereas the tetrahedral  $\text{FCIO}_3$  does not exhibit acid/base behavior and, in fact, the chemical reactivity of the two differs markedly [50]. The three known bromine oxofluorides,  $\text{FBrO}_2$ ,  $\text{F}_3\text{BrO}$  and  $\text{FBrO}_3$ , behave in an analogous fashion. All five of the above permutations are known for iodine. Perchloryl fluoride and perbromyl fluoride,  $\text{FCIO}_3$  and  $\text{FBrO}_3$ , are the most useful members of this family of compounds in their roles as mild effective fluorinating reagents with organic materials. Few generalizations can be made about synthetic routes to these compounds.

### Perfluoroalkyl organometallic compounds

The birthplace of perfluoroalkyl organometallic chemistry was Emeléus' laboratories at Cambridge. An important step towards what is now a very expansive organometallic field was taken when carbon tetraiodide was reacted with  $\text{IF}_5$  to form  $\text{CF}_3\text{I}$ , which when photolyzed or heated with mercury gave  $\text{CF}_3\text{HgI}$ . This half-mercurial or  $\text{CF}_3\text{I}$  itself was reacted directly with  $\text{Cd/Hg}$  to form  $(\text{CF}_3)_2\text{Hg}$  [52]. Bis(perfluoroalkyl)mercurials are soluble in, and recoverable from, water where a solution of low but definite electrical conductivity results. The lithium and magnesium derivatives are stable only below room temperature.

Trifluoromethyl iodide (prepared from  $\text{AgOC(O)CF}_3 + \text{I}_2 \rightarrow \text{AgI} + \text{CO}_2 + \text{CF}_3\text{I}$ ) received much attention from the Cambridge laboratories as a favorite precursor to trifluoromethyl-substituted Main Group compounds, particularly those of sulfur, phosphorus, arsenic, antimony and selenium by direct reaction with the elements. Exchange reactions between  $\text{CF}_3\text{I}$  and compounds of germanium, tin and lead gave mixed halo or alkyltrifluoromethyl derivatives [53]. At temperatures in excess of  $100^\circ\text{C}$ , it was possible to form  $(\text{CF}_3)_4\text{Ge}$  (15%) or  $(\text{CF}_3)_2\text{SnBr}_2$  (10%) when  $\text{GeI}_4$  or  $\text{SnBr}_4$  was

reacted with  $(\text{CF}_3)_2\text{Hg}$  [54, 55]. Thermally-induced decarbonylation reactions of trifluoroacetyl-substituted transition metal compounds provide a useful route to the trifluoromethyl derivatives [54].

Turning to much more exotic techniques, Lagow and his coworkers [55] demonstrated that  $\text{C}_2\text{F}_6$ , when exposed to a low-temperature glow discharge, was an excellent precursor to  $\cdot\text{CF}_3$ . The radicals displace halogen atoms stepwise from, for example,  $\text{BiI}_3$ , to form  $\text{Bi}(\text{CF}_3)_3$  in 32% yield. Lagow also showed that by using direct fluorination, metal alkyls could be converted to isolable metal perfluoroalkyls in addition to a large number of the partially fluorinated intermediates. Taking advantage of cocondensation techniques which Klabunde had applied largely to transition metal atom reactions with  $\text{CF}_3\text{I}$ , Lagow and Morrison [55] cocondensed trifluoromethyl radicals with a variety of metals and metalloids, such as Hg, Te, Bi, Sn and Ge, and in each case the trifluoromethyl derivative was prepared in fair [ $\text{Sn}(\text{CF}_3)_4$ , 8%] to good [ $\text{Hg}(\text{CF}_3)_2$ , 89%] yields. But more importantly, these workers were able to demonstrate that molecules containing a large number of trifluoromethyl groups were really quite stable thermally. This method also allows utilization of other free radicals, such as  $\text{CH}_3\cdot$  and  $\cdot\text{SiF}_3$ . Ultrasound excitation has been utilized to form  $\text{CF}_3\text{ZnI}$  from  $\text{CF}_3\text{I}$  and Zn, which was used subsequently with organic halides to give trifluoromethyl organic species [55].

Synthetic chemists invariably search for the simplest methods to arrive at their starting materials or to achieve the new compound. For this reason, the current method of choice for  $(\text{CF}_3)_2\text{Hg}$  is the thermal decarboxylation of  $\text{Hg}[\text{OC}(\text{O})\text{CF}_3]_2$ . However, it has been observed that bis(trifluoromethyl)-cadmium is much more reactive than the mercurial. It can be made by the metathesis of bis(trifluoromethyl)mercury and bis(methyl)cadmium in a basic solvent, such as tetrahydrofuran, glyme or pyridine. Because of its Lewis acidity, the cadmium compound is isolated as  $(\text{CF}_3)_2\text{Cd}\cdot\text{solvent}$ . Of these,  $(\text{CF}_3)_2\text{Cd}\cdot\text{glyme}$  appears to be the best choice for chemical reactivity with adequate thermal stability [54]. Employing a second route which utilizes perfluoroalkyl iodides with dialkyl cadmium in the presence of a variety of basic solvents, the high-yield syntheses of  $(\text{R}_f)_2\text{Cd}\cdot\text{solvent}$  ( $\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5, n\text{-C}_3\text{F}_7, i\text{-C}_3\text{F}_7, n\text{-C}_4\text{F}_9, \text{C}_6\text{F}_5$ ) is available. The analogous  $(\text{R}_f)_2\text{Zn}\cdot\text{solvent}$  ( $\text{R}_f = \text{CF}_3, \text{C}_6\text{F}_5$ ) compounds have also been prepared [56]. A more recent report of *F*-alkyl or *F*-aryl cadmium reagents directly from *F*-alkyl iodides or *F*-aryl bromides with cadmium metal is a major contribution [57]. The high-yield direct synthesis of a 50:50 mixture of perfluoroalkenyl cadmium compounds,  $(\text{F}_2\text{C}=\text{CF})\text{CdI}$  and  $(\text{F}_2\text{C}=\text{CF})_2\text{Cd}$ , by treating  $\text{CF}_2=\text{CFI}$  with cadmium powder in dimethylformamide should increase interest in the syntheses of new families of Main Group compounds.

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## BIOGRAPHIC NOTE

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Jean'ne M. Shreeve was born in Montana and educated at the Universities of Montana, Minnesota and Washington. It is her privilege to have worked with three of fluorine chemistry's finest contributors and gentlemen, Professor G. H. Cady, Professor H. J. Emeléus and Professor O. Glemser. Her entire professional career has been spent at the University of Idaho where she has been since 1961, rising through the professorial ranks to assume her present position as Professor and Head of the Chemistry Department in 1973. Her contributions to fluorine chemistry have been recognized by the American Chemical Society's Garvan Medal and the ACS Fluorine Division's Award. In 1983 her alma mater awarded her an honorary Doctor of Science degree. Her research interests include the syntheses and characterization of compounds which contain fluorine.



J. M. Shreeve