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# FLUORINATED HYPOFLUORITES AND HYPOCHLORITES

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## I. Introduction

The richness of the exciting field of fluorinated hypofluorites and hypochlorites is due in very large part to the imaginative work by Ruff and Lustig. Dudley (*92*) had suggested that $AgOSF_5$ and $AgOSO_2F$ were active intermediates in the AgF(I,II) catalytic fluorination of $OSF_4$ and $SO_3$ to give $SF_5OF$ and $FSO_2OF$, respectively. Because

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$CsOSF_5$ had been reported (*278*), a study of the fluorination of thionyl fluoride and thionyl tetrafluoride in the presence of CsF was undertaken (*237*). For the first time, $SF_5OF$ could be consistently isolated in yields greater than 95%! The existence of the trifluoromethoxides of alkali metals as stable entities was demonstrated by Redwood and Willis (*46, 221, 222*). Ruff, Pitochelli, and Lustig proceeded to demonstrate the alkali-metal (K, Rb, or Cs) fluorides catalyzed addition of fluorine across the carbon–oxygen double bond in perfluorocarbonyl compounds to form fluoroxy compounds in nearly quantitative yields (*238*). In 1968 Fox and co-workers extended this method to the essentially quantitative preparation of the first perfluoroalkyl hypochlorite, $CF_3OCl$, by simply substituting ClF for $F_2$ in reaction with $COF_2$ in the presence of CsF. In that paper they also announced $i$-$C_3F_7OCl$ and $SF_5OCl$ (*124*). The flood gates were open and much beautiful work was about to commence.

This is not meant to detract in any way from the excellent contributions of the Cady school at the University of Washington and of Prager and Thompson at the 3M Co., for it was their elegant work that invented, characterized, and studied a very large number of the fluoroxy compounds and hypofluorites known today (*175*).

A brief summary of the history of catalytic fluorination has been published (*175, 311*). Cady and co-workers have devoted considerable effort in attempting to understand the role played by silver fluoride(I,II) in the fluorination of $COF_2$ to $CF_3OF$ and $CF_3OOCF_3$. They concluded that (1) catalysts active at lower temperatures are generally the more ionic salts; (2) catalysts active at −78°C mostly catalyze the formation of $CF_3OF$; (3) catalysts that are initially active at 25–150°C cause the production of relatively high yields of $CF_3OOCF_3$; and (4) the percentage of $CF_3OF$ in the product apparently increases with reaction temperature when the same catalyst is used (*149*).

Although there are many variations, the three main methods of preparing the alkali-metal fluorides for their catalytic role are thermal dehydration accompanied by mechanical powdering, heating under vacuum, and the formation of a salt, which is subsequently decomposed, for example, the reaction with hexafluoroacetone in acetonitrile. Using $^{85}Kr$, Winfield and co-workers (*164*) have studied the surface areas of CsF, TlF, and RbF as a function of the pretreatment method used and have shown that the surface areas of CsF and TlF are increased markedly by any of these methods, with the surface of CsF being particularly enhanced by hexafluoroacetone. The surface area of RbF was less sensitive to pretreatment. That TlF shows little or no catalytic activity although its surface area can be greatly enhanced indicates that surface area is not the sole factor involved. In a review of the utilization of $^{18}F$-labeled inorganic compounds (*315*), it was shown that there is a correlation between $^{18}F$ exchange and catalytic ability; for example, exchange between $CF_3C(O)^{18}F$, $F^{18}FCO$, or $SF_3{}^{18}F$ and alkali-metal fluorides varies in the order Cs > Rb > K > Na > Li. CsF is the best catalyst whereas NaF and LiF have little or no catalytic activity. However, this correlation breaks down for ionic fluorides other than those of the alkali metals; for example, TlF, $Hg_2F_2$, $HgF_2$, and $LaF_3$ readily undergo $^{18}F$ exchange with $SF_3{}^{18}F$ but are not catalysts for the chlorofluorination of $SF_4$. Although much light has been shed on the subject of catalytic fluorination, there is still work to be done before complete predictability will be possible.

The present chapter is an effort to update the most recent accessible review on fluoroxy compounds and hypofluorites (*175*). No attempt has been made to cover the literature that was available prior to 1971 (except when needed for completeness) because this period was adequately handled earlier (*9, 16, 53, 135, 175, 200, 312*). Fluoroxy compounds used strictly as fluorinating agents are included in Section VI (*18, 19, 130, 160*). Although the hypochlorites of group VIa (*16*) and fluorinated compounds that contain positive chlorine have been reviewed more recently (*244*), the entire history of fluorinated hypochlorites has now been covered.

Suitable nomenclature for OCl-containing molecules presents little difficulty, with hypochlorite being a perfectly utilitarian term. However, for OF-containing molecules the situation is less straightforward. Therefore, the system used previously has been retained, that is, for perfluoroacyl and for inorganic OF compounds the term hypofluorite will be used. For perfluoroalkyl OF compounds the term fluoroxy is more suitable.

## II. Hypofluorous Acid

At the time of our last hypofluorite review (*175*), hypofluorous acid had just been synthesized and isolated by passing fluorine over cold water (*283*). Earlier, infrared bands were assigned to HOF, which was formed by photolysis of a mixture of $F_2$ and $H_2O$ that was frozen into a solid $N_2$ matrix at 14–20 K (*204*). Appelman (*9*) has described his historic synthesis as a result of a very simple experiment, whereby a drop of water was placed in a Kel-F tube with about 100 torr of fluorine gas, with the subsequent observation of a small HOF peak at mass 36, seen as a shoulder of the $F_2$ peak at mass 38 in a time-of-flight mass spectrometer.

At low temperature HOF is a white solid that melts at −117°C to a pale yellow liquid. The compound boils below room temperature (~HF) and has a vapor pressure of less than one torr at −79°C. Based on microwave studies, the O—H bond distance is 0.96(4) Å, the O—F bond distance 1.442 Å, and the HOF bond angle 97° (*152*). This is the smallest known oxygen bond angle. Appelman (*134*) rationalized this fact based on NMR studies of the molecule, which showed the fluorine to have a charge of about −0.5 e and the hydrogen to have a charge of about +0.5 e. Thus the smaller bond angle is a result of the electrostatic attraction between the ends of the molecule. This precludes the assignment of a +1 valence to fluorine except as a formalism. Matrix isolation (*121*) and gas-phase IR (*12*) spectral studies on relatively pure HOF gave fundamental bands at 886.0, 1359.0, and 3537.1 and 889.0, 1354.8, and 3578.5 $cm^{-1}$, respectively. The gas-phase spectrum of the deuterated molecule has also been recorded. A normal coordinate analysis of HOF and DOF is available (*205, 240*).

Photoionization (*37*) and photoelectron (*38*) studies are in close agreement for the first ionization potential of HOF at 12.70 eV. Ab initio LCAO MO SCF calculations gave 13.97, 14.94, and 17.16 eV for the first three ionization potentials (*153*). A value of −22.8 ± 1 kcal $mol^{-1}$ was found for the standard heat of formation of the molecule, and the proton affinity of OF is 5.8 eV (*37*). The total electric dipole moment of HOF is $\mu = |2.23 \pm 0.1\ OD|$ (*228*). The calculated value is somewhat higher (*126*).

As is to be expected for such an interesting three-atom system, HOF has been the subject of a very large number of theoretical studies. These include (1) establishment of general harmonic ab initio and semiempirical force fields (*42, 45, 202, 273*); (2) vibrational frequencies from anharmonic ab inito/empirical potential-energy functions (*44*); (3) calculation of magnetic shielding and susceptibility (*328*); (4) analytical potentials (*201*); and (5) molecular orbital theory of the hydrogen bond in $HOF–H_2O$ and $(HOF)_2$ (*79*).

Despite the strong tendency of HOF to decompose to HF and $O_2$ at room temperature, in Kel-F or Teflon apparatus and at pressures of about 100 torr the compound has a half-life of about 30 min. It sometimes decomposes explosively. Although its chemistry has not been studied exhaustively, HOF has been shown to act only as an oxygenating or as a hydroxylating agent, that is, as a donor of atomic oxygen or of its conjugate acid, $OH^+$.

Hypofluorous acid mimics the behavior of $F_2$ in many of its reactions; for example, in weakly acidic solutions the water is oxidized primarily to $H_2O_2$, whereas in alkaline solutions $O_2$ is the main oxygen product.

In addition, only in alkaline solutions is bromate oxidized to perbromate. It may well be that HOF is the reactive species when fluorine is employed in aqueous systems (*9*). However, this may be an oversimplification, because although $F_2$ produces $OF_2$ from neutral, acidic, or basic media, interaction of HOF with water has never been noted to produce $OF_2$.

$^{18}O$-Tracer studies show that the reactions of $H^{18}OF$ with $H_2O$ and with aqueous $HSO_4^-$ and $Cr(NH_3)_5N_3^{2+}$ lead to transfer of oxygen with formation of $HO^{18}OH$, $O_3SO^{18}OH^-$, and $Cr(NH_3)_5N^{18}O^{2+}$, respectively (*13*). It is interesting to note that in reactions of $F_2$ and HOF with aqueous $HClO_4$ solutions containing various complexes of Cr(III), in no case was the chromium oxidized (*294*). The readiness with which HOF transfers an oxygen atom to reducing substrates is consistent with NMR studies that indicate the HOF molecule to be polarized $HO^{\delta+}—F^{\delta-}$ (*134*).

A variety of aromatic compounds, for example, $\phi R$ [R = H, $CH_3$, $(CH_3)_3C$, $CH_3O$, $NO_2$, F, or Cl], $p$-$(CH_3)_2C_6H_4$, and naphthalene, undergo hydroxylation with HOF to form phenols (*11*). With octaethylporphyrin, HOF gives a new system—a prophyrin *N*-oxide—and possibly the *N,N'*-dioxide (*43*). Alkenes result in $\alpha$-fluoro alcohols as the major products, whereas acetylenes gave mixtures of aldehydes, ketones, and acyl fluorides, which very likely are formed by tautomerization of the $\alpha$-fluoro enol products formed initially (*185*). Although the expected Markownikoff addition products are usually found, on occasion anti-Markownikoff products are also formed. The reaction of ethynylbenzene with HOF gave 30% of the antiproduct and none of the Markownikoff. Hydrogen fluoride, which is a difficultly removed contaminant, may be part of the explanation. Mechanisms have been suggested.

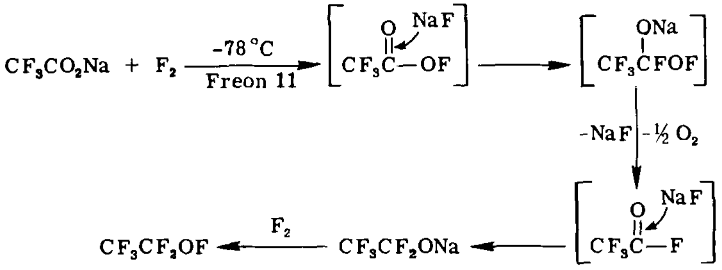
## III. Monofluoroxy Compounds or Monohypofluorites

### A. OF Bonded to Carbon

#### 1. *Fluoroxyperfluoroalkanes* ($R_fOF$)

Although the older methods of catalytic fluorination, over a AgF(I,II) catalyst at elevated temperatures (*52*), or the direct fluorination of partially fluorinated alcohols or salts (*217, 218*) are still of synthetic value, the most efficient and highest yielding route to these fluoroxy compounds is the fluorination of perfluoroalkyl ketones and perfluoroacyl fluorides in the presence of an alkali-metal fluoride (*173*, *238*). Nitrosyl fluoride has been used effectiely as a catalyst in place of MF (*317*). A discussion of the relative merits of various catalysts that have been employed can be found in Section I.

The first example of the production of fluoroxyperfluoroalkane via electrochemical fluorination (by bubbling $COF_2$/He through purified AHF in an electrolytic cell at 7°C to give 73 parts $CF_3OF$, 17 $CF_3OOCF_3$, and 10 $CF_4$) has been described by Abe *et al.* (*1*). Rozen has reported the *in situ* synthesis of $CF_3CF_2OF$ (*218, 291*) to form a stable oxidizing solution at −78°C via Scheme 1 (*230, 232*). The suggested



SCHEME 1

fluoroxy compound is not isolated, but its existence is supported by the synthesis of perfluoroalkyl ethers, for example,

$$C_6H_5CH{=}CHC_6H_5 + CF_3CF_2OF \xrightarrow[\text{Freon 11}]{-78^\circ C} C_6H_5CHFCH(OCF_2CF_3)C_6H_5$$

| | | |
|---|---|---|
| cis | DL-erythro (38%) | DL-threo (7%) |
| trans | DL-erythro (<5%) | DL-threo (28%) |

When treated with some stilbenes it produces stereospecific (syn addition) and regiospecific adducts.

A convenient procedure for the rapid synthesis of $^{18}$F-labeled $CF_3OF$ with $NiF_2\cdot CsF$ as catalyst is available. The preparation requires a fluorine-passivated Ni target and anhydrous conditions (*203*).

The number of new fluoroxyperfluoroalkanes that appeared during the 1970s was very limited. Standard methods were used. DesMarteau

$$CF_3C(O)N{=}C(CF_3)_2 + 5F_2 \xrightarrow[-60^\circ C]{KF} \underset{27\%}{CF_3CF(OF)NFCF(CF_3)_2}$$

$$CF_3C(O)NFCF(CF_3)_2 + 3F_2 \xrightarrow[-78^\circ C]{KF} CF_3CF(OF)NFCF(CF_3)_2$$

$$40\% \quad \nu_{OF} = 902\ \text{cm}^{-1} \quad \phi_{OF} = +164\ (213)$$

observed that when $(CF_3)_3COOSO_2F$ was subjected to fluorination at $-55^\circ C$ in the presence of CsF, $(CF_3)_3COF$ (*218*) as well as $(CF_3)_3COOF$ was formed (*327*). The former fluoroxy compound was also formed essentially quantitatively when $F_2/N_2$ was passed through a 50:50 mixture of $(CF_3)_3CONa$ and NaF at $-23^\circ C$ (*295*). Perhaps the first example of a fluoroxy compound with an ether linkage has appeared (*245*).

$$CF_3OCF_2C(O)F + F_2 \xrightarrow[25^\circ C]{CsF} CF_3OCF_2CF_2OF$$

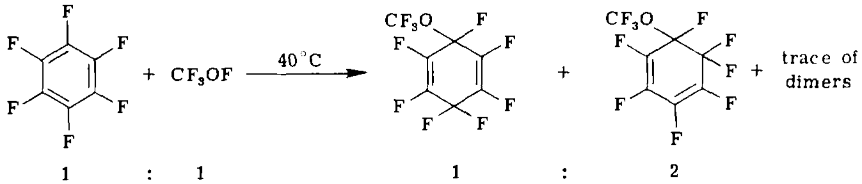
$$\nu_{OF} = 895\ cm^{-1}$$

$$\phi_{OF} = +138.8$$

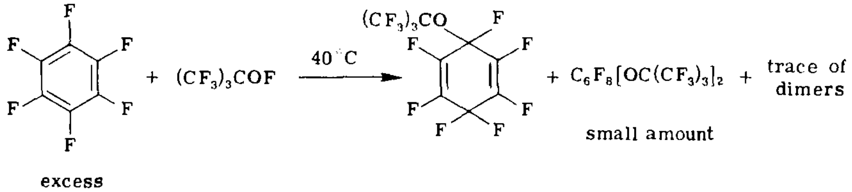
Most of the literature dealing with fluoroxyperfluoroalkanes pertains to electrophilic fluorination applications (Section VI). However, some other studies, usually involving $CF_3OF$, have appeared.

Structural studies of $CF_3OF$ which include IR and Raman spectra (*128, 166, 168, 274, 275, 309, 314*), microwave spectra (*49*), and electron diffraction (*84*), suggest $C_s$ symmetry. From Stark-effect measurements, $CF_3OF$ has been shown to have a small dipole moment ($\sim 0.3$ D). The computed dipole moment agrees well with this value. In addition, the HOMO is found to be largely an O—F $\pi^*$ orbital, and the O—F bond is also found to be the least ionic and weakest bond in the molecule (*206*). Using a Bendix time-of-flight mass spectrometer equipped with a Kel-F inlet system, a molecular ion (0.2 relative intensity) was observed for $CF_3OF$. The base peak was $CF_3^+$ (*140*). Calculations of the unimolecular decomposition of $CF_3OF$ have appeared (*56, 72*). Kinetic studies of the formation of $CF_3OOCF_3$ from $CF_3OF$ and $COF_2$ (*75*), the photochemical gas-phase fluorination of $COF_2$ between 15 and 80°C (*172*), thermal reactions between $CF_3OF$ and $NO_2$ (*76*), and the behavior of mixtures of $CF_3OF$, CO, $O_2$, and $CO_2$ exposed to 366-nm radiation at 35–55°C (*40*) have been reported. In studying the kinetics of the decomposition to $COF_2$ and $CF_3OF$, a bond energy of $44.5 \pm 0.8$ kcal $mol^{-1}$ was determined for $CF_3O$—F (*150*). This is in good agreement with the previous value of $43.5 \pm 0.5$ kcal $mol^{-1}$ (*74*). The reactions of $CF_3OF$ with $CH_4$, $CHCl_3$, $CHF_2Cl$, $CH_3F$, $CH_2F_2$, $CH_2Cl_2$, and $CH_2FCl$ were studied from 25 to 100°C and at 3–30 mm. $CF_3OF$ reacted with the dihalomethanes by a branched-chain mechanism (*289*).

It is interesting to compare the products obtained when $CF_3OF$ or $(CF_3)_3COF$ is treated with hexafluorobenzene (*296*). Addition occurs more readily with the latter fluoroxy compound. But if the $C_6F_6$ and



$(CF_3)_3COF$ are equimolar, the products are $C_6F_7[OC(CF_3)_3]$ (60%) and $C_6F_8[OC(CF_3)_3]_2$ (30%), plus dimers and a trace of the trifluoroxy adduct $C_6F_9[OC(CF_3)_3]_3$. The reaction between octafluorotoluene and $CF_3OF$ occurred only after 8 h at 100°C to give mainly $CF_3OOCF_3$ and perfluoromethylmethoxycyclohexadiene, with perfluoromethylmethoxycyclohexene and dimer in smaller amounts.



At −62°C, addition of $(CF_3)_3COF$ to $CF_3CF{=}CF_2$ gave perfluoro-*n*-propyl perfluoro-*t*-butyl ether in greater than 95% yield, suggesting an electrophilic attack by the O—F group. Analogously, the reaction with perfluoro-3,6-dioxy-5-methyl-*n*-non-1-ene gives greater than 95% addition of the perfluoro-*t*-butoxy group to the unsaturated terminal carbon atom (*295*).

Under photolytic conditions at −20°C, $(CF_3)_3COF$ undergoes a one-electron reduction in the presence of perfluorocycloolefins ($C_5F_8$ or $C_6F_{10}$) to give a mixture of products including $(CF_3)_3COOC(CF_3)_3$ (major) and simple adducts $C_5F_9OC(CF_3)_3$ or $C_6F_{11}OC(CF_3)_3$ as well as $(CF_3)_2CO$, $CF_4$, $C_5F_{10}$ or $C_6F_{12}$, and smaller amounts of vicinal $C_5F_8[OC(CF_3)_3]_2$ or $C_6F_{10}[OC(CF_3)_3]_2$. Similar conditions with $CF_3OF$ and $C_5F_8$ or $C_6F_{10}$ result in $C_5F_9OCF_3$ (83%) or $C_6F_{11}OCF_3$ (~100%). In the case of $C_5F_8$, small amounts of $(C_5F_8OCF_3)_2$ and $(C_5F_9)_2$ are formed (*297*). Surprisingly, although the reaction with $CF_3OF$ was run with that reagent in twofold excess, no evidence was found for $CF_3OOCF_3$.

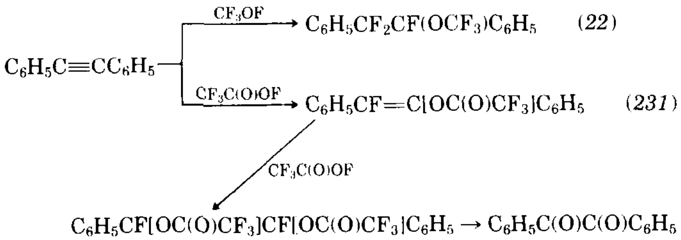
Fluoroxytrifluoromethane was found to be useful as a polymerization initiator for perfluoro-2-butyne (*59*). Radicals of the type $(CF_3O)_3S$ and $(CF_3O)_2SF$ have been detected via ESR spectra during the photolysis of $CF_3OF$ and peroxides containing dissolved OCS, $F_2SS$, $CS_2$, $Cl_2CS$, or $F_2CS$ (*199*). Similarly, with $SF_4$, radicals of the type $CF_3OSF_4$

are observed (*196*). An intense ESR spectrum observed in the UV-irradiated solid Kr/$CF_3OF$ at 10 K is attributed to the linear radical KrFKr having a $\Sigma_u$ ground state (*41*). Emission spectral measurements were made on diatomic xenon halides formed by the interaction of Xe with $CF_3OF$ (*306*).

### 2. *Fluoroacyl Hypofluorites* [$R_fC(O)OF$]

Just as Cady *et al.* (*52, 117*) have demonstrated that the presence of water is necessary to form $CF_3C(O)OF$ from trifluoroacetic acid and fluorine, Rozen has shown that, when $CF_3C(O)ONa$ is not strictly anhydrous, the main oxidant formed when the latter in Freon 11 is treated with fluorine at −78°C is $CF_3C(O)OF$ (*230*). Although Rozen did not isolate the hypofluorite, its reaction with *trans*-$C_6H_5CH{=}CHC_6H_5$ gave DL-*threo*-$C_6H_5CHFCH(OC(O)CF_3)C_6H_5$.

Using elemental fluorine diluted with nitrogen at −78°C with $CF_3C(O)ONa$ in an inert solvent (usually $CCl_3F$) to generate $CF_3CF_2OF$ (if anhydrous) and $CF_3C(O)OF$ (if damp), Rozen and coworkers have produced α-fluoroketones (*181, 230, 234, 235*). They suggested that the fluoroxy fluorine in $CF_3C(O)OF$ is more electrophilic in character than that in $CF_3OF$, based on the respective reaction products of diphenylacetylene. The 1-fluoro-2-trifluoroacetoxy compounds formed with stilbenes are readily hydrolyzed to the corresponding α-fluorohydrins (*231*).



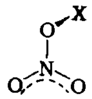
For completeness it should be mentioned that the first nonfluorinated acyl hypofluorite, $CH_3CO_2F$ (50–80%), was claimed to have been generated *in situ* by bubbling $F_2/N_2$ through suspensions of sodium fluoride, acetate, or trifluoroacetate in acetic acid/Freon 11 (1 : 9) at −78°C. Although it has not been isolated, the reaction products with $C_6H_5CH{=}CHC_6H_5$ are *threo*-$C_6H_5CH(OC(O)CH_3)CHFC_6H_5$ (45%) and *erythro*- (7%) (*233*).

## B. INORGANIC HYPOFLUORITES

### 1. *Group Va Hypofluorites*

*Nitryl Hypofluorite or Fluorine Nitrate* (*$O_2NOF$*). This is the only known hypofluorite in which an OF group is bonded to nitrogen (see Table I). Its high-yield synthesis results from the reaction of fluorine with $HNO_3$ or any alkali-metal nitrate (*51, 62, 239, 307, 316*). It has not been possible to reproduce others that have been reported (*62*). The kinetics of the unimolecular thermal decomposition reactions of $O_2NOF$ have been studied at 120, 130, and 140°C, at pressures from approximately 0.5 to 10–20 torr (*48*). The heat of formation of gaseous $O_2NOF$ has once again been determined with the value at $2.5 \pm 0.5$ kcal $mol^{-1}$ (*223*).

Although long ago low-precision electron-diffraction studies pointed to a nonplanar structure for $O_2NOF$, in which the N—O—F group is perpendicular to the $ONO_2$ plane (*212*), the geometry continues to be discussed. Coplanarity is favored, based primarily on analogy with the planar structures well established for the related molecules $HONO_2$ and $CH_3ONO_2$ (*15, 47, 73, 91, 136, 186*). However, perhaps now the definitive work has appeared from two different laboratories, using Raman polarization measurements to show that $O_2NOF$ and other halogen nitrates are indeed nonplanar (*67, 270*).



### 2. *Group VIa Hypofluorites*

*a. Pentafluorosulfur Hypofluorite* (*$SF_5OF$*). The preparation of this compound exemplifies the beauty of the Lustig and Ruff method for synthesis of hypofluorites through the use of alkali-metal fluorides (*237*). Based on the fact that it is possible to prepare a material having the composition $CsOSF_5$ (*66, 278*), they were able to demonstrate that thionyl fluoride or thionyl tetrafluoride could be catalytically fluorinated to $SF_5OF$ in the presence of CsF in yields greater than 95% (*237*). This is in sharp contrast to yields obtained via the AgF(I,II)-catalyzed fluorination of $SOF_2$ (*93, 94*).

The addition of $SF_5OF$ to olefins (*175, 216*) occurs readily to give only one product, which contains the components $SF_5$ and F. Penta-

$$SF_5OF\left\{\begin{array}{l} + CHCl{=}CHCl \xrightarrow{-183 \text{ to } 25^\circ C} \underset{81\%}{SF_5OCHClCHClF} \\[1em] + CH_2CCl_2 \xrightarrow{-183 \text{ to } 25^\circ C} \underset{71\%}{SF_5OCH_2CCl_2F} \\[1em] + CHBrCHBr \xrightarrow{23^\circ C} \underset{15\%}{SF_5OCHBrCHBrF} \end{array}\right.$$

fluorosulfur hypofluorite is much more reactive than $SeF_5OF$ (Table I). For EPR studies of the radical $ClF_4$, $SF_5OF$ was photolyzed with $Cl_2$ or HCl (*197*). When $SF_5OF$ was photolyzed in the presence of $SO_2$ and $OSF_2$, EPR spectra showed $FSO_2$ and $OSF_3$, respectively (*198*). Because of its facile synthesis, some use has been made of $SF_5OF$ in electrophilic fluorination applications. These are included in Section VI.

*b. Fluorosulfuryl Hypofluorite or Fluorine Fluorosulfate* (*$FSO_2OF$*). The standard synthesis of $FSO_2OF$ is the fluorination of sulfur trioxide in the presence of AgF(I,II) at 200°C in a flow reactor to give yields of approximately 60% (*95, 175*). Photolysis of $SO_3$–$F_2$ mixtures in Pyrex result in $S_2O_6F_2$ and $FSO_2OF$ (*116*). A rather novel route to produce pure $FSO_2OF$ has been described by Christe *et al.* (*69*). Little additional chemistry has appeared in recent years. This may reflect the treacherous nature of this material (Table I). However, one further olefin insertion and one chlorine abstraction reaction have been reported (*54*).

$$NF_4SbF_6 + CsSO_3F \xrightarrow[-78^\circ C]{AHF} NF_4SO_3F \xrightarrow[10^\circ C]{-\,AHF} NF_3 + \underset{\sim 100\%}{FSO_2OF}$$

$$CHCl{=}CCl_2 + FSO_2OF \xrightarrow{-78^\circ C} \underset{70\%}{CHClFCCl_2OSO_2F}$$

$$CHCl_3 + FSO_2OF \xrightarrow{-78^\circ C} \underset{80\%}{CHCl_2OSO_2F}$$

Experimental kinetic studies of the thermal reactions between $FSO_2OF$ and $N_2F_4$ (*308*) or CO (*304*) or CO and $O_2$ (*305*) and a theoretical calculation on the unimolecular decomposition of $FSO_2OF$ (*55*) are in the literature. Raman and IR spectral data suggest $C_s$ symmetry (*219*).

*c. Pentafluoroselenium Hypofluorite* (*$SeF_5OF$*). The initial synthesis of $SeF_5OF$ occurred in low yield (14%) via the reaction of $SeO_2$ and

TABLE I

INORGANIC HYPOFLUORITES

| Compound | Melting point (°C) | Boiling point (°C) | $\nu_{OF}$ cm$^{-1}$ | $\phi_{OF}$ | Comments | References |
|---|---|---|---|---|---|---|
| $ON_2OF$ | | | 927 | | Shock sensitive | (*67, 186*) |
| $FSO_2OF$ | −158.5 | −31.3 | 878 | 249 | Unpredictable, explosive | (*93, 95*) |
| $SF_5OF$ | −86.0 | −55.1 | 935 | 189 | Thermally stable to ~200°C | (*93, 94, 182*) |
| $SeF_5OF$ | −55 | −30 | 920 | 177.5 | Store at low temperature | (*191, 263, 265*) |
| $O_3ClOF$ | −167.3 | −15.9 | 885 | 219.4 | Shock sensitive | (*2, 71, 229*) |
| $OIF_4OF$ | −33.1 | 28.4 | 890 | 202 (trans)<br>176 (cis) | Slow decomposition in Teflon or stainless steel | (*68, 70*) |

$F_2/N_2$ in the presence of AgF(I,II) at 100°C (*191*). Later, Cady and Smith showed the yield could be tripled if KF and $SeOF_2$ were allowed to form $KSeOF_3$, which was then subjected to fluorination (*277*). Subsequently, Seppelt demonstrated that when $KSeOF_3$ was treated with fluorine an insoluble salt $KSeOF_5$ was formed (*261*). The latter can be further fluorinated to $F_5SeOF$. Seppelt has shown also that, if $Hg(OSeF_5)_2$ is used in place of the potassium salt, much higher yields of $SeF_5OF$ are obtained, with smaller quantities of $SeF_6$ present as a contaminant (*265*). The vibrational spectra of $F_5SeOF$ have been assigned (Table I) (*263*).

$$\underset{100\ \text{mmol}}{Hg(OSeF_5)_2} + \underset{260\ \text{mmol}}{F_2} \xrightarrow[14\ \text{h}]{25^\circ\text{C}} \underset{74\%}{SeF_5OF}$$

Few synthetic reactions with $SeF_5OF$ have been attempted. It is not as reactive as $SF_5OF$. However, with *c*-$C_5F_8$, $SF_4$, and CO $SeF_5OC_5F_9$, $SeF_5OSF_5$, and $SeF_5OC(O)F$ are obtained, respectively. The first two occur at 25°C on long standing, whereas with CO the reaction goes to completion after 12 h at 65°C (*277*).

### 3. *Group VIIa Hypofluorites*

*a. Perchloryl Hypofluorite or Fluorine Perchlorate* (*$O_3ClOF$*). The classic synthetic routes to $O_3ClOF$ are similar to those for $O_2NOF$, for example, bubbling elemental fluorine through 70% perchloric acid (*229*) or direct combination of fluorine with metal perchlorates (*175*). A new and convenient synthesis has been discovered (*71*). The thermal decomposition of $O_3ClOF$ has been studied at 65–100°C and found to give $ClO_2F$, ClF, and $O_2$ (Table I). The amount of ClF formed increased with temperature (*176*). Vibrational spectral studies have been carried out (*2*).

$$NF_4SbF_6 + CsClO_4 \xrightarrow[-78^\circ C]{AHF} CsSbF_6\downarrow + NF_4ClO_4$$

$$NF_4ClO_4 \xrightarrow{25^\circ C} NF_3 + \underset{\sim 100\%}{O_3ClOF}$$

$$C_3F_6 + O_3ClOF \xrightarrow[12\ h]{-45^\circ C} \underset{50\%}{CF_3CF_2CF_2OClO_3} + \underset{24\%}{CF_3CF(OClO_3)CF_3}$$

$$C_2F_4 + O_3ClOF \xrightarrow{-45^\circ C} \underset{68\%}{CF_3CF_2OClO_3}$$

$$CF_3I + O_3ClOF \xrightarrow{-45^\circ C} \underset{8\%}{CF_3OClO_3}$$

Very little reaction chemistry has been attempted with $O_3ClOF$; there are only a few references to remote (*290*) or unpublished work (*169*). However, Schack and Christe (*246*) have examined reactions with olefins and with $CF_3I$. The formation of both isomers with $C_3F_6$ is in sharp contrast to the exclusive Markownikoff-type additions observed for $ClOClO_3$ and $BrOClO_3$ reactions, which give 100% of $CF_3CFXCF_2OClO_3$ (*251*). This would suggest that the F—O bond in $FOClO_3$ is not strongly polarized in either direction, and it certainly does not support a significant positive charge on fluorine. Steric effects could account for the somewhat larger yield of the *n*-propyl isomer. The reaction with $CF_3I$ is more difficult to control than with olefins. The yield of $CF_3OClO_3$ was much smaller than when $ClOClO_4$ was used as the source of perchlorate.

*b.* cis- *and* trans-*Iodine(VII) Oxytetrafluoride Hypofluorite* (*OIF₄-OF*). The synthesis of $OIF_4OF$, the first iodine-containing hypofluorite, was one of the most elegant pieces of hypofluorite work during this period. A metathetical reaction between $NF_4SbF_6$ and $CsBrO_4$ in AHF gave only $FBrO_2$ and $O_2$. However, when $CsIO_4$ was substituted, the reaction was thought to proceed via the following (*68, 70*).

$$\mathrm{CsIO_4 + 4\ HF \rightleftharpoons CsIF_4O_2 + 2\ H_2O}$$

$$\mathrm{NF_4SbF_6 + CsIF_4O_2 \xrightarrow[-78^\circ C]{HF} CsSbF_6\downarrow + \underline{HOIF_4O + NF_4HF_2}}$$

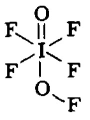
$$\mathrm{NF_3} + cis\text{–}trans\text{-}\mathrm{OIF_4OF} \xleftarrow{-30\ \text{to}\ 25^\circ\mathrm{C}}$$

$$81\%$$

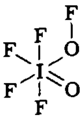
Fluorination reactions of $CsIO_4$ with $ClF_5$, $BrF_5$, $ClF_3$, or $F_2$ did not result in pure $CsIF_4O_2$, so they were less attractive reagents. Alkaline hydrolysis occurred according to

$$\mathrm{OIF_4OF + 6OH^- \rightarrow IO_4^- + 5F^- + 0.5O_2 + 3H_2O}$$

Physical properties have been determined for the cis–trans mixture. $OIF_4OF$ is colorless as a gas, pale yellow as a liquid, and white in the solid state. Vapor pressures may be obtained from the equation log $P_{\mathrm{mm}} = 7.62925 - 1432.0/T$ K over the temperature range −45.3 to 0°C. It is marginally stable at 25°C and can be handled in well-passivated metal and Teflon gear without rapid decomposition. When a sample was heated in a stainless steel cylinder to 120°C for 388 h, $IF_5$ and $O_2$ were formed. Addition across the double bond in $C_2F_4$ resulted only in $COF_2$, $CF_3CFO$, and $C_2F_6$. It has no Lewis-acid or -base properties, reacting with neither CsF nor $SbF_5$. The IR spectra of the gas and of the neon-matrix-isolated solid and the Raman spectra of liquid and solid $FOIF_4O$ have been recorded (Table I). The highest mass fragment in the mass spectrum has been assigned to $IF_4O^+$ (70 eV). The hypofluorite is much more stable than the corresponding hypochlorite.



trans



cis

## C. Rubidium and Cesium Fluoroxysulfates

In one of the most exciting breakthroughs in hypofluorite chemistry, Appleman *et al.* identified Fichter's (*97*) *vergängliches Oxidationsmittel* in the form of its rubidium and cesium salts as the fluoroxysulfate ion, $SO_4F^-$ (*10*). Fluorine (as a 20% mixture in nitrogen) was passed into a 1–2 *M* solution of $Rb_2SO_4$ or $Cs_2SO_4$ held at approximately 0°C to give a yellowish-white precipitate of $RbSO_4F$ or $CsSO_4F$. These compounds are the first known examples of ionic hypofluorites.

The solid salts, which only lose oxidizing power slowly at 25°C, detonate mildly at 100°C. Aqueous solutions decompose gradually with the formation of $O_2$, $H_2O_2$ and $HSO_5^-$. Using $H_2{}^{18}O$, it was found that each product contained one atom of $^{18}O$ (*293*). At 15°C in 0.01 $M$ $HClO_4$, the first-order rate constant $k = 3.6 \times 10^{-4}\ s^{-1}$, $\Delta H\ddagger = 16.8 \pm 0.4$ kcal $mol^{-1}$ and $\Delta S\dagger = -15.7 \pm 1.5$ cal $mol^{-1}$ $deg^{-1}$. Mechanisms for decomposition of aqueous solutions of and oxidations by $SO_4F^-$ have been postulated (*292, 293*).

$$MSO_4F \xrightarrow{100°C} MSO_3F + \tfrac{1}{2}O_2$$

Both salts in acetonitrile (more stable than in $H_2O$) give singlet resonance bands in their respective $^{19}F$-NMR spectra at $\phi + 132.3$, compared to $\phi + 37.5$ for $KSO_3F$. The O—F stretching frequency in the IR and Raman spectra is assigned to a band at 830 $cm^{-1}$ (*10*). The fluoroxysulfate anion in $RbSO_4F$ has distorted tetrahedral coordination, with each central sulfur atom bound to four oxygens (*118*). The S—O—F bond angle is 107.8°. Each Rb cation is coordinated to nine oxygen atoms and two fluorine atoms.

Aqueous solutions of the fluorooxysulfate salts are very powerfully oxidizing. Chloride, bromide, and iodide are oxidized first to the free halogens and then to higher states. In addition, V(IV) → V(V); Ce(III) → Ce(IV); Co(II) → Co(III); Mn(II) → Mn(III) → Mn(VII) (*10*). The heat of reaction of $CsSO_4F$ with aqueous HI has been determined by solution calorimetry. The standard heat of formation is $-1004.9 \pm 1.6$ kJ $mol^{-1}$ (*282*).

The fluoroxysulfate ion fluorinates aromatic compounds in acetonitrile at room temperature. Reaction of $CsSO_4F$ with PhOR (R = H, $CH_3$, $C_4H_9$, or $C_2H_5CHCH_3$) in $CH_3CN$ with a $BF_3$ catalyst gave a mixture of 2-$FC_6H_4OR$ and 4-$FC_6H_4OR$ (70–80%), the product ratio being dependent on the size of OR (*280*). Under similar conditions benzene gave fluorobenzene (30–35%), and naphthalene gave a mixture of 1- and 2-fluoronaphthalene in the ratio 5:1 (38–42%) (*281*). Phenanthrene and pyrene as well as phenol, anisole, biphenyl, and toluene (*141*) have been fluorinated without the use of a catalyst. The major product with toluene was benzyl fluoride. Because of their relative stability and ease of preparation, storage, and use, these fluoroxysulfate salts appear to have a considerable potential as synthetic reagents for organic chemistry.

## IV. Bisfluoroxy Compounds or Bishypofluorites

### A. OF BONDED TO CARBON

The use of alkali-metal-fluoride-catalyzed fluorination of appropriate oxygen-containing species enhances the ease of syntheses and the yields of bisfluoroxy compounds. However, Prager and Thompson have been remarkably successful in the preparation of several mono- and bisfluoroxy compounds, particularly via the mild fluorination of fluoroalkyl alcohols or ketones and sodium salts of perfluorocarboxylic acids or of hexafluoroacetone hydrate (*175*).

$$FOCF_2CF_2CF_2OF \xrightarrow[RH]{\Delta\ or} CF_4 + 2\,COF_2$$

$$\begin{array}{l} FC(O)(CF_2)_xC(O)F + 2F_2 \xrightarrow[-78^\circ]{CsF} FO(CF_2)_{x+2}OF \\ x = 2, 3 \end{array}$$

$$FC(O)OOC(O)F + 2F_2 \xrightarrow[-95^\circ C]{KF} \underset{95\%}{FOCF_2OOCF_2OF}$$

In 1966 Prager (*217*) reported the first bisfluoroxy compound, $FO(CF_2)_3OF$, which was obtained in a 2% yield by the direct fluorination of 1-hydroxy-3-trichloroacetoxypropane. Although it is stable at room temperature when pure, it is decomposed by heat or by chemical initiators, including hydrocarbons. This decomposition appears to occur in a manner analogous to that of monofunctional primary compounds having more than one carbon atom. Almost simultaneously, Lustig and co-workers (*173, 174, 238*) demonstrated the marked advantage of the low-temperature alkali-metal-fluoride-catalyzed fluorination of perfluoroalkyl acid fluorides or of bisfluorocarbonyl peroxide to produce bisfluoroxy compounds in high yield and a state of high purity. At 25°C in the presence of CsF, $CO_2$ was converted essentially quantitatively to the first geminal bisfluoroxy compound, $CF_2(OF)_2$ (*57, 137, 173*). This product was also obtained in somewhat smaller yields via the direct fluorination of sodium trifluoroacetate (2%) or of sodium oxalate (1–15%) (*165, 291*). In addition, in the former case, a second geminal bisfluoroxy compound, $CF_3CF(OF)_2$ (55%), was isolated. This compound was found as a product in the fluorination of the monosodium salt of perfluoroacetone hydrate in 3% yield, whereas $(CF_3)_2C(OF)_2$ occurred in 5% yield (*291*).

$$NaOC(CF_3)_2OH + F_2/N_2 \xrightarrow[temp.]{reduced} (CF_3)_2C(OF)_2 + CF_3CF(OF)_2 + others$$

Based on an earlier report by Cady and Cauble (*58*) of the CsF-catalyzed fluorination of $FC(O)OF$ to $CF_2(OF)_2$, DesMarteau and Sekiya (*259, 260*) reasoned that this route might prove to be a general one to $R_fCF(OF)_2$. They cleverly demonstrated that, at reduced temperatures in the presence of CsF, acidic hydrogens of perfluorocarboxylic acids react very readily with fluorine to form the acyl hypofluorite, which is then further catalytically fluorinated *in situ* to give geminal bisfluoroxy molecules.

$$R_fCO_2H + F_2 \xrightarrow[-78 \text{ or } -111^\circ C]{CsF} [R_fC(O)OF] \xrightarrow[F_2]{\text{fast}} [R_fCF(OF)_2]$$

$$R_f = CF_3(84\text{–}100\%);\ C_2F_5(96\%);\ C_3F_7(92\%);\ ClCF_2(100\%)$$

The thermal stability of the $R_fCF(OF)_2$ compounds decreases with increasing number of carbons, with the greatest change from two to three carbons. When $R_f = CF_3$, the parent compound is 98% recovered; when $R_f = C_2F_5$, 35% recovered; and when $R_f = C_3F_7$, 22% recovered after 8 h in Pyrex glass at 53°C. $ClCF_2CF(OF)_2$ was too explosive to measure. On the other hand, $CF_2(OF)_2$ is recovered 100% unchanged after 6 h at 150°C and 40% unchanged after 3 h at 250°C (*175*). All of the geminal bisfluoroxyalkanes are strong oxidizers and explosive and must be handled with care. The greatest tendency toward explosive decomposition was at higher pressures in the gas phase. The known bisfluoroxy compounds are given in Table II.

$$R_fCF(OF)_2 \xrightarrow{53^\circ C} R_fF + COF_2 + O_2$$

Very little chemistry of these bisfluoroxy compounds has been explored, primarily, with the exception of $CF_2(OF)_2$, because of their instability and, in the case of geminal compounds, the inconvenient low-yield syntheses that were available. However, the very stable and easily synthesized $CF_2(OF)_2$ has received some attention. Much of the early reaction chemistry has already been reviewed (*175*).

Although it has been demonstrated that $CF_2(OF)_2$ does not yield $CF_2(ONF_2)_2$ (*138*) with $N_2F_4$ in strict analogy with $CF_3OF$ (*127*), the desired product as well as the monoether hypofluorite has been produced in a slightly different way (*215*). Fluorinated amines and peroxy compounds have been prepared by the $F_2C(OF)_2$ oxidation of the adduct of KCN with $(F_2N)_2C{=}NF$ in a borosilicate pressure vessel (*285, 286*).

$$KF + HNF_2 \xrightarrow[-126 \text{ to } -80^\circ C]{F_2C(OF)_2} F_2C(ONF_2)_2 + F_2C(ONF_2)OF$$

$$CF_2(OF)_2 + KCN{:}\,(F_2N)_2C{=}NF \rightarrow$$
$$(F_2N)_2CF_2,\ CF_3OOC(O)F,\ CF_3OOOCF_3,\ CF_3OOCF_2OF,\ \text{etc.}$$

TABLE II

BISFLUOROXY COMPOUNDS

| Compound | Boiling point (°C) | $\nu_{O-F}$(cm$^{-1}$) | $\phi_{OF}$ | Comments | References |
|---|---|---|---|---|---|
| $FO(CF_2)_3OF$ | — | 886 | 146.0 | Stable at 25°C when pure | *(217)* |
| $FO(CF_2)_4OF$ | −119 (mp) | 886 | 146.7 | Stable at 25°C when pure | *(173)* |
| $FO(CF_2)_5OF$ | −102.9 (mp) | 890 | 146.9 | Stable at 25°C when pure | *(173)* |
| $FOCF_2OOCF_2OF$ | — | 939 | 158.6 | Stable at 25°C when pure | *(174)* |
| $CF_2(OF)_2$ | −64 | 916, 933 | 159.2 | $\Delta H_f^0 = -134.9 \pm 3$ kcal mol$^{-1}$ | *(115, 190)* |
| $CF_3CF(OF)_2$ | −35 | 895 | 150.0 | Greater stability than $C_2F_5OF$ | *(58, 291)* |
| $(CF_3)_2C(OF)_2$ | — | 888 | 148.0 | Extreme tendency to explode | *(291)* |
| $CF_3CF_2CF(OF)_2$ | ~0 | 885 | 154.3 | Decreasing stability with increasing chain length | *(260)* |
| $CF_3CF_2CF_2CF(OF)_2$ | ~40 | 870 | 153.8 |  | *(260)* |
| $ClCF_2CF(OF)_2$ | — | 881 | 150.1 | Very explosive | *(260)* |
| $SeF_4(OF)_2$ | 12.9 | 917 | 179.0 | Stable at 22°C | *(276)* |

In the presence of CsF and $COF_2$, $CF_2(OF)_2$ gave trifluoromethyl(fluoroformyl) peroxide, bistrifluoromethyl trioxide, and fluoroxytrifluoromethane (*8*). However, when $CF_2(OF)_2$ was treated with a mixture of $CsOCF_3$ and CsF at −78 to −5°C (10 h), small amounts of $CF_3OOOCF_3$ (20%) and $CF_3OOOCF_2OOCF_3$ were isolated as well as $O_2$ and large amounts of $CF_3OF$ (*85*). When both $CF_2(OF)_2$ and $COF_2$ were reactants, substantial quantities of $CF_3OOC(O)F$ formed.

Not too surprisingly, $CF_2(OF)_2$ has found an interesting role in thermal and photopolymerizations with hexafluorobenzene, in which copolymers of molecular weight about 2500 have been formed in addition to two new perfluoroethers (*299*). Similar reactions have been studied with hexafluorobicyclo[2.2.0]hexa-2,5-diene (*298*), perfluorobicyclo[2.2.0]hexene oxides (*300*), pentafluoropyridine (*301*), and octafluoronaphthalene (*302*). Use of $CF_2(OF)_2$ in electrophilic fluorinations is discussed in Section VI.

### B. OF Bonded to Selenium

The only known bishypofluorite which does not contain carbon is $SeF_4(OF)_2$ (*276*). The reaction of $KSeO_2F$ with fluorine at reduced temperatures gave *trans*-$FOSeF_4OF$ in about 16% yield. It is a stable gas at room temperature and obeys the vapor-pressure curve $\log P_{mm} = -1386/T + 7.726$ over the range 241–286 K. Some of its spectral data are in Table II. It undergoes alkaline hydrolysis to release oxygen and form $SeO_4^{2-}$.

$$KSeO_2F + 3F_2 \xrightarrow{-78°C} FOSeF_4OF + SeF_5OF + SeF_6 + O_2$$

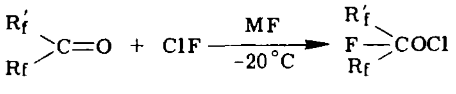
## V. Hypochlorites

### A. Polyfluoroalkyl and Pentafluorosulfur Hypochlorites ($R_fOCl$ and $SF_5OCl$)

### 1. *Preparation and Characterization*

The methods of preparation of $R_fOCl$ and of $SF_5OCl$ are essentially identical with those used for the analogous fluoroxy compounds and hypofluorites, using chlorine monofluoride in place of elemental fluorine. Some examples are as follows.

*a. Chlorofluorination in the Presence of MF.*



$$\mathrm{(R_f')(R_f)C{=}O + ClF \xrightarrow[-20°C]{MF} F{-}C(R_f')(R_f)OCl}$$

(123–125, 249, 324)

$R_f$ = F, $CF_3$, F, $CF_2Cl$

$R_f'$ = F, $CF_3$, $CF_3$, $CF_3$

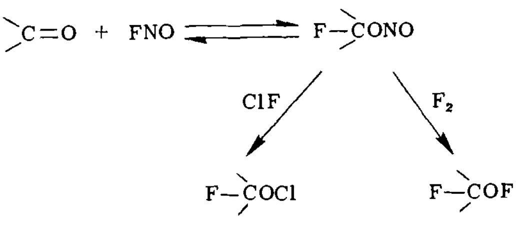
yield > 99% 91% 99%

M = Cs or, less often, K or Rb

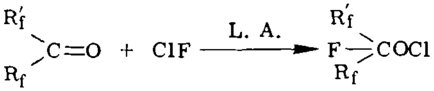
$$FC(O)(CF_2)_3C(O)F + 2ClF \xrightarrow[-20°C]{CsF} ClO(CF_2)_5OCl$$ (*125*)

$$OSF_4 + ClF \xrightarrow[-20°]{MF\ (M = K, Cs)} \underset{>95\%}{SF_5OCl}$$ (*125, 254*)

Also, using FNO, both fluorinations with fluorine and chlorofluorination with ClF occur probably via the formation of an α-fluorinated nitrite (*317*).



### b. *Chlorofluorination in the Presence of a Lewis Acid.*



$$R_f'R_fC{=}O + ClF \xrightarrow{L.\ A.} F{-}C(R_f')(R_f)OCl$$

Lewis acid = HF, $BF_3$, $AsF_5$, ≠ $PF_5$ (*318*)

It is interesting to note that Lewis acids do not catalyze fluorine addition to form fluoroxy compounds.

### c. *Fluoroalcohols with Positive Chlorine-Containing Molecules.*

$$R_fOH + ClF \xrightarrow{25°C} R_fOCl$$

$R_f$ = $(CF_3)_3C$, $(CF_3)_2CH$, $CH_3C(CF_3)_2$, and $CF_3CH_2$ (*324*)

The reactions of ClF with the esters $CF_3(CH_3)CHOS(O)CF_3$ at −78°C and $(CF_3)_2C(CH_3)OS(O)CF_3$ at 25°C formed $CF_3(CH_3)CFOCl$ and $(CF_3)_2CCH_3OCl$, respectively (*177*).

The attempted preparation of *t*-butyl hypochlorite resulted in a sharp detonation. Although no explosion occurred, reactions with $CH_3OH$ or perfluoropinacol gave none of the hypochlorites sought (*324*). The use of $Cl_2O$ as a source of positive chlorine was successful with $COF_2$ to give $CF_3OCl$ (*125*).

Fokin *et al.* (*114*) have used $ClOSO_2F$ as the source of positive chlorine in reaction with rather long-chain polyfluoroalcohols.

$$R_fCH_2OH + FSO_2OCl \xrightarrow{-HSO_3F} \underset{25\text{–}46\%}{R_fCH_2OCl}$$

$R_f$ = $H(CF_2)_2$, $H(CF_2)_4$, $H(CF_2)_6$, $O_2NCF_2$

Perfluoroalkyl hypochlorites and $SF_5OCl$ are more stable thermally than the alkyl hypochlorites. For example, $CF_3OCl$ decomposes slowly at 150°C, and the others have decreasing stability (*125, 324*). When thermal decomposition does occur, the general reaction is, for example,

$$CF_3OCl > (CF_3)_3COCl \sim CH_3C(CF_3)_2OCl \sim (CF_3)_2CHOCl \sim CF_3CH_2OCl > C_2F_5OCl \sim i\text{-}C_3F_7OCl > SF_5OCl$$

$$(CF_3)_3COCl \xrightarrow{\Delta} (CF_3)_2CO + Cl_2 + CF_3Cl + C_2F_6$$

and

$$i\text{-}C_3F_7OCl \xrightarrow{\Delta} CF_3C(O)F + CF_3Cl + (CF_3)_2CO + ClF$$

It is also interesting to note that although these hydrogen-containing fluorohypochlorites are stable to spontaneous decomposition, at least to 80°C, the analogous fluoroxy compounds either are not isolable or have only a very fleeting existence at low temperature. On the other hand, the fluorinated species are much more susceptible to hydrolysis than their alkyl analogs. A qualitative ordering of hydrolytic stabilities shows $(CF_3)_3COCl$ to be the least stable: $(CF_3)_3COCl < CH_3C(CF_3)_2OCl \sim (CF_3)_2CHOCl < CF_3CH_2OCl \ll (CH_3)_3COCl$.

*In situ* generation of partially fluorinated hypochlorites has been used considerably by J. C. Martin and co-workers in the preparation of S(IV) compounds. This preparative method, because it does not result in the synthesis and isolation of new hypochlorites, will be covered in Section V.A.2.*b*.

Vibrational spectral studies and normal coordinate analysis of $CF_3OCl$ have been carried out (*166, 309*). The low-frequency Raman spectrum of $CF_3OCl$ (l) was recorded below 300 $cm^{-1}$, and the $CF_3$ torsional modes were observed (*128*). Also, the vibrational spectra for $SF_5OCl$ have been analyzed (*87*). The low-pressure pyrolysis and UV photolysis of $CF_3OCl$ have been studied to obtain information on the initial decomposition steps. The decomposition products of $CF_3OCl$ were trapped at 8 K in an argon matrix, and the only detectable product was $COF_2$, identified by IR (*63*). Later, matrix-IR (*274*) and Raman (*275*) studies have identified $COF_2$, $CF_3OOCF_3$, $CF_3OF$, ClF, and COFCl. The photochemical decomposition of $CF_3OCl$ at 2537 Å was investigated between 20 and 30°C and total pressures between 45 and 450 torr. The only products formed were $CF_3OOCF_3$ and $Cl_2$. When the decomposition was induced by chlorine atoms at 3650 Å, the same products were observed (*88*). The kinetics of the photochemical reaction between $CF_3OCl$ and CO (*89*), and $CF_3OCl$ and $CF_2CCl_2$ have been examined (*90*).

### 2. *Reactions*

There are many strong attributes that favor fluorohypochlorite reaction chemistry compared to that of the analogous fluoroxy compounds, at least to the synthesis chemist, including higher product yields with concomitantly fewer side products, less harsh conditions, and shorter reaction times. The other side of the coin is their lower thermal and hydrolytic stabilities. Throughout Section V.A.2 these comparisons will be made so that the reader can draw his own conclusions.

*a. Oxidative Displacement and Oxidative Addition.* Advantage was taken of either the hydrolytic instability of $SF_5OCl$ or the positive character of the chlorine in $CF_3OCl$ or $SF_5OCl$ to prepare the first perfluorinated alcohol, $CF_3OH$, or pentafluoroorthosulfuric acid, $HOSF_5$ · $CF_3OH$ decomposes slowly at −20°C, whereas $SF_5OH$ begins to lose HF at −60°C. Fluoroxy compounds react very slowly with water or acid solution (*217*).

$$R_fOCl + HCl \xrightarrow{T} R_fOH + Cl_2$$

$R_f = CF_3, T = -120°C$ (*157, 267*)
$R_f = SF_5, T = -95°C$ (*266*)

With boron trichloride the chlorine is oxidatively displaced to give the first perfluoroalkyl borate esters. The thermal stability of the products is a function of the number of fluorine atoms attached to the α-carbon; thus $(CF_3O)_3B$ decomposes to $3F_2CO$ and $BF_3$ rapidly at 25°C, but $[(CF_3)_3CO]_3B$ is stable. The borates with fluorine atoms on the α-carbon can be stabilized by complexing with trimethylamine by blocking the α-fluoride shift (*319*). A similar displacement occurs with $PClF_4$ and $PCl_2F_3$. These perfluorobutoxyphosphoranes can be stored at 25°C, with the only decomposition being a very slow reorganization

$$3R_fOCl + BCl_3 \xrightarrow{T} B(OR_f)_3 + 3Cl_2$$

$R_f = CF_3,\ i\text{-}C_3F_7,\ t\text{-}C_4F_9$
$T = -20°C, -20°C, 25°C$

$$t\text{-}C_4F_9OCl + PClF_4 \xrightarrow{25°C} \underset{\sim 100\%}{t\text{-}C_4F_9OPF_4} + Cl_2$$

$$2t\text{-}C_4F_9OCl + PCl_2F_3 \xrightarrow{25°C} \underset{\sim 100\%}{(t\text{-}C_4F_9O)_2PF_3} + 2Cl_2$$

of $t\text{-}C_4F_9OPF_4$ to $PF_5$ and $(t\text{-}C_4F_9O)_2PF_3$ (*325*). This compound is also obtained, but in lower yield (15%), in an oxidative addition reaction between $PF_3$ and $(CF_3)_3COCl$ at 0°C (*189*). At 0°C, $(CF_3)_3COCl$ gave essentially quantitative yields of $P[OC(CF_3)_3]_3$ and $P[OC(CF_3)_3]_5$ with $PCl_3$ and $PCl_5$, respectively. $P[OC(CF_3)_3]_5$ hydrolyzes readily to $OP[OC(CF_3)_3]_3$. The latter molecule could not be obtained from $OPCl_3$ + $(CF_3)_3COCl$. Analogous reactions between trifluoromethyl hypochlorite and $PCl_3$, $PCl_5$, and $OPCl_3$ result primarily in fluorination products (*189*). However, with $OPCl_3$, mass spectral data indicate the existence of such species as $OP(OCF_3)_3$, $OP(OCF_3)_2Cl$, and $OP(OCF_3)Cl_2$, which on standing give white solids and volatile materials such as $COF_2$ and $OPF_3$, which would be expected by analogy with the instability of the perfluoroalkyl borate esters with fluorine atoms on the $\alpha$-carbon (*319*).

Oxidative addition reactions of $CF_3OCl$ and $(CF_3)_3COCl$ with compounds in which the coordination number of the central atom is increased by the addition of two $CF_3O$ or two $(CF_3)_3CO$ groups have provided a route to many new sulfuranes. A comparative study of the reactions of $(CF_3)_3COCl$ and $CF_3OCl$ indicates that the vast difference in behavior of these two hypochlorites can be attributed in large degree to the fact that $CF_3OCl$ is more stable, most of its reactions requiring photolysis, which suggests a free-radical mechanism. $(CF_3)_3COCl$ is less stable to thermolysis, hydrolysis, photolysis, and insertion reactions. Reactions of $(CF_3)_3COCl$ are carried out normally at 0°C. If photolytic conditions are employed, the $(CF_3)_3CO\cdot$ radical readily decomposes to the stable $(CF_3)_2CO$. It is not possible to carry out reactions of $(CF_3)_3COCl$ under rigorous conditions [e.g., photolysis of neat $CF_3OCl$ (or $SF_5OCl$)] because of its overall lower stability (*188*). The high yields (>90%) [compare 25% yield from $SF_5OF \xrightarrow{h\nu} SF_5OOSF_5 + F_2$ (*80*)]

$$CF_3OCl(SF_5OCl) \xrightarrow{h\nu} CF_3OOCF_3(SF_5OOSF_5) + Cl_2 \qquad (249, 254, 274)$$

make this an attractive route to these two peroxides, but it is only applicable to hypochlorite precursors that do not contain fluorine on the $\alpha$-carbon where, for example,

$$C_2F_5OCl \xrightarrow[25°C]{h\nu} CF_3Cl + COF_2$$

but for $(CF_3)_3COCl$ at low temperature,

$$(CF_3)_3COCl \xrightarrow[-78°C]{h\nu/\text{quartz}} \underset{30\%}{(CF_3)_3COOC(CF_3)_3}$$

and

$$CH_3C(CF_3)_2OCl \xrightarrow[25^\circ C]{h\nu} CH_3C(CF_3)_2OOC(CF_3)_2CH_3 \qquad (80)$$

The products of the oxidative addition reactions of $CF_3OCl$ and $(CF_3)_3COCl$ differ markedly (*188*), and, in fact, in all reactions attempted the only point of agreement is that neither can be caused to react with $(CF_3)_2SF_2$ under the conditions tried. In Table III some of the reactions are summarized. Although Gombler (*122*) had reported the synthesis of the first stable perfluoroalkyl-containing compound in which three-coordinate sulfur(IV) is bonded to sulfur (II), $CF_3S(O)SCF_3$, **A** (Table III) is the first sulfurane in which four-coordinate sulfur(IV) is bonded to sulfur(II). Although $CF_3OCl$ adds 2 mol of $CF_3O$ to each sulfur of $\overline{SCF_2SC}F_2$, under all conditions tried only 2 mol of $(CF_3)_3CO$ added to one sulfur in the ring **B**. X-Ray studies (*255*) of **B** show that both ring atoms occupy equatorial positions with the C—S—C angle of 77.4(6)° much reduced from the 120° required for the

TABLE III

REACTIONS OF $CF_3OCl$ AND $(CF_3)_3COCl$

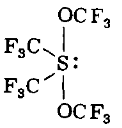
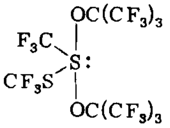
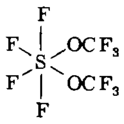
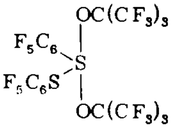
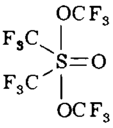
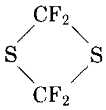
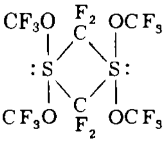
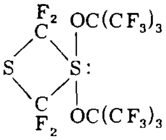
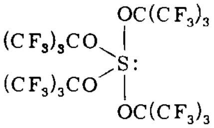
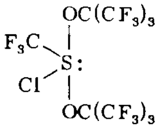
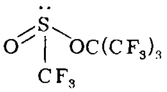
| Reagent | $CF_3OCl$ | $(CF_3)_3COCl$ |
|---|---|---|
| $CF_3SCF_3$ |  $(CF_3)_2S(OCF_3)_2$<br>65%<br>(*154*, *155*) | No reaction |
| $CF_3SSCF_3$ | $CF_3SF_3$, $COF_2$, $Cl_2$<br>$CF_3Cl$ (tr), $SF_4$ (tr) |  $(CF_3)(CF_3S)S[OC(CF_3)_3]_2$<br>**(A)**<br>(*187*) |
| $SF_4$ |  $SF_4(OCF_3)_2$<br>90–95%<br>(*156*) | No reaction |

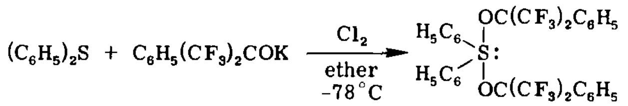
TABLE III (*Continued*)

| Reagent | $CF_3OCl$ | | $(CF_3)_3COCl$ | |
|---|---|---|---|---|
| $C_6F_5SSC_6F_5$ | | |  | (*187*) |
| $CF_3S(O)CF_3$ | <br>86% | (*155*) | No reaction | |
|  | <br>50% | (*154*, *155*) | <br>(**B**) 95% | (*188*, *285*) |
| $SCl_2$ | $COF_2$, $Cl_2$,<br>$SF_4(OCF_3)_2$ | (*188*) | <br>(**C**) 95% | (*188*) |
| $CF_3SCl$ | $CF_3Cl$, $COF_2$, $SF_4$,<br>$Cl_2$, $CF_3SF_3$ | (*188*) | <br>(**D**) | (*188*, *195*) |
| $CF_3S(O)Cl$ | $COF_2$, $Cl_2$, $SOClF$,<br>$SOCl_2$, $CF_3SO_2Cl$,<br>$CF_4$, $CF_3Cl$ | (*188*) | <br>95% | (*188*) |

ideal trigonal–bipyramidal structure. The axial positions are occupied by $(CF_3)_3CO$ groups that are bent over the ring away from the sulfur electron pair, precluding the oxidative addition of additional $(CF_3)_3CO$ groups to the second sulfur.

With either $CCl_3SCl$, $SCl_2$, $S_2Cl_2$, or $CS_2$, at 0°C $(CF_3)_3COCl$ oxidatively adds to sulfur, displacing all other ligands to give the hydrolytically stable $S[OC(CF_3)_3]_4$ (**C**, Table III). The behavior of $(CF_3)_3COCl$ toward $CF_3SCl$ or $CCl_3SCl$ is considerably different. As already noted with $CCl_3SCl$, **C** is obtained, but with $CF_3SCl$ oxidative addition occurs at sulfur with no C—S or S—Cl bond breaking to give **D**, which is quite a different type of chlorosulfurane, with three different ligands. In none of these cases was chlorine also introduced in the oxidative addition reactions.

Alcohols of the type hexafluoro-2-phenyl-2-propanol are converted to hypochlorites by chlorination of a suspension of the alkoxide in anhydrous $CFCl_3$ at −78°C. This can be treated with sulfides in $CH_2Cl_2$ at −78°C to prepare the alkoxysulfonium chloride, which reacts further with the alkoxide to give a sulfurane (*14, 122, 178, 179, 211*). The more convenient route is the treatment of an ether solution of the alkoxide from reaction of the alcohol with potassium metal and, for example, diphenyl sulfide with chlorine at −78°C.



Just as the fluorohypochlorites can be photolyzed neat to form peroxides, so they can combine with other free radicals.

$$2CF_3OCl(SF_5OCl) + N_2F_4 \xrightarrow{h\nu} \underset{71\%}{CF_3ONF_2}\,(\underset{14\%}{SF_5ONF_2}) \qquad (249, 254)$$

$$SF_5OCl + (FC(O)O)_2 \xrightarrow{h\nu} SF_5OC(O)F + SF_5OOC(O)F \qquad (16)$$

Oxidative addition or insertion reactions where the units $R_fO$ and Cl add to the central atom of the reactant are known and, in some cases, well studied. With CO or $SO_2$, perfluoroalkyl and pentafluorosulfur chloroformates or perfluorochlorosulfates are easily formed. $CF_3OC(O)Cl$ and $SF_5OC(O)Cl$ have also been synthesized using photolysis at 25°C (*249, 254*). Insertion of sulfur dioxide into the O—Cl bond occurred readily.

$$R_fOCl + CO \xrightarrow[25°C]{} \underset{\sim 100\%}{R_fOC(O)Cl}$$

$R = CF_3, C_2F_5, i\text{-}C_3F_7, (CF_3)_3C, SF_5, (CH_3)_2CH, (CF_3)_2C(CH_3), CF_3CH_2$ (*322–324, 326*)

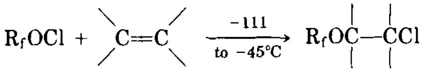
$$R_fOCl + SO_2 \xrightarrow{-20°C} \underset{\sim 50\%}{R_fOSO_2Cl}$$

$R_f = CF_3, C_2F_5, i\text{-}C_3F_7, (CF_3)_3C, (CF_3)_2CH, (CF_3)_2C(CH_3), CF_3CH_2$ (*320–322, 324*)

Again it should be noted that although $CF_3OF$ will react under photolytic conditions with CO to form the fluoroformate $CF_3OC(O)F$ (*17*), the chloroformate could be formed at 25°C. Similarly, the chlorosulfates were obtained at −20°C, but $CF_3OSO_2F$ from $CF_3OF$ and $SO_2$ required 180°C (*303*).

Both $CF_3OCl$ and $(CF_3)_3COCl$ react with mercury to give $COF_2$ and HgClF (*188*) and $(CF_3)_3COHgCl$ (*195*), respectively. The latter is a useful precursor for the introduction of $(CF_3)_3CO$ into a variety of compounds with labile halogen; for example, although $CF_3SCl$ would not react with $(CF_3)_3COH$ neat or in the presence of $(C_2H_5)_3N$, with the mercurial derivative ester formation proceeded smoothly (90% yield).

*b. Addition to Unsaturated Systems.* Perfluoroalkyl, polyfluoroalkyl, and pentafluorosulfur hypochlorites add readily and, in most cases, nearly quantitatively to unsubstituted and halogen-substituted terminal olefins (*7, 180*). With a few exceptions (e.g., $CF_2{=}CFCl$, $CF_3CF{=}CF_2$ and $CF_3OCH{=}CH_2$) the direction of addition to unsymmetric olefins is such that in the resulting ether the chlorine atom of the hypochlorite is bonded to the olefinic carbon with the greatest electron density. In cases where the difference in electron density be-



$$R_fOCl + {>}C{=}C{<} \xrightarrow[\text{to } -45°C]{-111} R_fO\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}Cl$$

| $R_f$ | $>C{=}C<$ |
|---|---|
| $CF_3$ | $CF_2{=}CF_2$, $CH_2{=}CH_2$, $CH_2{=}CHCl$, $CF_2{=}CH_2$ |
| $i\text{-}C_3F_7$ | $CF_2{=}CF_2$ |
| $(CF_3)_3C$ | $CF_2{=}CF_2$, $CH_2{=}CH_2$ |
| $(CF_3)_2CH$ | $CF_2{=}CF_2$ |
| $SF_5$ | $CF_2{=}CF_2$, $CH_2{=}CH_2$ |
| $H(CF_2)_4CH_2$ | $CF_2{=}CF_2$ |
| $H(CF_2)_6CH_2$ | $CF_2{=}CF_2$ |
| $O_2NCF_2CH_2$ | $CF_2{=}CF_2$ |
| $H(CF_2)_4CH_2$ | $CH_2{=}CHC_5H_{11}$ |
| $H(CF_2)_2CH_2$ | $CF_2{=}CFCF_3$ (acid catalyst) |

tween the two carbon atoms of the olefin is small, significant amounts of each isomer are found.

$$\underset{}{CF_3CF{=}CF_2 + CF_3OCl \xrightarrow{0^\circ C} CF_3CFClCF_2OCF_3 + CF_3CF(OCF_3)CF_2Cl} \quad (194)$$

$$7 : 3$$

$$CF_3OCH{=}CH_2 + CF_3OCl \xrightarrow{-111^\circ C} (CF_3O)_2CHCH_2Cl + CF_3OCHClCH_2OCF_3 \quad (7)$$

$$CF_2{=}CFCl + CF_3OCl \xrightarrow{-80^\circ C} CF_3OCFClCF_2Cl + CF_3OCF_2CFCl_2 \quad (180)$$

$$2.5 : 3$$

The highly fluorinated ethers are very stable compounds, for example when $C_2F_4$ is the substrate. They undergo essentially no change when held at 400°C or more for over 1 week or in contact with KOH pellets at 25°C. The less highly fluorinated ethers such as $CF_3OCH_2CH_2Cl$, which have chlorine and hydrogen bonded to vicinal carbon atoms, readily undergo dehydrohalogenation to give fluoroolefins which can be further treated with more hypochlorite. Attempts to add $CF_3OCl$ to either perfluoro-2-butene or perfluoro-2-butyne were unsuccessful up to 150°C (decomposition point of $CF_3OCl$) (*7*).

In the reaction of perfluoro-2-azabut-1-ene with $CF_3OCl$ or $CF_3OF$, the latter acts strictly as a fluorinating agent $\xrightarrow{250-300^\circ C}$ $CF_3(C_2F_5)NF$, whereas $CF_3OCl$ plays a chlorofluorinating role $\xrightarrow{-196 \text{ to } 25^\circ C}$ $CF_3(C_2F_5)NCl$ (*193*). The presence of an acid catalyst causes addition to trifluoromethyl isocyanate, heptafluorobutyronitrile, and bistrifluoromethyl ketene to occur (*113, 114*).

$$H(CF_2)_4CH_2OCl \left\{ \begin{array}{lll} + CF_3NCO & \xrightarrow[H^+]{70-75^\circ C} & CF_3NClC(O)OCH_2(CF_2)_4H \\ + C_3F_7CN & \xrightarrow[H^+]{110-115^\circ C} & C_3F_7C({=}NCl)OCH_2(CF_2)_4H \\ + (CF_3)_2CCO & \xrightarrow{H^+} & (CF_3)_2CClC(O)OCH_2(CF_2)_4H \end{array} \right.$$

### B. POLYFLUOROACYL AND POLYFLUOROALKANESULFONYL HYPOCHLORITES [$R_fC(O)OCl$ AND $R_fSO_2OCl$]

Chlorine derivatives of varying stabilities of several strong fluorinated acids have been synthesized. Although several perfluoroacyl hypofluorites and $FSO_2OCl$ are known and are discussed in this chapter, only very recently have the polyfluoroacyl and polyfluoroalkanesulfonyl hypochlorites been described.

### 1. *Preparation and Characterization*

The synthesis involves a metathesis reaction between a polyfluorocarboxylic acid or its sodium salt and a readily available source of positive chlorine.

$$R_fCO_2M + ClX \xrightarrow{T} R_fC(O)OCl + MX$$

$R_f = CF_3, C_2F_5, C_3F_7, HCF_2, ClCF_2, -CF_2-$; $X = F$; $M = H, Na$

$T = -111$ to $-78°C$ yields ~80–90% *(86, 287)*

$R_f = CF_3, ClCF_2$; $X = OSO_2F$; $M = H, Na$

$T = -78$ to $-45°C$ yields ~90% *(242)*

$$R_fSO_3H + ClF \xrightarrow{-78°C} R_fSO_2OCl + HF \quad (86, 148)$$

$R_f = CF_3, C_4F_9$ 80–100%

DesMarteau preferred the sodium carboxylate precursor because of fewer separation problems (*287*). Where a volatile acyl hypochlorite is formed, Schack has preferred the use of $ClOSO_2F$ with the carboxylic acid rather than ClF because $HSO_3F$ is less volatile than HF. When salts are used, $ClOSO_2F$ has been claimed to be superior to ClF in chlorinating anionic species (*242*).

$$R_fC(O)OCl \xrightarrow{22°C} R_fCl + CO_2$$

$$CF_3SO_2OCl \xrightarrow{22°C} CF_3Cl + SO_3$$

All of the polyfluoroacyl hypochlorites are thermally unstable at 22°C and are explosive. If samples are warmed in a closed system so that the partial pressure of the hypochlorite exceeds 20–50 torr, they explode without fail (*287*). $CF_3SO_2OCl$ slowly decomposes at 22°C, but no comment has been found about its explosiveness. The decomposition in each case proceeds as expected. At low pressure ($<$ 10 torr) in glass, their complete decomposition requires several hours. The relative order of stability at 22°C is $CF_3CO_2Cl > C_2F_5CO_2Cl > C_3F_7CO_2Cl > ClCF_2CO_2Cl > HCF_2CO_2Cl \gg CF_2(CF_2CO_2Cl)_2$. $CF_3C(O)OCl$ and $CF_3C(O)OF$ are about equally stable thermally. The Raman spectrum of $CF_3SO_2OCl$, which suggests $C_1$ symmetry, has been analyzed (*148*). Infrared and Raman spectra of most of these hypochlorites have been recorded.

### 2. *Reactions*

The reaction chemistry of these hypochlorites is typical of compounds that contain positive chlorine.

*a. Oxidative Displacement and Oxidative Addition.* A very powerful route to trifluoromethanesulfonate esters is now available via reactions of $R_fSO_2OCl$ with alkyl or haloalkyl halides. In the case of monohaloalkanes the yields in general are high, but low yields result with dihaloalkanes. It has not been possible to form tri- and tetrasubstituted compounds. All of the esters are colorless, stable compounds at 22°C and higher (*147*). However, when alkyl chlorides are employed multisubstitution occurs readily, that is, $CH_2Cl_2 \rightarrow (CF_3SO_3)_2CH_2$ (45%) + $CF_3SO_3CH_2Cl$ (35%); $(CH_2Cl)_2 \rightarrow (CF_3SO_3CH_2)_2$ (50%) + $CF_3SO_3CH_2CH_2Cl$ (50%); $(ClCH_2)_2CH_2 \rightarrow$ explosion at −55°C; and $HCCl_3 \rightarrow [(CF_3SO_3)_3CH]$ (unstable above 0°C) (*145*). In some cases, in which $CF_3SO_2OCl$ is too vigorous, $CF_3SO_2OBr$, which is a milder but less stable reagent, has been used.

$$CF_3SO_2OCl + RX \xrightarrow{-111 \text{ to } 22°C} XCl + CF_3SO_2OR$$

RX = $CF_3Br$ (95%), $C_2F_5Br$ (58%), $C_3F_7Br$ (65%), $CCl_2F_2$ (82%), $CBr_2F_2$ (44%), $CCl_3F$ (63%), $(CF_2Br)_2$ (62%), $CF_3SO_3CF_2Br$ (30%), *e*-$CF_3CO_2CHFCHFCl$ (80%), *t*-$CF_3CO_2CHFCHFCl$ (90%), *e*$CF_3SO_3CHFCHFBr$ (~100%) (*144, 147*)

$$2CF_3SO_2OCl + Br_2 \xrightarrow{-60,\ -20°C} 2CF_3SO_2OBr + Cl_2 \qquad (148)$$

With small molecules such as CO and $SO_2$, insertion into the O—Cl occurs at low temperature

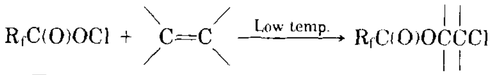
$$R_fC(O)OCl + CO \xrightarrow{-111 \text{ to } -75°C} R_fC(O)OC(O)Cl \xrightarrow{22°C} R_fC(O)Cl + CO_2$$

$$R_f = CF_3,\ C_3F_7 \qquad (86,\ 287)$$

and

$$CF_3C(O)OCl + SO_2 \xrightarrow{-111 \text{ to } -15°C} CF_3C(O)OSO_2Cl$$

*b. Addition to Unsaturated Systems.* Reactions of $CF_3SO_2OCl$ and $CF_3C(O)OCl$ provide a second useful route to esters. Both Schack (*242*) and DesMarteau (*144, 146, 288*) have demonstrated the relative ease with which these two types of hypochlorites saturate olefinic double bonds. It should be noted that in every case the addition reactions were



$$R_fC(O)OCl + \rangle C{=}C\langle \xrightarrow{\text{Low temp.}} R_fC(O)O\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}Cl$$

(*64, 242, 288*)

| R | $\rangle C{=}C\langle$ |
|---|---|
| $CF_3$ | $CF_2{=}CF_2$ (54%); $CF_2{=}CH_2$ (94%); $CF_2{=}CFCl$ (65%) |
| $CF_3$ | $CF_2{=}CCl_2$ (81%); $CH_2{=}CH_2$ (33%); *cis*-$CFH{=}CFH$ (*e*-64%); *trans*-$CFH{=}CFH$ (*t*-65%); $CF_3CF{=}CF_2$ (84%) |
| $CF_2Cl$ | $CF_2{=}CF_2$ (42%); $CF_2{=}CH_2$ (93%); $CF_3CF{=}CF_2$ (74%) |
| $C_2F_5$ | $CF_2{=}CF_2$ (65%); $CF_2{=}CH_2$ (80%) |
| *n*-$C_3F_7$ | $CF_2{=}CF_2$ (66%); $CF_2{=}CH_2$ (80%) |
| $HCF_2$ | $CF_2{=}CF_2$ (<1%); $CF_2{=}CH_2$ (95%) |

regiospecific, suggesting concerted polar addition. Invariably, the positive chlorine is found at the most electronegative carbon. The addition of $CF_3C(O)OCl$ to *cis*- and *trans*-$CFH{=}CFH$ gives a single different diastereomer, erythro and threo, respectively. Therefore, the reactions are stereospecific.

The behavior of $CF_3SO_2OCl$ exactly mimics that of the polyfluoroacyl compounds, with addition occurring at low temperature to give only one structural isomer in each case (*144, 146*). Also, *cis*- and *trans*-$CHF{=}CHF$ form a single, different diastereomer.

All of the new esters are stable in glass at 22°C, and all have good thermal stability at considerably higher temperatures, with the majority of the carboxylates approximately being 100% recovered after 10 h at 200°C. Most of the trifluoromethanesulfonates show no decomposition to at least 100°C. The carboxylate esters with $\alpha$-fluorine in the carbalkoxy group are readily decomposed to acid fluorides by fluoride ion (KF but not NaF).

## C. FLUOROSULFURYL HYPOCHLORITE (CHLORINE FLUOROSULFATE) ($FSO_2OCl$)

### 1. *Preparation and Characterization*

Fluorosulfuryl hypochlorite was invented by Cady and Gilbreath via the extended thermal reaction of chlorine with peroxydisulfuryl difluoride (*120*). Later workers have demonstrated that ClF and $SO_3$ will react to form the yellow $FSO_2OCl$, essentially quantitatively after a slow warm-up to 25 from −196°C (*129, 252*). The Raman spectrum (*219*) of liquid $FSO_2OCl$ and the IR spectra of the gas and solid (*65, 313*) have been assigned. $C_s$ symmetry is suggested.

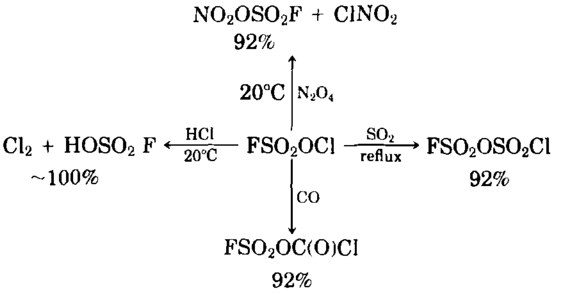
### 2. *Reactions*

One of the more useful reactions of $FSO_2OCl$, now that it can be synthesized by a route that does not require $S_2O_6F_2$, is to subject it to UV radiation to provide an alternate synthesis of $S_2O_6F_2$. A somewhat novel use is to spray a mixture of $FSO_2OCl$ and $H_2O_2$ containing 20% $H_2O$ and 1% NaOH on the bottom of a vessel at −78° to leave a gas stream that contains approximately 40% singlet $O_2$ (*214*).

$$ClOSO_2F \xrightarrow[2\text{–}4\ h]{h\nu} \underset{94\text{–}97\%}{FSO_2OOSO_2F} + Cl_2 \qquad (243)$$
$$25^\circ C$$

As has been cited previously, $FSO_2OCl$ is a valuable alternate source of positive chlorine for use as a precursor of other hypochlorites (*64, 114, 242*).

*a. Oxidative Displacement and Oxidative Additions.* Fluorosulfuryl hypochlorite reacted predictably with small molecules,



$$\begin{tikzcd} & \underset{92\%}{NO_2OSO_2F + ClNO_2} & \\ \underset{\sim100\%}{Cl_2 + HOSO_2F} & FSO_2OCl \arrow[l, "HCl", "20^\circ C"'] \arrow[u, "20^\circ C", "N_2O_4"'] \arrow[r, "SO_2", "reflux"'] \arrow[d, "CO"'] & \underset{92\%}{FSO_2OSO_2Cl} \\ & \underset{92\%}{FSO_2OC(O)Cl} & \end{tikzcd}$$

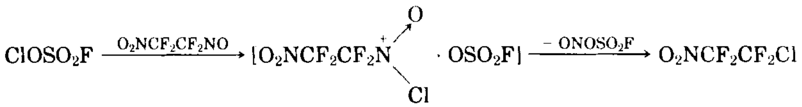
(*102, 119*)

However, with ozone the previously known $ClO_2OSO_2F$ and oxygen resulted (*241*).

This reactive molecule is insensitive to naked flame and mechanical effects, but at approximately 20°C it reacts explosively with $H_2O$ and $(CH_3)_2CO$, induces combustion of $C_6H_6$ and $C_6H_{12}$, and reacts vigorously with chlorocarbons and polyfluorinated lubricants (*111*). However, at −100°C it reacts with an excess of $C_6H_6$ to give $C_6Cl_6$ in 80% yield (*100, 104*). A similar behavior has been noted with 1,3,5-$Cl_3C_6H_3$ at −25°C (*108*). The chlorination reaction is substantially slowed when a nitro group is introduced into the aromatic ring. At 25°C, 1,3,5-trinitrobenzene does not react at all with $ClOSO_2F$.

$$O_2NC_6H_5 + FSO_2OCl \xrightarrow{-10\text{ to }25^\circ C} \underset{60\%}{O_2NC_6Cl_5} + \underset{x\,=\,1,\,2,\,3,\,4}{O_2NC_6H_xCl_{5-x}}$$

The complex of $FSO_2OCl$ with $SbF_5$ has more chlorinating activity than $FSO_2OCl$ alone. At 20°C this reagent chlorinates pentafluorobenzene and 4,4′-dihydroperfluorobiphenyl to pentafluorochlorobenzene and 4,4′-dichloroperfluorobiphenyl in 95 and 60% yields, respectively (*103, 108*). The reactive species has been claimed to be $Cl(FSO_2OSbF_5)$. The latter reacts with $C_6F_6$ to give $C_6F_6Cl^+$. However, $FSO_2OCl$, unaided by $SbF_5$, will substitute the nitroso group by chlorine in perfluoronitrosoalkanes. Other nitro derivatives have been realized by using salts of nitro compounds with $FSO_2OCl$ (*111*). In two very nice



$$ClOSO_2F \xrightarrow{O_2NCF_2CF_2NO} [O_2NCF_2CF_2\overset{+}{N}(\rightarrow O)(Cl)\cdot OSO_2F] \xrightarrow{-ONOSO_2F} O_2NCF_2CF_2Cl$$

reactions, Schack and co-workers have used $FSO_2OCl$ to prepare $ClOClO_3$ and $SeF_5Cl$ from appropriate salts.

$$RC(NO_2)_2M + FSO_2OCl \xrightarrow[-30\text{ to }0°C]{CCl_2FCClF_2} RC(NO_2)_2Cl$$

$$R = NO_2,\ CN;\ M = K,\ Na$$

$$MClO_4 + FSO_2OCl \xrightarrow{-45°C} MSO_3F + ClOClO_3 \qquad (250)$$

$$M = Cs,\ NO_2$$

$$CsSeF_5 + FSO_2OCl \xrightarrow{25°C} CsOSO_2F + SeF_5Cl \qquad (253)$$

Fokin and co-workers have synthesized perfluoroacyl fluorosulfates from perfluoroacyl chlorides in the presence of fluorosulfuric acid at

$$R_fC(O)Cl + FSO_2OCl \xrightarrow[20°C]{HSO_3F} R_fC(O)OSO_2F + Cl_2$$

$$R_f = CF_3,\ C_3F_7,\ C_8F_{17}$$

20°C (*105*). Perfluoroalkyl halides $R_fX$ ($R_f = C_{1-10}$ perfluoroalkyl; X = Cl, Br, I) result from treating the perfluorocarboxylic acid or its salt with $FSO_2OCl$ (*247, 248*). It is likely that the corresponding acyl hypochlorite is the unstable intermediate.

$$R_fC(O)OM + FSO_2OX \xrightarrow{25-50°C} R_fCl + CO_2 + NaOSO_2F$$

$$M = H,\ Na,\ Ag,\text{ or }CF_3C{=}O;\ X = Cl,\ Br;\ R_f = CF_3\ (90\%),\ ClCF_2\ (85\%),\ CF_3CF_2\ (79\%),\ C_7F_{15}\ (78\%),\ CF_2CF_2CF_2\ (86\%)$$

Additionally, both the Soviet and the Rocketdyne workers have demonstrated that $FSO_2OCl$ is an excellent reagent for substitution halogen atoms in haloalkanes, halofluorocarbons, and various esters and polyfluoroethers. Reactions of chlorofluorocarbon ethers that can be readily obtained from addition of hypochlorites to perfluoroolefins (*7, 180*) with $FSO_2OCl$ proceed very slowly (2 or 3 weeks, 110–140°C) when 10–20 mol % bromine is added, but in high yield (*245*). Pure $FSO_2OCl$ does not produce appreciable reaction under the same conditions, which suggests the reactive reagent is $FSO_2OBr$ generated *in situ*.

$$RCH_2Cl + FSO_2OCl \xrightarrow{-30°C} RCH_2OSO_2F + Cl_2$$

$$R = Cl, CH_2Cl, COOC_4H_9, COOC_2H_5 \qquad (105)$$

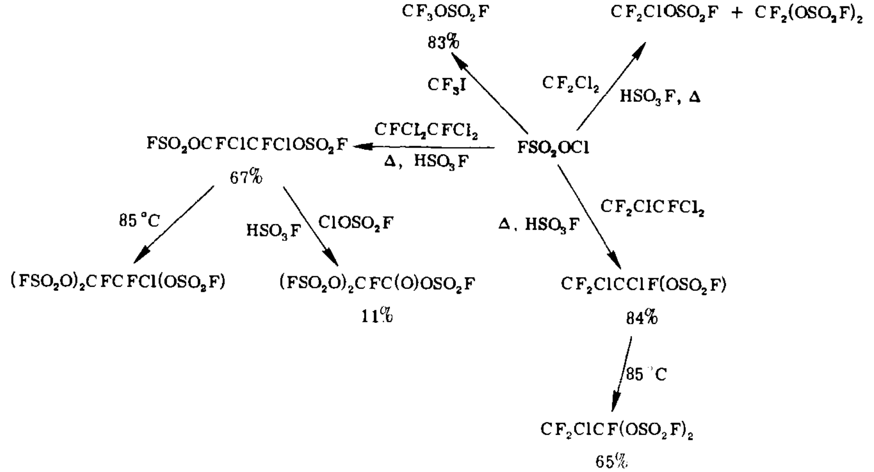
$$HCCl_2CCl_2H + FSO_2OCl \rightarrow HCCl_2CClHOSO_2F \xrightarrow{FSO_2OCl}$$

$$\underset{3:1}{Cl_2CHCH(OSO_2F)_2 + (FSO_2OCHCl)_2} \qquad (108)$$

$$R_fOCF_2CF_2Cl + FSO_2OCl \xrightarrow{Br_2} R_fOCF_2CF_2OSO_2F + Cl_2$$

$$R_f = CF_3\ (90\%),\ SF_5\ (71\%)$$

It has been claimed that the following reactions did not proceed, even at elevated temperatures, without excess fluorosulfuric acid (*110, 112*).



On the other hand, under strictly anhydrous conditions the displacement of halogen from halofluorocarbons by fluorosulfate has been carried out in high yields, with reactivity decreasing I > Br > Cl and with no intentional addition of fluorosulfuric acid (*248*). Under the condi-

TABLE IV

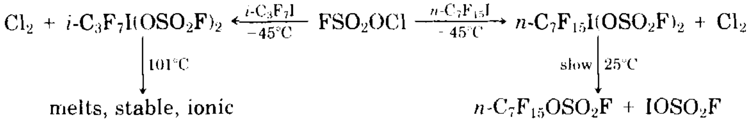
REACTIONS OF $ClOSO_2F$ AND $ClOSO_2F/Br_2$

| Reactant | Temperature (°C) | Product (%) |
|---|---|---|
| $ClCF_2CF_2Cl$[a] | 130 | $ClCF_2CF_2OSO_2F$ (90) |
| $ClCF_2CF_2Cl$[b] | 140 | $ClCF_2CF_2OSO_2F$ (89)<br>$FSO_2OCF_2CF_2OSO_2F$ (6) |
| $CF_3CFClCF_2Cl$[b] | 25 | $CF_3CFClCF_2OSO_2F$ (76) |
| $CF_3CFBrCF_2Br$[a] | 25 | $CF_3CFBrCF_2OSO_2F$ (70) |
| $n$-$C_7F_{15}I$[a] | 25 | $n$-$C_7F_{15}OSO_2F$ (85) |
| $CF_3CF_2Cl$[b] | 130 | $CF_3CF_2OSO_2F$ (22) |
| $ClCF_2CF_2OSO_2F$[b] | 140 | $FSO_2OCF_2CF_2OSO_2F$ (31) |
| $CF_3CF_2Br$[a] | 25 | $CF_3CF_2OSO_2F$ (96) |
| $BrCF_2CF_2Br$[a] | 25 | $BrCF_2CF_2OSO_2F$ (40) |
| $BrCF_2CF_2Br$[a] | 65 | $FSO_2OCF_2CF_2OSO_2F$ (64) |
| $i$-$C_3F_7I$[a] | −45 | $[(i\text{-}C_3F_7)_2I]^+[I(SO_3F_4)]^-$ (~100) |

[a] With $ClOSO_2F$.
[b] $ClOSO_2F/Br_2$.

tions used, it was demonstrated that (1) iodides reacted regardless of being primary or secondary; (2) only primary bromides or chlorides reacted; (3) the reactivity of $FSO_2OCl$ was enhanced by the addition of catalytic amounts of bromine, but not sufficiently to cause reaction with secondary bromides or chlorides; and (4) several primary chlorides were unreactive, that is, $C_2F_5Cl$, $C_7F_{15}Cl$, $CF_3CFClCF_3$, $CF_3CFClCF_2Cl$, $ClCF_2CF_2OSO_2F$, and $CF_3CFClCF_2OSO_2F$ (Table IV).

The iodide reactions are particularly interesting, with $-OSO_2F$ first oxidatively adding to iodine, followed by slow elimination of $IOSO_2F$ in the $n$-heptyl case (*248*). It has been demonstrated that the combination of fluorosulfonation of a fluorocarbon halide with $FSO_2OCl$, conversion



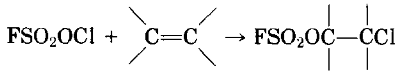
$$\begin{tikzcd}
Cl_2 + i\text{-}C_3F_7I(OSO_2F)_2 \arrow[d, "101^\circ C"] & FSO_2OCl \arrow[l, "i\text{-}C_3F_7I"', "-45^\circ C"] \arrow[r, "n\text{-}C_7F_{15}I", "-45^\circ C"'] & n\text{-}C_7F_{15}I(OSO_2F)_2 + Cl_2 \arrow[d, "slow"', "25^\circ C"] \\
\text{melts, stable, ionic} & & n\text{-}C_7F_{15}OSO_2F + IOSO_2F
\end{tikzcd}$$

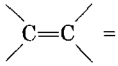
of the fluorosulfate to an alkali-metal perfluorocarboxylate with an alkali metal hydroxide, and subsequent further reaction of the perfluorocarboxylate with $FSO_2OCl$ provide a route to a high-yield, chain-shortening reaction.

*b. Addition to Unsaturated Systems.* At temperatures between −20 and 20°C, $FSO_2OCl$ adds with ease to hexafluorobenzene, with the products obtained dependent upon the stoichiometry used (*109*). Additions to olefins, with the exception of $CF_2{=}CFCl$, from which two isomers were obtained, were according to Markownikoff's rule and in high yield (90–95%) (*102, 106–108, 120, 194*). Reactivity of $FSO_2OCl$ with olefins in increasing order of vigor is $CF_2{=}CF_2 < CFCl{=}CFCl \simeq CF_2{=}CF_2Cl > CF_3CF{=}CF_2 < (CF_3)_2C{=}CF_2$ (*107*). Bistrifluoromethyl ketene reacted easily at −70°C (*106*). Complete saturation occurs with acetylene in Freon 113 at −25°C to give $Cl_2CHCH(OSO_2F)_2$ (>90% yield) and $(FSO_2OCHCl)_2$ (5–7%). The former compound has high thermal and hydrolytic stability. However, with propyne and 2,2-dimethyl-3-pentyne, product decomposition results below 25°C (*108*).

$$C_6F_6 + FSO_2OCl \xrightarrow{\text{Freon 113}} C_6F_6Cl(OSO_2F) + C_6F_6Cl_2(OSO_2F)_2 + C_6F_6Cl_3(OSO_2F)_3$$

bp (°C): 60 (30 torr) 70 (1 torr) 110 (1 torr)


$$FSO_2OCl + \;{>}C{=}C{<} \rightarrow FSO_2OC{-}CCl$$


$= CF_3CF{=}CF_2, C_2F_3Cl, C_2F_2Cl_2, C_2F_4, C_2Cl_4, CF_2{=}C(CF_3)_2,$
$C_2HCl_3$ (slow decomposition)

With nitriles the products obtained are a function of the stoichiometry of the reaction (*108*).

$$\underset{1:1}{R_fCN + FSO_2OCl} \xrightarrow{-45 \text{ to } -35^\circ C} R_fC({=}NCl)OSO_2F$$

$R_f = CF_3OCF_2$ (79%), $n$-$C_3F_7$ (89%), $n$-$C_4F_9$ (61%), $CF_2NO_2$ (90%)

$$\underset{1:2}{R_fCN + 2FSO_2OCl} \rightarrow R_fC({=}NCl)OSO_2F + R_fC(O)OSO_2F + S_2O_5F_2$$

$R_f = n$-$C_3F_7$, $n$-$C_4F_9$

The products found can be rationalized as follows.

$$R_fCN \xrightarrow{FSO_2OCl} R_fC({=}NCl)OSO_2F \xrightarrow{FSO_2OCl}$$
$$[R_fC(OSO_2F)_2NCl_2] \xrightarrow{FSO_2OCl} R_fC(O)OSO_2F + S_2O_5F_2 + [NCl_3]$$

When $FSO_2OCl$ is treated with the sodium salt of dinitroacetonitrile, the yield of the chloro derivative is reduced because monoaddition at the nitrile function occurs as well (*111*).

$$\mathrm{FSO_2OCl}\left\{\begin{array}{llll} + \ \mathrm{CF_3NCO} & \xrightarrow[25^\circ\mathrm{C}]{-78\ \mathrm{to}} & \mathrm{CF_3N(Cl)C(O)OSO_2F} & (279) \\ & & \quad 96\% & \\ + \ \mathrm{CF_3C(O)NCO} & \xrightarrow{25^\circ\mathrm{C}} & \mathrm{CF_3C(O)N(Cl)C(O)OSO_2F} & \\ & & \quad {\sim}90\% & \\ + \ \mathrm{(NF_2)_2C{=}NF} & \xrightarrow{-78^\circ\mathrm{C}} & \mathrm{ClFNC(NF_2)_2OSO_2F} & (98,\ 101) \\ & & \quad 76\% & \\ + \ \mathrm{C_2F_5N{=}CF_2} & \xrightarrow{-78^\circ\mathrm{C}} & \mathrm{C_2F_5N(Cl)CF_2OSO_2F} & (193) \end{array}\right.$$

In the majority of cases with molecules that contain carbon–nitrogen double bonds, saturation with $FSO_2OCl$ occurs with ease. However, with $(CF_3)_2C{=}NF$, fluorine abstraction was found. With ClNSO, sulfur–nitrogen bond breaking occurs with concomitant formation of thionyl fluorosulfate (*167*).

$$\mathrm{(CF_3)_2C{=}NF + FSO_2OCl} \xrightarrow[-78\ \mathrm{to}\ 20^\circ\mathrm{C}]{\mathrm{N_2}} \underset{74\%}{\mathrm{(CF_3)_2C{=}NOSO_2F}} \qquad (99)$$

## D. PENTAFLUOROSELENIUM HYPOCHLORITE ($SeF_5OCl$)

Because $OSeF_4$ is unstable, $SeF_5OCl$ cannot be obtained in a manner analogous to that for $SF_5OCl$. However, chlorine monofluoride reacts readily with $Hg(OSeF_5)_2$ to form the thermally stable but easily hydrolyzed straw-yellow $SeF_5OCl$. It melts at −115°C and boils at 31.5°C. With $H_2O$, $SeF_5OH$ and $Cl_2O$ have been found. The IR and Raman spectra of $SeF_5OCl$ have been assigned (*263*), and the $^{19}F$-NMR spectrum has been reported (*262, 265*).

$$\mathrm{Hg(OSeF_5)_2 + ClF} \xrightarrow{25^\circ\mathrm{C}} \underset{93\%}{\mathrm{SeF_5OCl}} \mathrm{+ HgF_2} \qquad (265)$$

Although $SeF_5OCl$ should be a useful precursor to new compounds that contain the $SeF_5O$ group, little reaction chemistry has been reported. However, it has been demonstrated that compounds with iodine(I) and iodine(III) are possible but of low stability (*265*). Dibromomethane gives $CH_2(OSeF_5)_2$ with $SeF_5OCl$ (*139*).

$$\mathrm{SeF_5OCl}\left\{\begin{array}{lll} + \ \mathrm{ICl} & \xrightarrow{\mathrm{CCl_3F}} & \mathrm{SeF_5OI + Cl_2} \\ & & \quad \text{brown} \\ + \ \mathrm{ICl_3} & \xrightarrow{\mathrm{CCl_3F}} & \mathrm{(SeF_5O)_3I + 3Cl_2} \\ & & \quad \text{orange–red} \end{array}\right.$$

## E. Pentafluorotellurium Hypochlorite ($TeF_5OCl$)

The essentially quantitative preparation of $TeF_5OCl$ was realized via the reaction of chlorine monofluoride with $Hg(OTeF_5)_2$ at 25°C. The yellow liquid (mp −121°C; bp 38.1°C) is hydrolyzed easily to $Cl_2O$ and $TeF_5OH$ (*269*). The gas-phase IR and liquid Raman spectra of $TeF_5OCl$ have been assigned (*263*), and the $^{19}$F-NMR spectrum has been discussed (*262*).

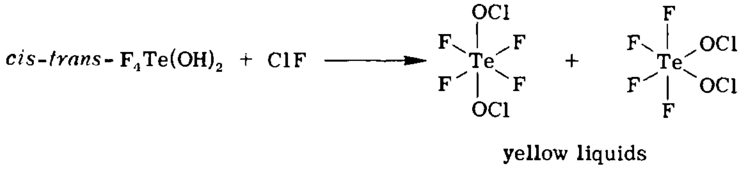
The greater stability of hexavalent tellurium permits the formation of stable iodine derivatives. Also, the reaction of bromine with $TeF_5OCl$ gives the stable, red $TeF_5OBr$ (*264*).

$$ICl_3 + 3TeF_5OCl \rightarrow \underset{\text{orange}}{I(OTeF_5)_3} + 3Cl_2$$

$$I(OTeF_5)_3 + I_2 \leftarrow \underset{\text{brown}}{3IOTeF_5}$$

## F. *cis*-and *trans*-Tetrafluorotellurium Bishypochlorite [$TeF_4(OCl)_2$]

A mixture of *cis*- and *trans*-$F_4Te(OH)_2$ is obtained when $TeF_5OH$ and $Te(OH)_6$ are melted together. This mixture, when treated with ClF, gave the first bishypochlorites. When these bishypochlorites were treated with elemental bromine, the rather unstable red liquid *cis*- and *trans*-$TeF_4(OBr)_2$ formed (*268*).



## G. *cis*- and *trans*-Iodine(VII) Oxytetrafluoride Hypochlorite ($OIF_4OCl$)

Demonstrating the usefulness of $FSO_2OCl$ as a source of positive chlorine, Christe and co-workers were able to synthesize the first iodine hypochlorite:

$$CsIF_4O_2 + FSO_2OCl \xrightarrow{-78°C} CsOSO_2F + OIF_4OCl \qquad (70).$$

Because of its high reactivity and thermal instability, this orange liquid was not well characterized. However, based largely on its gas-phase IR spectrum ($\nu_{OCl}$ = 763 cm$^{-1}$), which is similar to that of the more stable $OIF_4OF$, with stretching modes shifted to slightly lower frequencies, its existence is likely. Attempts to isolate fluorocarbon derivatives of $OIF_4OCl$ by addition to $C_2F_4$ at 25°C resulted in products such as $COF_2$, $CF_3COF$, $ClCF_2OF$, $C_2F_5Cl$, and $IF_5$.

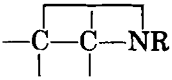
## VI. Applications

A detailed discussion of the applications of $R_fOF$ as versatile and useful electrophilic fluorinating reagents or as general reagents for C-fluorinations under free-radical conditions is beyond the scope of this chapter. The interested reader is urged to peruse reviews of the subject (*18, 19, 130, 160*). However, what follows are notes on the specific applications of primarily $CF_3OF$ and also $CF_2(OF)_2$, $SF_5OF$, $FSO_2OF$, $CF_3CF_2OF$, $CF_3C(O)OF$, and other $R_fOF$ species.

Cady and Allison (*4*) first demonstrated that $CF_3OF$, under photolytic conditions, adds essentially quantitatively to $C_2H_4 \rightarrow CF_3OC_2H_4F$ and, with benzene in $CCl_3F$ at −78°C, gives $C_6H_5F$ (65%) and $C_6H_5OCF_3$ (10%). The first workers to use $CF_3OF$ as a fluorinating reagent under non-free-radical conditions were Shreeve and Ratcliffe, who demonstrated that $CF_3OF$ smoothly fluorinated $CF_3SCl$ to $CF_3SF_3$ (95–100%) at −78°C (*220*). Others have used $CF_3OF$ to fluorinate organic sulfides oxidatively, but the claimed fluorosulfuranes and fluoropersulfuranes have not been isolated (*81, 82*). Cyclic difluorophosphoranes result from the respective cyclic phosphines (*60, 78, 83*). Stable alkoxyaryltrifluoroperiodanes have been synthesized from 2,5-$CH_3IC_6H_3C(CF_3)_2OH$ or 2-$IC_6H_4C(CH_3)_2OH$ with $CF_3OF$ (*5, 6*).

Action may occur at carbon, for example, $CF_3OF$ reacts with activated olefins to convert 3-methoxycholest-2-ene to 2$\alpha$-fluorocholestanone (*24*); at aromatic rings, 2,6-dimethylphenol → 6-fluoro-2,6-dimethyl-2,4-cyclohexadienone (*3, 23, 142, 207*); at unactivated and deactivated unsaturated linkages of steroids (*21, 22, 61*); with photolysis, $c\text{-}C_6H_{12} \rightarrow c\text{-}C_6H_{11}F$ (44%) (*161*); and with fluorination of a wide variety of organic compounds, for example, $CH_3C(O)OH \rightarrow FCH_2C(O)OH$ and 4-$(C_6H_5CH_2CH_2)C_6H_4C(CH_3)_2NH_2 \rightarrow$ 4-$(C_6H_5CF_2CF_2)C_6H_4C(CH_3)_2NH_2$ [with $CF_3OF$, $SF_5OF$, or $CF_3CF_2OF$ in the presence of a free-radical-producing initiator (*158, 159*)]. $(CF_3)_3COF$, $(CF_3)_2C(OF)C_2F_5$, $SF_5OF$, $CF_2(OF)_2$, and $CF_3OF$ act as electrophilic fluorinating reagents in solution in the absence of radical initiators (*34*). With $CF_3OF$, 5-fluorouracil is prepared directly from uracil (*133, 192, 227*); 5-fluorocytosine and its nucleosides directly from cytosine, cytidine, etc. (*224, 226*); griseofulvin to its 5-fluoro derivative (*33*). Photofluorination of diarylsulfones, for example, $4\text{-}O_2NC_6H_4SO_2C_6H_4NHC(O)CH_3\text{-}4 + CF_3OF \xrightarrow{h\nu} 4\text{-}O_2NC_6H_4SO_2C_6H_3FNHC(O)CH_3\text{-}3,4$ [which, when hydrolyzed → $4\text{-}O_2NC_6H_4SO_2C_6H_3FNH_2\text{-}3,4$, which is useful as poultry feed additives for treatment and prophylaxis of Marek's disease (*143*)]. $CF_3OF$ is used in synthesis of *N*-fluoroamines, for example, *p*-$RC_6H_4CH{=}NR' \rightarrow$ *p*-$RC_6H_4CF_2NFR'$ and the intermediates *p*-$RC_6H_4CF{=}NR'$ (*170*) and direct preparation of 2′-amino-2′-deoxy-5-fluorouridine (*271*). Tetrahydropyrimidine-2,4-diones react to form 6-oxygenated 5-fluoropyrimidinediones (*20*), and fluorination of naphthalene and anthracene derivatives (*209*) occurs with $CF_3OF$. $CF_3OF$ adds across double bonds in *cis—trans*-stilbenes (*28*). With $CF_3OF$, $SF_5OF$, and $CF_2(OF)_2$, secondary sulfonamides react to form *N*-fluoro derivatives (*26, 35, 131, 132*). Schiff bases with $CF_3OF$ in alcohol media react to form *N,N*-difluoroamines (*30*). Fluorination may occur at saturated carbons, for example, with adamantanes and steroids (*27, 31, 32*). Antidepressant properties have been claimed for trifluoromethoxy azepines or azepinones (*25, 162*).

With $CF_3OF$ the following transformations occur: methyl acetyl glycyrrhetate → monofluoroderivative (*236*); phenanthrenes → fluorinated K-region ketones (*210*); D-lactal hexaacetate → 2-deoxy-2-fluorolactose (*50, 151*); 2,3-benzofuran in methanol → fluorinated methoxy adduct (*29*). Reaction also occurs with diazoketones, for example, $C_6H_5C(O)CHN_2 \rightarrow C_6H_5C(O)CHF_2$ (14%) + $C_6H_5C(O)CHF(OCF_3)$ (10%) (*171, 310*); with 2-aminothiols and thiolamino acids in HF(l) → aminoalkyl fluorides and fluoroaminoacids, for example, D-penicillamine → D-3-fluorovaline (*163*).

5-Fluorouracil derivatives have been reportedly obtained from cytosine derivatives by using $FSO_2OF$ in aqueous solution (?) (*284*). With $CF_3OF$, [*carboxy*-$^{14}C$]orotic acid is fluorinated to [*carboxy*-$^{14}C$]-5-fluoroorotic acid (*272*); 2′,3′,5′- tri-*O*-acetyluridine to 5-fluorouridine, (*225*), and 2′-deoxyuridine to 5-fluoro-2′-deoxyuridine (*77*). Substituted uracils are fluorinated to 5-fluorouracil derivatives (*96*), and with 1,1-diphenylethylene a mixture of $(C_6H_5)_2C(OCF_3)CH_2F$, $(C_6H_5)_2C(CH{=}C(C_6H_5)_2)CH_2F$, $(C_6H_5)_2CHCH_2F$, $(C_6H_5)_2C{=}CHF$, and $(C_6H_5)_2C(OCF_3)CHF_2$ is obtained (*208*). $CF_3OF$ also reacts with a protected 2-*C*-cyano-2-deoxyglycal and a protected 3-amino-3-deoxyglucal to give 2-deoxy-2-fluoropyranose derivatives (*39*); a trichloromethiazide (6-chloro-3-dichloromethyl-7-sulfamoyl-3,4-dihydro-2*H*-1,2,4-benzo[*e*]thiadiazine 1,1-dioxide) to form a 5-fluoroderivative (*36*); N-nonsubstituted aziridines to give  $-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-NR$ [R = F, C(O)F (*256, 257*)];

and N-substituted aziridines via ring opening and 1,3-addition of F on N and $OCF_3$ on C (*256, 258*). $\alpha$-Fluorocarbonyl compounds $R_2CFC(O)R'$ (R = H, alkyl, cycloalkyl, aryl, optionally substituted by halogen or alkoxy; R′ = H, alkyl, haloalkyl, cycloalkyl, silyl, OH, alkoxy, aryloxy, amino, and *S*-heterocycle; RR′ = diradical) result from conversion of carbonyl compounds $R_2CHC(O)R'$ to their silyl enol ethers, following by fluorination with $CF_3OF$ ($CCl_3F$, −70°C) (*183, 184*).

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