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Fluorinated compounds that contain catenated oxygen, sulfur or nitrogen atoms

Robert L. Kirchmeier and Jean'ne M. Shreeve
Department of Chemistry, University of Idaho, Moscow, ID 83843 (U.S.A.)
R.D. Verma
Department of Chemistry, Panjab University, Chandigarh-160014 (India)

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A. INTRODUCTION

With the exception of compounds of carbon, it would appear that molecules containing catenated atoms of other elements are relatively unstable. While there is no element that can compete with carbon in the number of catenated atoms or in the numbers of compounds that contain such chains of atoms, it is also possible to prepare stable catenated species of other elements, especially when fluorine atoms or fluorinated groups are present. It is interesting to note the surprising thermal stability of catenated nitrogen compounds, e.g. pyrolysis of $CF_3N{=}NCF_3$ at 325°C or at 483°C gives 50 or 30% yields, respectively, of $(CF_3)_2NN(CF_3)_2$. At first glance this is a truly remarkable stability until one considers the thermal stabilities of the related chalcogen compounds, i.e. CF_3OOCF_3 (can be prepared at >325°C) and $CF_3S_xCF_3$ ($x=1$–4) (stable to at least 300°C). The stability of the higher oxygen compounds decreases markedly with CF_3OOOCF_3, decomposing at ~70°C, and with $CF_3OOOOCF_3$, not yet synthesized. However, a sharp decrease in thermal stability is not observed either for fluoroalkyl-substituted catenated sulfur compounds as indicated above or for the analogous nitrogen compounds. Earlier workers had prepared fluoro-substituted triazanes which were stable at least to their boiling points (~70°C). In addition, we have reported the new tetrazanes, $[CF_3(CF_3CF_2)NNR_f]_2$ ($R_f=CClF_2$, CF_2CF_3, $CF(CF_3)OR_f$) and the exciting more highly substituted species $[CF_3(C_2F_5)NNCF_2N(CF_3)N(C_2F_5)CF_3]_2$. These materials are very stable hydrolytically, shock insensitive and stable in glass to at least 100°C. Our aim in this review is to give the reader a broad picture of the advances made in fluorinated compounds that contain catenated oxygen, sulfur or nitrogen atoms.

B. OXYGEN FLUORIDES

The oxygen fluorides constitute a group of compounds composed of the two most electronegative elements. These materials are high-energy oxidants and have attracted considerable attention in the past as possible oxidizers in fuels for rocket propulsion systems. Several earlier reviews covered the syntheses and chemistry of these compounds [1–6]. The well-established oxygen difluoride, OF_2, is stable at room temperature, whereas the higher oxygen fluorides or polyoxygen fluorides are thermally unstable and decompose ultimately into fluorine and oxygen. In this section, we briefly cover only the polyoxygen fluorides, O_nF_2 ($n=2, 4–6$).

(i) Dioxygen difluoride

The synthesis of various oxygen fluorides has been accomplished by the flow reactions of F_2 and O_2 in an electric discharge or sometimes also by photolytic and radiolytic reactions. First synthesized by Ruff and Menzel [7,8], O_2F_2 has, in the meantime, been prepared by exposing a mixture of oxygen and fluorine to 3 meV bremsstrahlung [9,10], a glow discharge [1,3], an electric discharge (4–5 KV, 2 mA) [11], and photolysis (365 nm [12] or 1000 W Xe–Hg arc lamp [13], or after codeposition in argon [14]). Additionally, photolysis of mixtures of oxygen difluoride and oxygen neat [15] or in nitrogen, argon and oxygen matrices [16] forms O_2F_2. Ozone when photolyzed with fluorine gives O_2F_2 in addition to OF_2 [17].

Dioxygen difluoride is a pale yellow solid which melts at −153°C and boils (extrapolated) at −57°C [18]. The mechanism of its reactions is explained primarily by cleavage of the O–F bond leading to the formation of F atoms and OOF radicals. The formation of two OF radicals by cleavage of the O–O bond is energetically disfavored [19]. A microwave investigation [20], recently confirmed by an electron diffraction study [21], shows the molecule to have a zig-zag skewed chain structure (similar to H_2O_2) with a dihedral angle of 87.5°, a long O–F bond (157.5 pm) and a short O–O bond (121.7 pm). This type of structure has also been confirmed by several ab initio [22,23] and semiempirical (CNDO/2) [24], MINDO [18], extended Hückel [25] SCF.MO calculations [25]. The vibrational spectrum of the molecule has been studied many times [11,13,14,16,26–28]. The infrared spectrum of O_2F_2 in the gas phase [13] has the following important vibrations (cm^{-1}): ν_{O-O} 1210, ν_{O-F} 630, δ_{O-O-F} 366. A very large chemical shift (830–865 ppm) downfield from CCl_3F indicates considerable deshielding, probably due to the long O–F bond [29,30].

Dioxygen difluoride has been recognized as one of the most potent of all molecular oxidative fluorinating agents [3]. It reacts with most substances at cryogenic temperatures. Inadequate cooling or rapid combination of reagents can cause explosions [31]. Various reactions of O_2F_2 have been described [1,3,5,6].

Based on the observation that the O–F bond is the weakest bond in the molecule, it would seem likely that reactions of O_2F_2 could provide routes to other molecules which contain catenated oxygen atoms [32–48]. However, this phenomenon has been observed in only a few instances, viz.

$SO_2 + O_2F_2 \xrightarrow{-160^\circ C} FSO_2OOF + \text{others}$ [34]

$COF_2 + O_2F_2 \rightarrow CF_3OOOF$ [40,41]

$CF_3CF{=}CF_2 + O_2F_2 \rightarrow n\text{- and i-}C_3F_7OOF$ [42]

$BF_3 + O_2F_2 \xrightarrow{-126^\circ C} O_2BF_4$ [9]

$MF_x + O_2F_2 \xrightarrow{\text{var. } T} O_2MF_{x+1}$

M = P,	As,	Sb,	Bi,	V*,	W,	Mo
X = 5,	5,	5,	5,	5,	6,	6
	[44–46]*		[11]		[47]	

In more recent work, the versatility of O_2F_2 as a superb and controllable fluorinating agent has surfaced, e.g. with xenon at −78°C, XeF_4 is formed [33]. Low-temperature synthesis of actinide fluorides [35,48], e.g. PuF_6 or UF_6, by the action of O_2F_2 on PuF_4, PuO_2, PuO_2F_2 or U_3O_8 at room temperature or below has technological significance because direct fluorination of actinide substrates was achieved previously only by high-temperature fluorination except when KrF_2 was employed [49]. This suggests the feasibility of O_2F_2 utilization in the recovery of actinides from refractory and highly impure oxides. The potency of O_2F_2 as an oxidative fluorinating agent allows reactions at low temperature and thus avoids many of the problems associated with fluoride volatility. Dioxygen difluoride has obvious potential, not only for many applications in the nuclear industry but for low-temperature synthesis of high-valent fluorides, which otherwise are difficult to prepare, and as a starting material for the preparation of many dioxygenyl compounds.

(ii) Polyoxygen difluorides

(a) Trioxygen difluoride, O_3F_2

The actual existence of O_3F_2, although claimed, has never been proved [6]. The authors of this review accept the argument that the species so identified is, in fact, a mixture of O_2F_2 and O_4F_2 (or ·OOF) based on the definitive ^{19}F and ^{17}O nuclear magnetic resonance work by Solomon et al. [50,51]. The reaction chemistry attributed to "O_3F_2" can be rationalized by the presence of the above species [50,52,53]. The non-existence of O_3F_2 contrasted with the more stable CF_3OOOF and CF_3OOOCF_3 is a good example of the stabilizing effect of perfluoroalkyl groups.

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*$O_2V_2F_{11}$.

(b) Tetraoxygen difluoride, O_4F_2

Electric discharge of mixtures of oxygen and fluorine [54,55] or oxygen and oxygen difluoride [56], and radiolysis of oxygen and fluorine [9] provide routes to tetraoxygen difluoride. The formation of O_4F_2 very likely arises from the dimerization of O_2F radicals, which is part of the mechanism suggested for the formation of blue and violet compounds in the reactions of oxygen fluorides or O_2^+ salts [37]. Presumably O_4F_2 is formed by sublimation of O_2AsF_6 followed by the condensation of the vaporized species at −196°C [57].

Not unexpectedly, O_4F_2 is considerably less stable than O_2F_2, decomposing at −183°C. The red-brown solid melts to a similarly colored liquid at −191°C. However, at −196°C the pure compound can be stored for weeks without decomposition [55]. Electron resonance measurements on O_4F_2 confirm the existence of the equilibrium $O_4F_2 \rightleftharpoons 2\cdot OOF$ with a constant of 8×10^{-5} [5,58]. Based on vibrational spectral analysis, molecular vibrations are assigned to ν_{O-O}, ν_{O-F} and δ_{OOF} at 1516, 584, and 376 cm^{-1}, respectively [59]. Few studies of the reaction chemistry of O_4F_2 have been reported. For comparison purposes, it is interesting to mention the reaction of O_4F_2 with SO_2 where the products are similar to those obtained with O_2F_2. While simple fluorination predominates, O_4F_2 is a superior source of $\cdot OOF$, as evidenced by the yield of FSO_2OOF obtained (32% compared with 5%) [60]. As with O_2F_2, O_4F_2 forms a dioxygenyl salt with BF_3 [53].

(c) Pentaoxygen difluoride, O_5F_2 and hexaoxygen difluoride, O_6F_2

The last of the catenated oxygen fluorides are O_5F_2 and O_6F_2. These are prepared by electric discharge through F_2–O_2 mixtures of the appropriate molar ratio at −196°C [61]. Pentaoxygen difluoride is a red-brown liquid at −183°C where it decomposes, while O_6F_2 is a stable dark-brown, crystalline solid at −213°C. On warming, both decompose quickly, forming lower oxygen fluorides and ozone. Additional work to support these formulations has not been carried out and the only characterization has resulted from analysis of the oxygen and fluorine released on decomposition.

C. FLUORINATED PEROXIDES

Trifluoromethyl peroxygen derivatives of non-metals are of considerable interest because of their relative high thermal stability. In many instances, these compounds are unique and provide the only examples of a C–O–O–X molecular skeleton. Some of them, for example, CF_3OOF and CF_3OOCF_3, are of considerable chemical interest due to their photochemical reactivity. In recent years, a large number of fluorinated peroxides with highly electronegative fluorine-containing groups have been synthesized and studied. The simple fluoroalkyl peroxides, R_fOOR_f, are analogous in type to the well-known peroxides, but differ greatly both in their methods of preparation and in their properties. However, the existence of polyoxides, e.g.

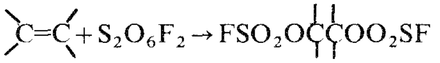
R_fOOOR_f which have no parallel alkyl analogs, is another unique example which illustrates clearly the special position of fluorinated groups in stabilizing compounds with catenated oxygen atoms.

(i) Bis(fluorosulfuryl)peroxide, FSO_2OOSO_2F

Bis(fluorosulfuryl)peroxide was first reported in 1955 [62], but first isolated in a pure state as a side product in the preparation of fluorine fluorosulfate [63]. Several other methods are now available, including the low-temperature electrolysis of an alkali metal fluorosulfate in HSO_3F [64], the reaction of fluorine with excess SO_3 in a flow system at 100°C with AgF_2 as catalyst [65,66], the reactions of xenon fluorides with HSO_3F/SO_3 [67–71], photolysis of a mixture of F_2 and SO_3 [72,73] or photolysis of $ClOSO_2F$ (ClF with SO_3) [74]. Bis(fluorosulfuryl)peroxide is a colorless compound that melts at $-55.4°C$ and boils at 67.1°C. At 100°C, the O–O bond is cleaved (bond energy 92 kJ $mole^{-1}$) to form yellow-brown $\cdot SO_3F$ radicals. This reaction is reversible. The chemistry of $S_2O_6F_2$ is essentially that of these radicals. Based on the Raman spectrum, $S_2O_6F_2$ is a staggered non-planar molecule with ν_{O-O} at 801 cm^{-1} [75]. A single resonance has been observed at 40.4 ppm in the ^{19}F NMR spectrum [76,77].

The reaction modes of $S_2O_6F_2$ may include oxidation, oxygenation and/or fluorosulfonation. It often reacts with organic compounds with explosion, making precautions necessary. Since it is easily hydrolysed by water to HSO_3F and oxygen, all operations must be carried out under anhydrous conditions.

Bis(fluorosulfuryl)peroxide does not oxidize xenon or gold, but it reacts with a variety of transition metals to give products in which the maximum oxidation state is attained. On heating, rhenium and niobium [78] give $ReO_3(SO_3F)$, $ReO_2(SO_3F)_3$ and $NbO(SO_3F)_3$. Reactions often proceed to completion more readily if metal carbonyls are used, e.g. $Mo(CO)_6$ and $W(CO)_6$ are converted to $MoO_2(SO_3F)_2$ and $WO(SO_3F)_4$, respectively [79,80]. Fluorosulfate radicals add to unsaturated molecules and, in many cases, in order for the reaction to be controlled, diluents, such as N_2, or an inert solvent, such as CCl_3F, or reduced temperature are required.



$$>C=C< + S_2O_6F_2 \rightarrow FSO_2OCCOO_2SF$$

$>C=C< = C_2F_4$, c-C_5F_8, $CF_3CF=CF_2$ [79], c-C_4F_6 [81], $ClCF=CF_2$, $H_2C=CHF$, $CH_2=CHCl$ [82]

$$XC\equiv N + S_2O_6F_2 \xrightarrow{\Delta} XC(OSO_2F)_2N(OSO_2F)_2$$

X=Cl, CF_3 [6]

Members of the halogen family and the chalcogens S, Se, Te were reacted with $S_2O_6F_2$ to give a variety of products which are primarily a function of the stoichiometry and the solvent used. In the absence of a solvent, F_2, Cl_2, Br_2 and I_2 are converted to fluorosulfates: $FOSO_2F$, colorless [65,83], $ClOSO_2F$, red-yellow [84,85], $BrOSO_2F$, red-brown [87], $Br(OSO_2F)_3$ [86,87], $IOSO_2F$, black [88], $I(OSO_2F)_3$ yellow [87], $I_3(OSO_2F)$ [88], $I_7(OSO_2F)$ [89]. These compounds are analogous to the known interhalogen compounds, with $\cdot OSO_2F$ behaving as a pseudohalogen which is also exemplified by the formation of the complex anions, $K[I(SO_3F)_4]$ [90] and $K[Br(SO_3F)_4]$ [91].

Gillespie and Passmore [92] have generated compounds that contain various polyatomic, catenated cations by reacting S, Se and Te with $S_2O_6F_2$, indicating its high oxidizing power, i.e. S_{16}^{2+}, S_8^{2+}, S_4^{2+}, Se_8^{2+}, Se_4^{2+}, Te_4^{2+}, Te_n^{2+}. Under moderating conditions of solvent and low temperature, it is possible to abstract hydrogen with $\cdot OSO_2F$ from organic compounds to form fluorosulfuric acid and organic fluorosulfates [6].

(ii) Bis(pentafluorosulfur)peroxide, F_5SOOSF_5

The first preparation of bis(pentafluorosulfur)peroxide was reported in 1954 [93] during fluorination of sulfur but higher yields are obtained from $SF_5OF + SOF_2$, photolysis of SF_5OF [94] or photolysis of SF_5Cl and O_2 [95]. Bis(pentafluorosulfur)peroxide is a thermally stable, colorless compound which melts at -53.5°C, and boils at 49.4°C. Its hydrolytic stability is reminiscent of organic peroxides with large substituent groups, such as di-*t*-butyl peroxide. The O–O bond dissociation energy in F_5SOOSF_5 is 234.3 kJ mole^{-1} and thus it is not as reactive as FSO_2OOSO_2F. This is demonstrated both by the dearth of reports of successful reactions and by the low yields of predicted products when reactions do occur [96]. Side reactions which involve oxygenation or fluorination or both often occur with F_5SOOSF_5. An electron diffraction study [93] indicates a structure similar to that of H_2O_2. As in SF_6, the fluorine atoms in the SF_5 groups are arranged octahedrally with a S–F bond length of 156 ± 2 pm. In the ^{19}F NMR spectrum, through-space coupling has been observed. An $AB_4B'_4A'$ system is observed with $\delta_A = 57.7$, $\delta_B = 56.5$ ppm with the latter assigned to the equatorial fluorine. The following coupling constants have been reported: $J_{AB} = 152.3 \pm 0.5$, $J_{AB'} = J_{AA'} = 0.0 \pm 0.2$, $J_{BB'} = 4.3 \pm 0.2$ Hz.

(iii) Pentafluorosulfur(fluorosulfuryl)peroxide, F_5SOOSO_2F

On photolysis, equimolar quantities of F_5SOOSF_5 and $S_2O_6F_2$ yield F_5SOOSO_2F [96]. In the presence of excess KF, SOF_4 can be reacted with $S_2O_6F_2$ to give F_5SOOSO_2F in 40% yield [97]. It is a colorless liquid that boils at 54.1°C.

(iv) Pentafluorosulfur(fluorocarbonyl)peroxide, $F_5SOOC(O)F$

Equimolar mixtures of F_5SOOSF_5 and $F(O)COOC(O)F$ on photolysis give $F_5SOOC(O)F$ which boils at ~25°C [98]. It is stable at room temperature but is easily hydrolyzed in aqueous base.

$$F_5SOOC(O)F+10OH^- \rightarrow 6F^- + SO_4^{2-} + CO_3^{2-} + 5H_2O + 0.5O_2$$

It attacks mercury and oxidizes aqueous iodide solution.

(v) Bis(tetrafluoropentafluoroxysulfur)peroxide, $F_5SOSF_4OOSF_4OSF_5$

This peroxide is obtained as one of the products when SF_5OF, SF_4 and O_2 are heated at 75°C for 12 h [99]. This symmetrical material boils at 59°C (20 Torr).

(vi) Fluoro(fluorosulfuryl)peroxide, FSO_2OOF

This compound can be considered as a formal derivative of FOOF. From ESR studies it has been established that, upon photolysis, FSO_2 and OOF radicals are predominantly formed [100] which is analogous to $FOOF \rightarrow F + OOF$ [58]. It is readily synthesized by photolysis of oxygen difluoride and SO_3 using radiation energies lower than 365 nm to prevent activation of any molecules other than OF_2 [76,101] or by the reaction of SO_2 with either O_2F_2 or O_4F_2 to give 5% and 32% yields, respectively, in $CFCl_3$ solvent at −183°C [6]. Fluoro(fluorosulfuryl)peroxide is a pale-green liquid that boils at 0°C and which is thermally stable up to 50°C [101].

Little reaction chemistry of FSO_2OOF is known. However, it is interesting to compare the rate and products of reaction with SO_2 with that between FSO_2OF and SO_2 [102]

$$FSO_2OOF + SO_2 \xrightarrow[1\,h]{25°C} SO_2F_2 + S_2O_5F_2 + O_2$$

$$FSO_2OF + SO_2 \xrightarrow[6\,days]{25°C} S_2O_5F_2$$

(vii) Bis(perfluoroalkyl)peroxides, R_fOOR_f

The simplest of the bis(perfluoroalkyl)peroxides, bis(trifluoromethyl)peroxide, was prepared in low yields by Swarts in 1933 [103] by the electrolysis of trifluoroacetate solutions. Better methods have been developed [104–107], e.g. the reaction of CO with F_2 in the presence of AgF_2 as catalyst at 180°C

$$2CO + 3F_2 \xrightarrow{AgF_2} CF_3OOCF_3\ (60\%)$$

There are very few general preparative reactions available. The equations given below illustrate a few of the reactions employed [6,108].

$$CF_3OCl \xrightarrow{h\nu} CF_3OOCF_3 + Cl_2$$

$$(CF_3)_3COCl \xrightarrow[-78^\circ C]{h\nu} (CF_3)_3COOC(CF_3)_3 + Cl_2$$

$$RC(CF_3)_2OH + ClF_3 \rightarrow RC(CF_3)_2OOC(CF_3)_2R \qquad (R = CF_3,\ C_2F_5,\ CH_3)$$

$$XeF_2 + C_6F_5OH \rightarrow Xe + HF + C_6F_5OOC_6F_5$$

$$CF_3CO_2M + F_2 \rightarrow CF_3OOC_2F_5 + MF \qquad (M = \text{metal})$$

Preparation of CF_3OOCF_3 and CF_3OOOCF_3 via electrochemical fluorination by bubbling COF_2/He through purified AHF in an electrolytic cell at 7°C has been reported [109]. Oxidation of the adduct of KCN with $(F_2N)_2C{=}NF$ by $CF_2(OF)_2$ also yields peroxy compounds and fluorinated amines [109].

$$\begin{aligned} CF_2(OF)_2 + KCN \cdot (F_2N)_2C{=}NF \rightarrow (F_2N)_2CF_2 &+ CF_3OOC(O)F \\ &+ CF_3OOOCF_3 + CF_3OOCF_2OF \text{ etc.} \end{aligned}$$

Reaction of octafluorobutene and CF_3OF at 100°C for 8 h gives mainly CF_3OOCF_3 [110]. The vibrational spectra have been measured with the band at 886 cm^{-1} assigned to ν_{O-O} [111,112]. The ^{19}F NMR has a single band at $\delta = -69.0$. The oxygen–oxygen distance in CF_3OOCF_3 is 141.9 pm [114].

Most of the reaction chemistry of these perfluoroalkyl peroxides has been studied through bis(trifluoromethyl)peroxide. It does not react readily with aqueous iodide and UV irradiation is required to enhance the reaction rate [104]. This is quite different from the behavior of the much more reactive $S_2O_6F_2$ or F(O)COO-C(O)F [115–117].

$$+ CF_3OOCF_3 \xrightarrow[10\,d]{130^\circ C} NF_2OCF_3$$

$$N_2F_4 + S_2O_6F_2 \xrightarrow{25^\circ C} NF_2OSO_2F$$

$$+ F(O)COOC(O)F \xrightarrow{25^\circ C} FC(O)ONF_2$$

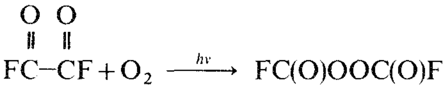
The CF_3O group can be transferred [118] in the reaction of CF_3OOCF_3 with C_3F_6 to give ethers of the type $CF_3O(C_3F_6)_nOCF_3$ $(n = 2–4)$. Under photolytic conditions, CF_3OOCF_3 oxidizes SF_4 to $(CF_3O)_2SF_4$ in 10% yield [119].

(viii) Bis(fluoroformyl)peroxide, FC(O)OOC(O)F

Bis(fluoroformyl)peroxide is readily synthesized at 25°C by mixing the reactants in a flow system [108,120].

$$F_2 + CO + O_2 \rightarrow \underset{(90\%)}{FC(O)OOC(O)F}$$

It has also been prepared in lower yields from the photolysis of oxalyl fluoride and oxygen [121]. This method utilizes readily available materials, and does involve less hazardous materials.



$$FC(O)-C(O)F + O_2 \xrightarrow{h\nu} FC(O)OOC(O)F$$

(46%)

Low-energy photolytic reaction between CO and OF_2 also results in the formation of the peroxide [122]. Many of the higher members of this family have been prepared using a method analogous to that for non-fluorinated compounds [6].

$$R_fC(O)Cl + Na_2O_2 \xrightarrow{-15^\circ C} R_fC(O)OOC(O)R_f$$

(80%)

These peroxides are normally prepared immediately prior to their use and allowed to react in dilute solutions or stored below 25°C because of their sensitivity to shock.

Some synthetic reactions have been carried out with FC(O)OOC(O)F. For example, Cauble and Cady [123] obtained FC(O)OF in addition to CF_3OOCF_3, $FC(O)OOCF_3$ and CF_3OOOCF_3 from the photolytic reaction of F_2 and the peroxide. With N_2F_4, $FC(O)ONF_2$ was obtained [117]. Photolysis with SO_2 yielded $FC(O)OSO_2F$ [124]. A reversible reaction of FC(O)OOC(O)F with KF led to the formation of a new cyclic peroxide, $\overline{OCF_2OOC}{=}O$ [125].

(ix) Bis(trifluoromethyl)trioxide, CF_3OOOCF_3

Based on thermodynamic calculations [126] and experimental evidence [127], non-fluorinated alkyl trioxides should have a sufficient half-life to be isolable only well below 25°C. In comparison, the perfluoroalkyl trioxides are stable at and above 25°C. The first reported preparation of a perfluoroalkyl trioxide was by the photolysis of hexafluoroazomethane and oxygen [128]. Fluorination of metal trifluoroacetates forms several trioxides in comparatively lower yields [113,129]

$$CF_3COOM + F_2/N_2 \rightarrow CF_3OOOCF_3 + CF_3OOOC_2F_5 + C_2F_5OOOC_2F_5$$

(1–5%) (<1%) (trace)

but the reaction of OF_2 and COF_2 in the presence of CsF gives CF_3OOOCF_3 in better yields [130–132].

$$OF_2 + COF_2 \xrightarrow{CsF} CF_3OOOCF_3$$

(10–80%)

The mechanism for this reaction was postulated as a nucleophilic displacement of

CF_3O^- by OF_2 and subsequent rapid reaction of the CF_3OOF formed. This was confirmed by using ^{17}O labelled COF_2 and OF_2 [133]. Other methods of preparation include

$$CF_3OOSO_2F + CF_3OF \xrightarrow{CsF} \underset{(20\%)}{CF_3OOOCF_3} + SO_2F_2 \qquad [97]$$

$$(CF_3)_2CO + F_2 + O_2 \xrightarrow{h\nu} \underset{(60\%)}{CF_3OOOCF_3} \qquad [134]$$

$$CF_2(OF)_2 + CsOCF_3 \xrightarrow{CsF} CF_3OF + CsOOCF_3 \qquad [135,136]$$

$$CsOOCF_3 + CF_2(OF)_2 + CF_3OF \rightarrow CF_3OOOCF_3 + CF_3OOOCF_2OOCF_3$$

$$CF_3OOF + KOCF_3 \rightarrow CF_3OOOCF_3 \qquad [137]$$

Vibrational and nuclear magnetic resonance data have been obtained for CF_3OOOCF_3 [131,138,139] and $CF_3OOOCF_2OOCF_3$ [136]. The compound $CF_3OOOCF_2OOCF_3$ is one of a very few examples of a molecule containing both trioxide and peroxide linkages. Its thermal stability is, however, lower than that of CF_3OOOCF_3 and $CF_3OOOC_2F_5$, undergoing explosive decomposition to CF_3OOOCF_3, COF_2, and O_2 at 40°C.

The following reactions show that CF_3OOOCF_3 is a convenient source of both CF_3O and $OOCF_3$ groups [140,141], thus providing a route to compounds with catenated oxygen atoms.

$$+ C_2F_3Cl \rightarrow CF_3OOCF_2CFClOCF_3 + CF_3OCF_2CFClOOCF_3$$

$$+ SO_2 \rightarrow CF_3OOSO_2OCF_3 \quad (31\%)$$

$$+ SF_4 \rightarrow cis\text{-}CF_3OOSF_4OCF_3 \quad (21\%)$$

$$CF_3OOCF_3 + S_2O_6F_2 \rightarrow CF_3OOSO_2F \quad (80\%)$$

$$+ N_2F_4 \rightarrow CF_3ONF_2 \quad (50\%)$$

$$+ SO_3 \rightarrow CF_3OOSO_2OCF_3 \quad (92\%)$$

$$+ CO \rightarrow CF_3OOC(O)OCF_3 \quad (29\%)$$

With C_2H_4, C_2F_4, C_2F_3Cl, hexafluoropropene, perfluorobutene-2 and perfluorocyclopentene, the typical products $CF_3OOCRR^1CR^2R^3OCF_3$ and CF_3OCRR^1-$CR^2R^3OOCF_3$ are obtained in 50–80% yields ($R = H$, F, Cl, alkyl or perfluoroalkyl). Evidence supports the radical nature of these reactions involving the initial addition of CF_3O to the alkene.

Perhaps surprisingly, the perfluoroalkyl trioxides are stable at 25°C when stored in glass or metal containers. Bis(trifluoromethyl)trioxide, which melts at −138°C and boils at −16°C, undergoes slow decomposition to CF_3OOCF_3 and O_2 at 70°C [130]. By using ^{19}F NMR, the $t_{1/2}$ of this decomposition at 25°C was determined to be 65 weeks [113]. Based on these data, the bond dissociation energy, $D(CF_3O\text{–}OOCF_3)$, was calculated to be 116–120 kJ mol^{-1} (compared with ~ 92 kJ mol^{-1} for $S_2O_6F_2$ and $\sim 80 \pm 24$ kJ mol^{-1} for alkyl trioxides [126]).

Although the synthesis of bis(trifluoromethyl)tetraoxide has been suggested, definitive characterization is lacking. It may have been formed in low yield from the fluorination of trifluoroacetate salts but the solitary piece of evidence is a resonance peak at $\varnothing$ −69 in the ^{19}F NMR spectrum of a mixture [113].

(x) Trifluoromethylhydroperoxide, CF_3OOH and pentafluorosulfurhydroperoxide, F_5SOOH

Trifluoromethylhydroperoxide can be prepared by hydrolysis of fluoroformyl(trifluoromethyl)peroxide, $CF_3OOC(O)F$ [136,142–144]. It is a stable, water-like liquid whose decomposition is catalyzed by HF and metal fluorides. In the presence of CsF, a small amount of CF_3OOOCF_3 is formed. In the IR spectrum, a sharp band at 3580 cm^{-1} has been assigned to ν_{OH}, a band at 1383 cm^{-1} to δ_{OOH} and a weak band at 862 cm^{-1} to the ν_{O-O} band. The ^{19}F NMR spectrum contains a single peak at $\delta = -72.3$ ppm, and in the ^{1}H spectrum a resonance is observed at $\delta = 9.2$ ppm [144]. Not surprisingly, CF_3OOH behaves as a weak protic acid, and readily forms trifluoromethyl peroxides with various substrates [144]. With acid fluorides, trifluoromethylperoxy esters are formed in high yields. The synthesis and properties of such compounds, e.g. $CF_3C(O)OOCF_3$, $CH_3C(O)OOCF_3$, $CF_3OOC(O)CF_2CF_2CF_2C(O)OOCF_3$, $CF_3OOC(O)CF_2CF_2CF_2C(O)F$ and $CF_3CF(OF)OOCF_3$ have been described [144]. CF_3OOH can be fluorinated in the presence of CsF to give CF_3OOF [145].

When CF_3OOH is reacted with $P_2O_3F_4$ and $P_2O_2F_4$, CF_3OOPOF_2 (87%) and CF_3OPOF_2 (65%) are formed, respectively [146]. Both of these materials decompose slowly at 22°C. The peroxide CF_3OOPOF_2 melts at −88.6°C and boils at 15.5°C.

Pentafluorosulfurhydroperoxide, F_5SOOH, which is prepared by the hydrolysis of $F_5SOOC(O)F$ with a stoichiometric amount of water at 0°C, is a colorless compound that melts at −55.6°C and boils at 0°C (150 Torr) [147,148]. When heated to 85°C, it decomposes to give SOF_4, HF and O_2. A strong Raman band at 735 cm^{-1} has been assigned to ν_{O-O}. Its reaction chemistry parallels that of CF_3OOH, forming pentafluorosulfurperoxy esters in high yields with acid fluorides in the presence of NaF [144,149]. Both SF_5OOH and CF_3OOH can be reacted with $CF_3N{=}CF_2$ to give $F_5SOOCF_2NHCF_3$ and $CF_3OOCF_2NHCF_3$, respectively. Elimination of HF from these compounds gives 2-trifluoromethyl-3,3-difluorooxazirine, CF_3NCF_2O [150]. Both CF_3OOH and SF_5OOH react with F_2 in the presence of CsF to give

CF_3OOF and SF_5OOF, respectively. These hydroperoxides with ClF at very low temperature (−110°C) give CF_3OOCl [151] and SF_5OOCl [152]. Chloroperoxytrifluoromethane, CF_3OOCl, is a stable yellow gas at room temperature. It boils at −22°C and melts ~ −132°C. The ν_{O-O} band is assigned at 813 cm^{-1}.

Both CF_3OOCl [153] and SF_5OOCl [152] undergo addition reactions with alkenes forming trifluoromethylperoxy and pentafluorosulfurperoxy derivatives, respectively. The additions are unidirectional and proceed by an electrophilic mechanism in which the positive chlorine adds to the more negative carbon. Reactions with C_2H_4, C_2F_4, C_2F_3Cl, CF_2CCl_2 and *cis*-CFHCFH take place below 0°C, whereas C_3F_6 and c-C_5F_8 were unreactive under all conditions tried. With *cis*-CFHCFH, the reaction is stereospecific. The resulting peroxides have been characterized spectroscopically.

Trifluoromethylhydroperoxide with N_2O_5 at −35°C (20 h) and CF_3OOF with N_2O_4 at −10°C (5 days) give CF_3OONO_2 in good yield. A colorless moisture-sensitive liquid, CF_3OONO_2 (b.p. 0.9°C extrapolated) undergoes slow thermal decomposition at 22°C [154].

In the preparation of SF_5OOF via fluorination of SF_5OOH in the presence of CsF, an unstable product believed to be SF_5OOOSF_5 is formed [148]. This material could not be separated from F_5SOOSF_5 and its existence is subject to some uncertainty. The ^{19}F NMR spectrum shows a single AB_4 pattern very similar to that of SF_5OOSF_5. This is analogous to that observed in the ^{19}F NMR spectra of CF_3OOOCF_3 relative to CF_3OOCF_3 [113,129,136].

The gas-phase electron diffraction study [155] and a microwave spectrum study [156] show that the structure of CF_3OOF is like that of FOOF having short O–O and long O–F and C–O bonds. The molecular structures of CF_3OOH and CF_3OOCl by gas phase electron diffraction studies have also been determined [155]. The hydro and chloro derivatives are typical peroxides.

*(xi) Perfluoro-*tert*-butyl peroxygen derivatives, $(CF_3)_3COOX$: [$X = SO_2F$, $C(O)F$, $C(O)OCF_3$, H, Cl, F, CF_2OF, CF_2CF_2Cl, $CFClCF_3$, $C(CF_3)_3$]*

The perfluoro-*t*-butoxy group is highly electronegative, as is shown by the properties of the alcohol [157] and the existence of the stable halogen derivatives, $(CF_3)_3COX$ (X = Cl, F) [158,159], and is capable of stabilizing certain unusual structures containing oxygen–oxygen bonds. Comparison of peroxygen derivatives containing CF_3O and SF_5O groups demonstrates greater thermal stability for the trifluoromethyl derivatives in all cases. With the $(CF_3)_3CO$ group, comparable or even better thermal stability of compounds can be achieved. For example, nearly every one of the following materials is prepared in high yield and is stable (except as noted) at least to its boiling point [137,160–164]: $(CF_3)_3COOSO_2F$ (80.5°C), $(CF_3)_3COOC(O)F$ (60.9°C), $(CF_3)_3COOC(O)OCF_3$ (m.p. −30°C), $(CF_3)_3COOH$ (72°C), $(CF_3)_3COOCl$ (unstable), $(CF_3)_3COOF$ (m.p. −16°C), $(CF_3)_3COOCF_2OF$

(74°C), $(CF_3)_3COOCF_2CF_2Cl$, $(CF_3)_3COOCFClCF_3$, $(CF_3)_3COOOC(CF_3)_3$, and $(CF_3)_3COOC(CF_3)_3$ (unstable).

(xii) Bis(pentafluoroselenium)peroxide, SeF_5OOSeF_5, and bis(pentafluorotellurium)peroxide, TeF_5OOTeF_5

Bis(pentafluoroselenium)peroxide, $F_5SeOOSeF_5$, forms from the reaction of F_2 with SeO_2. Irradiation of $Xe(OSeF_5)_2$ and $Xe(OTeF_5)_2$ gives $F_5SeOOSeF_5$ and $F_5TeOOTeF_5$, respectively, in almost quantitative yields. Both are stable compounds with $F_5SeOOSeF_5$ melting at −61.5°C and boiling at 74°C while $F_5TeOOTeF_5$ melts at −39°C and boils at 81.5°C. The stretching frequencies assigned to ν_{O-O} are at 903 and 907 cm^{-1}, respectively. These high-energy modes indicate a much smaller tendency for the oxygen–oxygen bond to dissociate to form radicals than is the case for FSO_2OOSO_2F where $\nu_{O-O} = 798\ cm^{-1}$ [165].

D. FLUORINATED DISULFANES AND POLYSULFANES

A large number of disulfanes and polysulfanes have been prepared and studied in recent years. We have, however, included only those disulfanes which are either analogous to the fluorinated peroxides discussed in an earlier section or the ones whose chemistry has been extensively studied in our laboratories.

(i) Fluorine disulfanes and polysulfanes, S_nF_2 (n = 2–4)

Sulfur analogues of O_nF_2 ($n = 2$–4), i.e. S_2F_2, S_3F_2 and S_4F_2 have been reported. Reaction of sulfur vapor with either AgF or HgF_2 produces both isomers FSSF and SSF_2 which are separated by distillation. Using ^{19}F NMR and mass spectral studies, S_3F_2 and S_4F_2 are also detected. The infrared, Raman, photoelectron and UV spectra have been reported [166]. The conversion of FSSF to the more stable isomer SSF_2 is catalyzed by BF_3. Chlorofluorodisulfane results from a partial exchange of halogen atoms between SSF_2 and ClSSCl. The UV and ^{19}F NMR spectra of ClSSF have been recorded. The stabilizing effect observed when a trifluoromethyl group(s) replaces a fluorine atom(s) is interesting and typical, e.g. in order of increasing stability $FSSF < CF_3SSF < CF_3SSCF_3$.

(ii) Trifluoromethyl disulfane, CF_3SSH

Trifluoromethyl disulfane, which is obtained in about 70% yield by a metathetical reaction between H_2S and CF_3SCl, boils at 35.4°C, and melts at −164 ± 2°C [167,168]. The vibrational spectra of gaseous CF_3SSH [167] favor the structure of a disulfane over the isomeric thiothionyl compound. Its mass spectrum shows a molecular ion peak along with other fragmentation peaks compatible with the proposed structure [167]. Vibrational and gas-phase electron diffraction studies of CF_3SSH have recently been reported [169].

In Pyrex glass, CF_3SSH decomposes slowly to give CF_3SH and S. A sealed sample decomposes within four weeks at 33°C to give 33% CF_3SH and 5% CF_3SSSCF_3. Water initiates the decomposition and after prolonged standing $CF_3S_4CF_3$, CS_2, COS and SiF_4 are identified. Even ether dried over sodium contains sufficient water to catalyze the decomposition [167].

The reaction chemistry of $CF_3(S)_nH$ ($n=1$–3) is governed by the acidic nature of the proton, which enables it to undergo metathesis reactions with compounds having labile halogens. The reaction between CF_3SSH and Cl_2 at −78°C gives predominantly CF_3SSCl and $CF_3S_nCF_3$ ($n=2$–4) [167]. In the presence of CsF at low temperature, the following type of reaction occurs,

$$CF_3SSH + RX \xrightarrow[-60^\circ C]{CsF} CF_3SSR + HX$$

(R = FC(O) [170], $CF_3C(O)$, FC(O)C(O),

$FC(O)(CF_2)_3C(O)$ (X = F, Cl) [171], $CF_3C(O)S$ [172])

The resulting compounds are those expected from nucleophilic displacement of the labile halide in RX by CF_3SS^-. It is also possible, using the appropriate stoichiometry, to obtain disubstituted products, e.g.

$$RF_2 + 2CF_3SSH \xrightarrow[-25^\circ C]{MF} (CF_3SS)_2R + 2HF$$

($R = C(O)(CF_2)_3C(O)$, C(O), C(O)C(O) (M = Cs, K) [171])

These substituted trifluoromethyl disulfanes are colorless, moderately volatile liquids which can be stored in Pyrex glass at 25°C for short periods. However, at −78°C they are stable indefinitely.

The infrared spectra of the compounds show characteristic absorption bands for the CF_3SS group at ~1185 and 1110 cm^{-1} as well as a carbonyl stretch for $CF_3SSC(O)$, which is markedly lower than the carbonyl stretch in the fluorine and trifluoromethylperoxy analogs. Typically, while substitution of a fluorine by CF_3OO shifts the absorption band of the adjacent carbonyl to lower energy by ~30 cm^{-1} (e.g. $CF_3C(O)F$, 1890 cm^{-1} (ν_{CO}) compared with 1859 cm^{-1} in $CF_3C(O)OOCF_3$ [143]), substitution by a CF_3SS group has a much larger effect, e.g. $CF_3C(O)SSCF_3$, 1768 cm^{-1}. The ^{19}F NMR spectra of the compounds show a resonance assignable to CF_3SS group(s) at approximately ($\delta = -45$) in all of the compounds studied. The mass spectra contain appropriate fragmentation patterns and isotopic ratios. All compounds studied give mass spectral peaks for CF_3SS^+ as well as recombination peaks for $CF_3S_nCF_3$ ($n=3, 4$). The more stable compounds $CF_3C(O)SSCF_3$ and $CF_3SSC(O)C(O)F$ also show molecular ion peaks [171].

(iii) Trifluoromethyltrisulfane, CF_3SSSH

Trifluoromethyl trisulfane is synthesized by allowing a mixture of excess H_2S and CF_3SSCl to warm slowly from −196 to 25°C (8 h). The product is recovered by low-temperature vacuum distillation. An excess of H_2S is used to minimize formation of bis(trifluoromethyl)pentasulfane via a competing reaction

$$CF_3SSCl + CF_3SSSH \rightarrow CF_3S_5CF_3 + HCl$$

CF_3SSSH can be manipulated in a glass line with little or no decomposition. However, it decomposes slowly into S and CF_3SH on standing in Pyrex glass at 25°C [168]. It is a volatile colorless liquid at 25°C. A strong molecular ion peak and a peak at 97 $(S_3H)^+$ accompanied by a supporting fragmentation pattern are present in its mass spectrum.

(iv) Chloro(trifluoromethyl)disulfane, CF_3SSCl

Chloro(trifluoromethyl)disulfane is prepared by the sequence of reactions

$$(CF_3)_2NSCl \xrightarrow[(C_2H_5)_2O,\,HgCl_2]{Hg(SCF_3)_2} \underset{(85\%)}{(CH_3)_2NSSCF_3} \xrightarrow{HCl} \underset{(90\%)}{CF_3SSCl}$$

The second step is carried out in a metal vessel [173]. It has also been prepared by the reaction of CF_3SH with SCl_2 in 60–70% yield [172].

$$CF_3SH + SCl_2 \rightarrow CF_3SSCl + HCl$$

Equimolar quantities of the reactants are employed to preclude the formation of bis(trifluoromethyl)trisulfane. UV photolysis of an equimolar mixture of CF_3SSCF_3 and SCl_2 or S_2Cl_2 for 6–12 h forms CF_3SSCl in 5–20% yield [172]. Reaction of CF_3SSH with chlorine gives CF_3SSCl in 64% yield [174]. CF_3SSCl is a yellow liquid that boils at 68.5°C. A singlet appears at $\delta = -48.2$ (CCl_3F) in its ^{19}F NMR spectrum. The gas-phase IR spectrum contains an absorbance band at 492 cm^{-1} assigned to ν_{S-Cl}. The gas-phase UV spectrum includes bands at 198 and 243 nm, and a molecular ion peak is observed in the mass spectrum. Raman spectra of the solid and IR spectra of matrix-isolated samples of CF_3SSCl and CF_3SSF have been reported [169].

The reaction mode of CF_3SSCl is that of a typical acid chloride where the SCl bond is broken to form CF_3SS-containing species [172]. In metathetical reactions with compounds that contain labile hydrogen or metal salts, hydrogen chloride or metal chlorides are formed. No evidence is found for breaking the S–S bond to form CF_3S- and S–Cl-containing compounds. This is in contrast with the reactions of

S_2Cl_2 where both S–S and S–Cl bonds break [175]. Some reactions of CF_3SSCl are summarized below [172].

$+R_2NH \rightarrow CF_3SSNR_2{}^a$

$+LiR \rightarrow CF_3SSR^a$

$+H_2S \rightarrow (CF_3)_2S_5$

$+CF_3SH \rightarrow CF_3SSSCF_3$

$+RSH \rightarrow CF_3SSSR^a$

$+AgX \rightarrow CF_3SSX^b$

CF_3SSCl

$+MeSH \rightarrow MeSSSCF_3$

$+EtSH \rightarrow EtSSSCF_3$

$+AcSH \rightarrow AcSSSCF_3$

$+CF_3C(O)SH \rightarrow CF_3C(O)SSSCF_3$

$+AgNCO \rightarrow CF_3SSNCO$

$+(CF_3)_2C{=}NLi \rightarrow CF_3SSN{=}C(CF_3)_2$

(a = alkyl, b = pseudohalogen)

In the presence of mercury, at 0, −78 or 120°C, CF_3SSCl gives HgS and unidentified solid products. CF_3SSCl reacts with ClF (to give CF_3SF_3, SF_4 and Cl_2) in either metal or glass. With alkali metal fluorides, reaction either does not occur or CF_3SSCl is converted into CF_3SSCF_3 or CF_3SSSCF_3 [176]. However, reaction with activated KF at 120°C yields CF_3SSF, CF_3SSSCF_3 and $CF_3S_4CF_3$ [174]. Fluoro(trifluoromethyl)disulfane has been identified by ^{19}F NMR, IR and mass spectral analysis [174]. When exposed to sunlight or UV light through Pyrex glass, CF_3SSCl interacts with olefins via a free radical mechanism [172].

$+\ CH_2{=}CH_2 \rightarrow CF_3SSCH_2CH_2Cl$

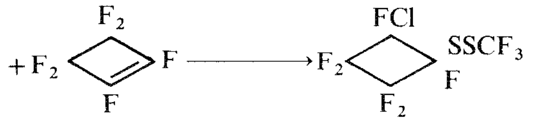
$CF_3SSCl+\ CFCl{=}CFCl \rightarrow CF_3SSCFClCFCl_2$

$+\ CF_2{=}CFCl \rightarrow CF_2ClCFClSSCF_3$ (80%), $CF_3SSCF_2CFCl_2$,

CF_3SSSCF_3, CF_2ClCF_2Cl

$$+CF_2{=}CF_2 \rightarrow CF_3SS(CF_2CF_2)_nCl \qquad (n=1,2)$$

$$CF_3SSCl + CF_3CF{=}CF_2 \rightarrow \underset{\text{(main product)}}{CF_3SSCF(CF_3)CF_2Cl} + CF_3CFClCF_2SSCF_3$$



With ammonia, CF_3SSCl reacts at −80 to −60°C to give the unstable compounds $(CF_3SS)_nNH_{3-n}$ $(n=1,2)$ which have only been identified spectroscopically [177]. Reaction with CF_3SNH_2 or $(CF_3S)_2NH$ in the presence of pyridine or Et_3N yields $CF_3S(CF_3SS)NH$ and $(CF_3S)_2(CF_3SS)N$, respectively. $CF_2ClSSCl$ reacts analogously with $(CF_3S)_2NH$ [177]. Reactions with CF_3COOH, polyfluoroalcohols and $(CF_3)_2NOH$ do not yield substitution products. With $KSC(S)OC_2H_5$ in petroleum ether at −20°C, $CF_3SSSC(S)OC_2H_5$, which boils at 41°C/0.1 Torr, is obtained [173].

CF_3SSI has been synthesized by reacting CF_3SSH with *N*-iodosuccinimide at −120°C. It is a red solid which decomposes to $(CF_3SS)_2$ and I_2 above −100°C. $(CF_3)_2S_3$ is also observed. The iodosulfane has been characterized by its Raman spectrum at −196°C and also by its ^{19}F NMR and UV/Vis spectra [169].

(v) Bis(trifluoromethyl)disulfane, CF_3SSCF_3

Previous methods for preparing perfluoroalkyl polysulfides have been reviewed [178]. For example, trifluoromethyl radicals produced by heating CF_3I react with elemental sulfur to form bis(trifluoromethyl)polysulfanes, containing 2–4 sulfur atoms [179]. Bis(trifluoromethyl)di-, tri- and tetrasulfanes are more stable than their non-fluorinated analogues. An alternate method is the reaction of CS_2 with IF_5 [180]. However, the most often used preparation for bis(trifluoromethyl)disulfane is the reaction of NaF with thiocarbonyl chloride or trichloromethylsulfenyl chloride in tetramethylenesulfone [181]. Other similar procedures may be used [182].

CF_3SSCF_3 has been obtained in low yield [183] by the reaction of $CHCl_3$ with S and KF in tetramethylenesulfone at 120–180°C for 20 h. Heating CF_3I with S at 390–420°C at atmospheric pressure in a continuous flow system yields CF_3SSCF_3 (81%) [184]. Reaction of $S_8[AsF_6]_2$ with C_2F_4 in SO_2 at −78°C yields predominantly CF_3SSCF_3 and $CF_3SSC_2F_5$ [185]. Reactions of sulfur vapor with CF_3 radicals (from C_2F_6) under the influence of a radio frequency (13.56 MHz, plasma synthesis) form CF_3SSCF_3 and polysulfanes [186,187]. Reaction of SF_6 with CS_2 at 485–495°C and 1350–4000 atmospheres yields CF_3SSCF_3 and other products [188]. Reaction of CF_3SH with $S_2O_6F_2$ (1 : 1 mole ratio) from −183 to 25°C gives the disulfane in 30% yield along with $S_2O_5F_2$, SO_2 and S [189]. Photolysis of $CF_3C(O)OSCF_3$ forms CF_3SSCF_3 in 25% yield [190]. Reaction of CF_3SCl with $(FCO)_2NCl$, $(CF_3)_2NCl$ or $(CF_3)_2C{=}NCl$ in the presence of mercury [191] or with

$(CF_2NCl)_3$ [176] or CF_3SPF_2 [192] yields CF_3SSCF_3 as a by-product. Pyrolysis of anhydrous $(CF_3S)_3N$ at 340°C results in the formation of CF_3SSCF_3 and $CF_3S_4CF_3$ as well as others [177]. Decomposition of CF_3SSBr occurs slowly at 20°C to give CF_3SSCF_3 and S_2Br_2 [173]. With CF_3SPF_2, CF_3SCl gives CF_3SSCF_3 and PF_2Cl. Hydrolysis of CF_3SPF_2 occurs rapidly to give CF_3SH and PF_3 accompanied by traces of CF_3SSCF_3, SiF_4 and fluorophosphoric acid, while hydrolysis of $CF_3SP(O)F_2$ yields mainly CF_3SSCF_3 [192]. Reaction of $LiSCF_3$ with *cis*-$SF_4(OCF_3)_2$ or SF_5Cl in diethyl ether at -78°C forms CF_3SSCF_3 as well as other products [193]. This disulfane, CF_3SSCF_3, is one of the products of the reaction of $Hg(SCF_3)_2$ with $CF_3S(O)Cl$ [194]. In the presence of $CF_3SF_2SCF_3$ [195,196], CF_3SF forms CF_3SF_3 and CF_3SSCF_3. In the reaction of CF_3SCl with CH_3OPCl_2 at -90°C, the unstable intermediate $CF_3SP(OCH_3)Cl_3$ reacts with additional CF_3SCl to give CH_3OPCl_4 and CF_3SSCF_3 [197].

This compound is a stable liquid which boils at 34°C. Electron diffraction studies show that it has a staggered configuration with C_2 symmetry [198]. The S–S bond distance is 206 pm. The Raman spectrum of liquid CF_3SSCF_3 and the IR spectrum of the gaseous compound are known [199]. Both ^{19}F and ^{13}C nuclear resonance spectra [195,200] and the mass spectra at 20 and 70 eV have been recorded [187,201].

(a) *Reactions of CF_3SSCF_3*

The disulfane reacts with fluorine in a continuous flow reactor at -120°C to give CF_3SF_3 after 38 h and CF_3SF_5 after 72 h [202]. Fluorination of CF_3SSCF_3 with CoF_3 at 170°C yields CF_3SF_5, SF_2 and SF_4 [203]. Reaction with ClF at 25°C for 10 h gives CF_3SF_4Cl in 79% yield [204]. It also reacts with excess ClF_3 in CF_2Cl_2 (-196 to -78°C) to give CF_3SF_3. Detonation has occurred when either ClF or ClF_3 was treated with CF_3SSCF_3 in the absence of a solvent [205]. Reaction of CF_3OCl with CF_3SSCF_3 which occurs at 0°C results in the cleavage of the S–S bond to form CF_3SF_3, Cl_2 and COF_2 as well as trace amounts of CF_3Cl and SF_4 [206]. With $(CF_3)_3COCl$ (-196 to 0°C), the sulfurane $CF_3(CF_3S)S[OC(CF_3)_3]_2$ forms in which four-coordinated sulfur(IV) is bonded to sulfur(II) [206,207].

Reaction of SF_6 and CF_3SSCF_3 in a gold tube at 540°C (24 h) forms C, S, CF_4, C_2F_6, C_3F_8, C_4F_{10}, C_5F_{12} and CS_2 [188]. With bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, CF_3OSO_2F forms in 58% yield [189]. Photolysis of an equimolar mixture of CF_3SSCF_3 and SCl_2 or S_2Cl_2 gives CF_3SSCl in low yield [208]. UV irradiation of a mixture of CF_3SSCF_3 and H_2S gives CF_3SH and sulfur [209].

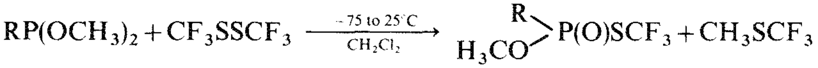
Under UV irradiation, CF_3SSCF_3 adds to $F_2C{=}CFX$ ($X = F$, Cl or CF_3) to give $CF_3S(CF_2CFX)_nSCF_3$ ($n \leq 4$). The alkene $CF_2{=}CH_2$ reacts similarly to give $CF_3SCF_2CH_2CH_2CF_2SCF_3$ [210,211]. The $CF_3S\cdot$ radical formed by photolysis of CF_3SSCF_3 also adds to $(CH_3)_2C{=}C{=}C(CH_3)_2$ [212] and $(CH_3)_3CN{=}S{=}NC(CH_3)_3$ [213]. A large variety of additional olefins have been reacted with CF_3SSCF_3 [214].

Photochemically generated CF_3S radicals (from CF_3SSCF_3 in cyclopropane) add to sulfanes, R^1SR^2 to form sulfuranyl radicals $R^1R^2S\dot{-}SCF_3$ (R^1 = alkyl; R^2 = alkyl/deuterated alkyl groups). The ESR spectra have been reported. Evidence is presented indicating that the radicals are non-planar with the unpaired electron occupying a σ^* orbital [215,216]. A similar type of reaction has been observed with monoselenides, R^1SeR^2 in cyclopropane, leading to radicals of the type $R_1R_2Se{-}SCF_3$ [217].

Upon irradiation, CF_3SSCF_3 reacts with dimethyl diallylmalontate forming a mixture consisting of 48% cyclic and 14% acyclic substitution products [218]. Similarly, with geranyl acetate, cyclic and acyclic products are formed in varying amounts depending on the reaction conditions used [218]. CF_3SSCF_3 reacts with 4,5-diphenyl-1-(2-tetrahydropyranyl)imidazole in THF/ether/hexane following the addition of LiC_4H_9 to form 4,5-diphenyl-1-(2-tetrahydropyranyl)-2-trifluoromethylimidazole (m.p., 104–105°C) [219].

The disulfane catalyzes decomposition [220] or transylidation [221] of stable sulfur ylides. Phosphetanes are oxidized by CF_3SSCF_3 to give difluorophosphoranes (two conformers) [222]. CF_3SSCF_3 reacts with $(CF_3P)_4$ in a Pyrex tube at 200°C to form $(CF_3S)_2PCF_3$ [223]. With $(CF_3)_2PP(CF_3)_2$, $(CF_3)_2S_2$ gives $(CF_3)_2PSCF_3$ in quantitative yield [223]. With $As_2(CF_3)_4$, the disulfide reacts at 95°C to yield $(CF_3)_2AsSCF_3$ [224]. With $(C_6H_5P)_5$ at 120°C in a Carius tube (15 h), CF_3SSCF_3 forms $C_6H_5P(SCF_3)_2$. The reaction with $C_6H_5P[Si(CH_3)_3]_2$ at 120°C (40 h) provides a route to $C_6H_5P(SCF_3)_2$ and $(CH_3)_3SiSCF_3$. Reaction with $C_6H_5PCl_2$ and zinc yields $C_6H_5P(SCF_3)_2$ [225].

Phosphoric acid derivatives react with CF_3SSCF_3 as follows [226]:



$$RP(OCH_3)_2 + CF_3SSCF_3 \xrightarrow[CH_2Cl_2]{-75\text{ to }25^\circ C} \overset{R}{\underset{H_3CO}{>}}P(O)SCF_3 + CH_3SCF_3$$

($R = OCH_3$, $N(C_2H_5)_2$)

$$(C_2H_5O)_2P(OH) + CF_3SSCF_3 \xrightarrow{-20\text{ to }20^\circ C} (C_2H_5O)_2P(O)SCF_3 + CF_3SH$$

With $(CH_3)_3GeH$ at 20°C, S–S bond breaking occurs to give an equilibrium mixture with CF_3SH. Cleavage by $(CH_3)_3SnH$ yields CF_3SH and $CF_3SSn(CH_3)_3$. In the latter case, conversion is 50% at 0°C and is complete at 20°C [227]. Copper metal reacts with $(CF_3)_2S_2$ to give $CuSCF_3$, which can be reacted with aryl iodides to form trifluoromethylaryl sulfides in good yield [228].

(vi) Bis(pentafluorophenyl)disulfane, $C_6F_5SSC_6F_5$

Bis(pentafluorophenyl)disulfane is formed either from C_6F_5SH and SbF_5 at 20°C (95% yield) or from $C_6F_5S(O)F$ in HF at 70°C (in 50% yield) [229]. Pentafluorobenzene reacts with S in liquid SO_2 in an autoclave at 90°C (2 h) to yield a mixture containing 10% $C_6F_5SSC_6F_5$ [230]. By reacting C_6F_5SH with MCl_3 (M =

In, Tl, Rh) [231] or $AlCl_3$, $FeBr_3$ or $CrCl_3$ [232], $C_6F_5SSC_6F_5$ is formed in 8–12% yield. The formation of $C_6F_5SSC_6F_5$ has been observed as a product of the hydrolysis of C_6F_5SCl with 15% NaOH solution [233]. It is also formed as a result of the oxidation of C_6F_5SH with 2-(benzenesulfonyl)-3-phenyloxaziridine [234] and from the reaction of C_6F_5Cl/HSO_3F with water [235]. A mixture of sulfides, $C_6F_5S_nC_6F_5$ ($n=2, 3$), is formed by the reaction of C_6F_5SSCl with H_2S in a 2 : 1 molar ratio in a sealed tube [236]. Pentafluorothiophenol reacts with S_2Cl_2 in CCl_4 to give $C_6F_5S_4C_6F_5$ [230]. $C_6F_5SSC_6F_5$ is also obtained together with C_6F_5SCl by chlorination of the product of the reaction of C_6F_5Cl with copper and sulfur [237]. Thermal decomposition of $Ti(SC_6F_5)_4$ above 70°C results in $C_6F_5SSC_6F_5$ [238]. Reactive nucleophiles such as C_6F_5SLi readily attack *cis*-$SF_4(OCF_3)_2$, SF_5X ($X=$ Cl, Br), CF_3SF_4Cl and $C_6F_5SF_4CF_3$ (molar ratios of 3 : 1 to 4 : 1 in diethyl ether at -78°C) to form $C_6F_5S_nC_6F_5$ ($n=2, 3$) [193].

A colorless solid, $C_6F_5SSC_6F_5$ melts at 49–52°C. It forms orthothombic crystals (1.94 g cm^{-3}). Important bond lengths and angles are S–S = 205.9 pm, S–C = 177.0 pm, $\angle SSC = 101.3°$. The dihedral angle is 76.5° and the angle between the planes of the rings is 39.3° [239]. The ^{19}F NMR [240,241], UV [242] and mass spectra [243] are known.

The reaction of $C_6F_5SSC_6F_5$ with ammonia (1 : 3 molar ratio) in a sealed tube at 25°C yields $NH_4SC_6F_5$ and $C_6F_5SNH_2$. The latter compound decomposes on vacuum sublimation to give $(C_6F_5S)_2NH$ and ammonia [241]. A blue solution is formed in SbF_5 which exhibits a strong ESR signal due to the presence of a radical cation. After 5 h at 20°C, 80% $C_6F_5SSC_6F_5$, 10% C_6F_5SH and 10% pentafluorobenzenesulfonyl fluoride are isolated after pouring this reaction mixture into water [229]. With perfluorolefins in the presence of SbF_5, perfluorinated aliphatic/aromatic sulfanes are found [244]. $C_6F_5SSC_6F_5$ and $C_6F_5S_4C_6F_5$ react with C_6F_5SH in SbF_5 to give $C_6F_5SC_6F_5$ in excellent yield [229,230]. Addition of $C_6F_5SSC_6F_5$ exhibits an influence on the free radical reaction of sulfenyl chlorides with hydrocarbons in a manner similar to cyclohexane or toluene. Substitution products C_6F_5SR ($R=$ C_6H_{11}, $C_6H_5CH_2$) are formed accompanied by the products usually obtained from the sulfenyl chloride reaction [245]. Germanium is oxidized by $C_6F_5SSC_6F_5$ at 350°C to $Ge(C_6F_5)_4$ [246].

(vii) Some polysulfanes

(a) Bis(trifluoromethyl)polysulfane, $CF_3S_nCF_3$ (n = 3–5)

Bis(trifluoromethyl)trisulfane is prepared by reacting CF_3SSCl with CF_3SH [172,208]. The trisulfane is also formed as a by-product in the reaction of CF_3SH with SCl_2 [208], and on reaction of $LiSCF_3$ with *cis*-$SF_4(OCF_3)_2$ or SF_5Cl [193]. Both the tri-and tetrasulfanes are obtained on decomposition of CF_3SSH in glass vessels [167]. The trisulfane has also been obtained from the reaction of CF_3SCl with H_2S [167]. CF_3SSCl with active KF [174], CF_3SSH with Cl_2, and sulfur vapor and C_2F_6 under plasma conditions [187] give trisulfanes. The gas-phase reaction of

CF_3SSCl with H_2S gives high yields of $CF_3S_5CF_3$ [173,208]. CF_3SSSCF_3 and $CF_3SSSSCF_3$ have been characterized by their ^{19}F NMR, IR and mass spectra [187].

(b) *Trifluoroacetyl(trifluoromethyl)trisulfane,* $CF_3C(O)SSSCF_3$

This compound is prepared in high yield when $CF_3C(O)SH$ is reacted with CF_3SSCl at 20°C (0.5 h) [172], and in 5% yield together with $CF_3C(O)SSCF_3$, when $CF_3C(O)SCl$ is reacted with CF_3SSH at −25°C [171]. Spectral parameters have been reported for this compound [172].

(c) *Trifluoromethyl(pentafluoroethyl)polysulfane,* $CF_3S_nC_2F_5$ (n = 3–5), *bis(pentafluoroethyl)polysulfane,* $C_2F_5S_nC_2F_5$ (n = 3–6); *2-oxo-1,1,2-trifluoroethyl(trifluoromethyl)polysulfanes,* $CF_3S_nCF_2C(O)F$ (n = 3, 4); *2-oxo-1,1,2-trifluoroethyl(pentafluoroethyl)polysulfane,* $C_2F_5S_nCF_2C(O)F$ (n = 3–5), *and bis(2-oxo-1,1,2-trifluoroethyl)polysulfanes,* $FC(O)CF_2S_nCF_2C(O)F$, (n = 3, 4)

$CF_3SSSC_2F_5$ and $C_2F_5SSSC_2F_5$ are formed by the reaction of $CF_2{=}CF_2$ with SbF_5, and excess sulfur in liquid SO_2 [247]. Reaction of $S_8[AsF_6]_2$ either neat or dissolved in liquid SO_2, SOF_2 or SO_2F_2 with $CF_2{=}CF_2$ [185] yields the tri- and tetrasulfanes. A mechanism for the formation of these polysulfanes has been proposed [185,248]. The penta- and hexasulfanes are formed only in small amounts. If SO_2 is used as the solvent, $CF_3S_nC_2F_5$, $C_2F_5S_nCF_2C(O)F$ ($n = 3$–5), $FC(O)CF_2S_nCF_2C(O)F$ and $CF_3S_nCF_2C(O)F$ ($n = 3, 4$) can be identified spectroscopically [248]. $C_2F_5S_nC_2F_5$ ($n = 3, 4$) is also obtained by the reaction of neat $S_4[AsF_6]_2$ or $S_8[AsF_6]_2$ with C_2F_4 [185]. $CF_3S_nC_2F_5$ ($n = 3, 4$) and $C_2F_5SSSC_2F_5$ are also formed in the plasma reaction of sulfur vapor and C_2F_6 [187].

(d) *Bis(pentafluorophenyl)polysulfanes,* $C_6F_5S_nC_6F_5$ (n = 3, 4)

The trisulfane is formed together with the disulfane when $LiSC_6F_5$ reacts with *cis*-$SF_4(OCF_3)_2$, SF_5Cl, SF_5Br or CF_3SF_4Cl [193]. The analogous reaction with *cis*-$CF_3SF_4CF_3$ yields only the trisulfane. The reaction of $Pb[SC_6F_5]_2$ with SCl_2 or S_2Cl_2 in benzene yields $C_6F_5S_3C_6F_5$ or $C_6F_5S_4C_6F_5$, respectively [240]. Reaction of C_6F_5SH with S_2Cl_2 in CCl_4 at 80°C (3 h) gives $C_6F_5SSSC_6F_5$ in 95% yield [230]. $C_6F_5SSSC_6F_5$ is isolated from the reaction of equimolar amounts of C_6F_5SCl and H_2S and also by the reaction of C_6F_5SSCl with H_2S (2 : 1 molar ratio) in a sealed tube [236].

The tri- and tetrasulfanes are solid compounds and have been characterized by various spectral techniques [240]. Molecular ions are observed for both compounds in their mass spectra. An interesting feature of the mass spectra of $(C_6F_5)_2S_n$ ($n = 3, 4$) is the presence of traces of higher polysulfanes up to $C_6F_5S_6C_6F_5$ presumably formed in the probe prior to sublimation in the source. From the Raman spectra, ν_{S-S} is found at 484 and 457 cm^{-1} for $n = 3$ and 4, respectively.

E. REACTIONS OF DISULFANES WITH METAL CARBONYLS AND COMPLEXES

Three main preparative routes have been developed for trifluoromethylthio complexes. Grobe and Kober [249] prepared the complexes by studying the thermal reactions of CF_3SX ($X=SCF_3$, SCH_3, SC_6H_5, Cl) with $Mn_2(CO)_{10}$. Others utilized photochemical reactions of $(CF_3)_2S_2$ with a variety of low-oxidation-state cyclopentadienyl and carbonyl complexes [250]. King and Welcman [251] used metathetical reactions of $AgSCF_3$ with metal carbonyl halides. In this section, only the reactions of CF_3SSCF_3 and $C_6F_5SSC_6F_5$ with metal carbonyls and complexes are included to emphasize another important aspect of the chemistry of disulfanes. Oxidative addition reactions of $(R_f)_2S_2$ provide a convenient route for the preparation of organometallic derivatives containing the R_fS moiety, ($R_f=CF_3$, C_6F_5). Table 1 includes some of the compounds obtained, their yields and the reaction conditions used.

Bis(trifluoromethyl)disulfane under photolysis with some organometallic compounds in low oxidation states gives trifluoromethylthio derivatives. On reaction of complexes with other ligands, the SCF_3 ligand remains coordinated in most cases. Davidson and Sharp [250] reported the formation of $[(\pi\text{-}C_5H_5)M(CO)_3(SCF_3)]$, ($M=Mo$, W); $[Fe(CO)_3(SCF_3)]_2$, $[Fe_2(CO)_6(SCF_3)]_2S$, $[(\pi\text{-}C_5H_5)Ni(SCF_3)]_2$, $[(\pi\text{-}C_5H_5)Mo(CO)_2(SCF_3)]_2$, $[Fe(CO)_2PPh_3(SCF_3)]_2$ and $[(\pi\text{-}C_5H_5)NiPPh_3(SCF_3)]$. It is probable that all of these reactions proceed through an intermediate $\cdot SCF_3$ radical, whereas some of the compounds seem to have been obtained by photochemical decarbonylation. Usually, the simple trifluoromethylthio derivatives are the major products and, once formed, are stable. Spectroscopic studies [250] indicate that the structures of these SCF_3 derivatives are analogous to the structure of the corresponding alkylthio and arylthio derivatives [260]. Where two bridging SCF_3 groups are present there is a possibility of *syn* and *anti* isomers. NMR spectroscopy is helpful in assigning structures of these compounds.

Oxidative addition reactions of CF_3SSCF_3 with Pt(0), Pd(0) and Ni(0) complexes offer a simple route to $[M(SCF_3)_2(PPh_3)_2]$ derivatives. $[Pt(SCF_3)_2(PPh_3)_2]$ is a greenish yellow product having a molecular weight of 911 in dibromomethane [252]. The ^{19}F NMR spectral data show the presence of approximately equal quantities of two compounds which can be assigned as *cis* and *trans* isomers.

In the case of $[Pd(SCF_3)_2(PPh_3)_2]$, only 10% of the *cis* isomer is obtained compared with about 50% in the corresponding platinum complex, but this is consistent with the known isomer ratio in other complexes [261]. With $Ni(PPh_3)_4$, CF_3SSCF_3 reacts even in the absence of irradiation to give a low yield of *trans*-$[Ni(SCF_3)_2(PPh_3)_2]$. The *trans* square planar geometry is confirmed by the diamagnetism of the complex and by the appearance in the ^{19}F NMR spectrum of a single triplet due to coupling with two equivalent phosphorus atoms [252].

Photolytic reactions between disulfanes and some manganese and nickel carbonyl complexes produce unstable $Mn(CO)_5SR$ and $[(\pi\text{-}C_5H_5)Ni(CO)SR]$ ($R=CF_3$,

TABLE 1

Reactions of $(R_f)_2S_2$ with metal carbonyls and complexes

Reactants	Products	Yield (%)	Reaction conditions	Ref.
$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2{}^a$	$[(\pi\text{-}C_5H_5)Mo(CO)_3SCF_3]$	28	Hexane, *hv*, 25°C, several h	250
$[(\pi\text{-}C_5H_5)W(CO)_3]_2{}^a$	$[(\pi\text{-}C_5H_5)W(CO)_3SCF_3]$	31	Hexane, *hv*, 25°C, several h	250
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2{}^a$	$[(\pi\text{-}C_5H_5)Fe(CO)_2SCF_3]$	55	Hexane, *hv*, 25°C, several h	250
$[(\pi\text{-}C_5H_5)Mo(CO)_3I]^a$	$[(\pi\text{-}C_5H_5)Mo(CO)_3SCF_3]$	28	Hexane, *hv*, 25°C, several h	250
$Fe_2(CO)_9{}^a$	$[Fe(CO)_3SCF_3]_2$,	20, 0.5	Hexane, *hv*. 25°C, several h	250
	$[Fe_4(CO)_{12}S(SCF_3)_2]$,	0.3, 0.1		
	$[Fe(CO)_3S]_2$, $[Fe(CO)_3]_3S$	respect.		
$Fe(CO)_5{}^a$	$[Fe(CO)_3SCF_3]_2$,	26, 0.5	Hexane, *hv*, 25°C, several h	250
	$[Fe_4(CO)_{12}S(SCF_3)_2]$	respect.		
$(\pi\text{-}C_5H_5)_2Ni^a$	$[(\pi\text{-}C_5H_5)_2Ni(SCF_3)]_2$	47	Hexane, *hv*, 25°C, several h	250
$Pd(PPh_3)_4{}^a$	*cis*-$[Pd(SCF_3)_2(PPh_3)_2]$	10	Pentane, *hv*, 25°C, 30 min	252
	trans-$[Pd(SCF_3)_2(PPh_3)_2]$	90		
$Ni[PPh_3]_4{}^a$	*trans*-$[Ni(SCF_3)_2(PPh_3)_2]$	–	Heptane, *hv*, 25°C, 45 min	252
$Pt[PPh_3]_4{}^a$	*cis*-$[Pt(SCF_3)_2(PPh_3)_2]$	45	Pentane, *hv*, 25°C, 30 min	252
$[Mn(CO)_5]_2{}^a$	$[Mn(SCF_3)(CO)_5]$,	~90	Pentane, *hv*, −10°C, 24 h	253
	$[Mn(CO)_4SCF_3]_2$			
$[(\pi\text{-}C_5H_5)Ni(CO)_2]_2{}^a$	$[(\pi\text{-}C_5H_5)Ni(SCF_3)_2]$	~90	Pentane, *hv*, 25 h	253
$Mo(CO)_6{}^a$	$[Mo(CO)_4(SCF_3)]_2$	5.5	Pentane, *hv*, 40 h	253
$W(CO)_6{}^a$	$[W(CO)_4(SCF_3)]_2$	80	Pentane, *hv*, 40 h	253
$[(\pi\text{-}C_5H_5)Co(CO)]^a$	$[(\pi\text{-}C_5H_5)Co(SCF_3)]_2$	–	Pentane, *hv*, 50 h	254
$MnCo(CO)_9{}^a$	$[Mn(CO)_5(SCF_3)]$,	–	Pentane, 90°C, 15 h	255
	$[Mn(CO)_4(SCF_3)]_2$	45		
$HMn(CO)_5{}^a$	$[Mn(CO)_5(SCF_3)]$	–	Benzene, −22°C, 10 min	256
$HRe(CO)_5{}^a$	$[Re(CO)_5(SCF_3)]$	45	Benzene, 35°C, ~2 days	256
$HMn(CO)_5{}^a$, $HRe(CO)_5{}^a$	$[Mn(CO)_5(SCF_3)]$,			
	$[Re(CO)_5(SCF_3)]$	–	Benzene	256
	$[MnRe(CO)_8(SCF_3)_2]$			

$[C_6H_{11}NC)_4Rh][BPh_4]$[a]	$[(C_6H_{11}NC)_4Rh(SCF_3)_2][BPh_4]$	80	CH_2Cl_2	257
$Co_2(CO)_8$[b]	$[C_6F_5SCo(CO)_3]_2$	80	Hexane, 20°C, 2 h	258
$Pd_2[Ph_2PCH_2PPh_2]_3$[b]	$[Pd_2(Ph_2PCH_2PPh_2)_2(SC_6F_5)_2]$	80	CH_2Cl_2	259
$Pd_2(Ph_2PCH_2PPh_2)_2(SC_6H_5)_2$[b]	$[Pd(Ph_2PCH_2PPh_2)_2(SC_6F_5)_2]$	79	CH_2Cl_2	259
$[Mn(CO)_5]_2$[b]	$[Mn(CO)_5(SC_6F_5)]$	92	Pentane, *hv*, −10°C, 24 h	253
$[(\pi\text{-}C_5H_5)NiCO]_2$[b]	$[(\pi\text{-}C_5H_5)Ni(SC_6F_5)]_2$	~90	Pentane, *hv*, 25 h	253
$[(\pi\text{-}C_5H_5)Co(CO)_2]$[b]	$[(\pi\text{-}C_5H_5)Co(CO)(SC_6F_5)_2]$	75	Pentane, 20°C, 3 days	254
$[(n\text{-}C_4H_9NC)_4Rh][BPh_4]$[b]	$[(n\text{-}C_4H_9NC)_4Rh(SC_6F_5)_2][BPh_4]$	48	Acetone	257

[a] $(CF_3)_2S_2$; [b] $(C_6F_5)_2S_2$

C_6F_5) complexes, which dimerize through decarbonylation [253]. CF_3SSCF_3 has been shown previously to react with $Mn_2(CO)_{10}$ [249,250,255,262] to form the thio-bridged species $[Mn(CO)_4(SCF_3)]_2$. Davidson and Sharp [253] were not able to isolate pure $CF_3SMn(CO)_5$, but have identified the product by comparison of its IR spectrum with that of $CF_3SRe(CO)_5$ and $C_6F_5SMn(CO)_5$ [251,263]. Spectroscopic characterization of $CF_3SMn(CO)_5$ and $CF_3SRe(CO)_5$ has also been described [256].

Bis(pentafluorophenyl)disulfane reacts similarly to give $C_6F_5SMn(CO)_5$ [251], which also undergoes decarbonylation to $[Mn(CO)_4(SC_6F_5)]_2$. The monomeric complexes, $[(\pi\text{-}C_5H_5)Ni(CO)SR]$ ($R = CF_3$, C_6F_5) are formed when $[(\pi\text{-}C_5H_5)Ni(CO)]_2$ is irradiated in the presence of the appropriate disulfane in a closed system [250,253].

Irradiation of $[\pi\text{-}(C_5H_5)Fe(CO)_2(SCF_3)]$ in hexane for 30 h produces olive-green crystals of the dimer, $[(\pi\text{-}C_5H_5)Fe(CO)(SCF_3)]_2$, in 72% yield as a mixture of two isomers. These isomers have been characterized by their IR and NMR spectra.

Irradiation of Group VI hexacarbonyls with CF_3SSCF_3 in hexane by using unfiltered radiation produces insoluble polymeric materials which were not characterized. However, by using a filtered UV source, the complexes $[M(CO)_3(SCF_3)]_2$ ($M = Mo$, W) are obtained.

Reactions of transition metal trifluoromethylthiolates with other ligands have been carried out to investigate the stability of complexes containing a metal–sulfur bond. Substitution [250,264], bridge cleavage [250,264] and the complete expulsion of the thio group can occur. Triphenylphosphine reacts with $[Fe(CO)_3(SCF_3)]_2$ to give $[Fe_2(CO)_5(PPh_3)(SCF_3)_2]$ in a *syn*:*anti* isomer ratio of 1:14 as a red oil that has been characterized spectroscopically. Nitric oxide causes complete substitution of CO in $[Fe(CO)_3(SCF_3)]_2$ to form $[Fe(NO)_3(SCF_3)]_2$.

In general, thiolate derivatives of cobalt are polymeric showing considerable complexity, although it has been pointed out that the presence of strongly electronegative substituents on sulfur should reduce the tendency to polymerization. The products of the reactions between dicarbonylcyclopentadienyl cobalt and $C_6F_5SSC_6F_5$ depend on the reaction conditions. In the absence of a solvent, a 1:1 molar ratio of the reactants gives a dark green air-sensitive solid $[(\pi\text{-}C_5H_5)Co(SC_6F_5)]_2$ at room temperature. In pentane solution on irradiation above $-10°C$, black crystals of $[(\pi\text{-}C_5H_5)Co(CO)(SC_6F_5)_2]$ are formed. A solution of $[(\pi\text{-}C_5H_5)Co(CO)(SC_6F_5)_2]$ heated above 50°C gives $[(\pi\text{-}C_5H_5)Co(SC_6F_5)]_2$ and an additional green complex thought to be $[(\pi\text{-}C_5H_5)Co_2(SC_6F_5)_3]$.

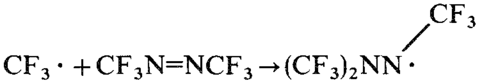
The reaction between carbonylcyclopentadienyl cobalt and CF_3SSCF_3 in the dark gives an ill defined purple-black solid, but under photolytic reaction conditions in pentane gives the air-sensitive green-black solid $[(\pi\text{-}C_5H_5)Co(SCF_3)]_2$. The main spectral features of these complexes are known [254]. Balch et al. [257] have obtained a yellow crystalline product $[(C_6H_{11}NC)_4Rh(SCF_3)_2][BPh_4]$, and the orange compound $[(n\text{-}C_4H_9NC)_4Rh(SC_6F_5)_2][BPh_4]$ by the reaction of CF_3SSCF_3 with $[(C_6H_{11}NC)_4Rh][BPh_4]$ in CH_2Cl_2, and of $C_6F_5SSC_6F_5$ with $[(n\text{-}C_4H_9NC)_4Rh][BPh_4]$ in CH_3CN, respectively.

F. CATENATED NITROGEN COMPOUNDS

The first member of the series, tetrafluorohydrazine, N_2F_4, has been reviewed recently [265]. In this section, the chemistry of some substituted hydrazines, e.g. $(R_f)_2N_2(R_f)_2$, fluorinated triazanes and tetrazanes is covered.

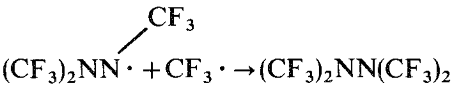
(i) Tetrakis(trifluoromethyl)hydrazine, $(CF_3)_2NN(CF_3)_2$

Dimethylamine diluted with nitrogen on fluorination with F_2 at 285° (32 h) gives $(CF_3)_2NN(CF_3)_2$ [266]. Fluorination of mono-, di- and trimethylamines under these reaction conditions leads to mixtures of several fluorinated amines which may be accounted for readily by free radical mechanisms [266]. Hexafluoroazomethane is decomposed by light (2537 Å) to yield nitrogen, C_2F_6, $(CF_3)_2NN(CF_3)_2$ and perfluorohexamethyltetrazane [267]. The relative amounts of various products vary with the pressure. Compounds of higher molecular weights are produced more abundantly at higher pressures. The initial step in this photolysis is the heterolytic decomposition of hexafluoroazomethane into a molecule of nitrogen and two $CF_3\cdot$ radicals which may react with one another to form hexafluoroethane or with the parent material to form a new radical.

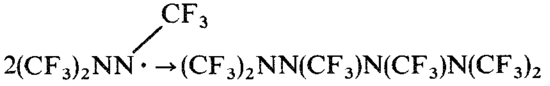


$$CF_3\cdot + CF_3N{=}NCF_3 \rightarrow (CF_3)_2N\overset{CF_3}{N}\cdot$$

Further reaction of $CF_3\cdot$ with the hydrazo radical may form perfluorotetramethylhydrazine or two hydrazo radicals can combine to form perfluorohexamethyltetrazane.

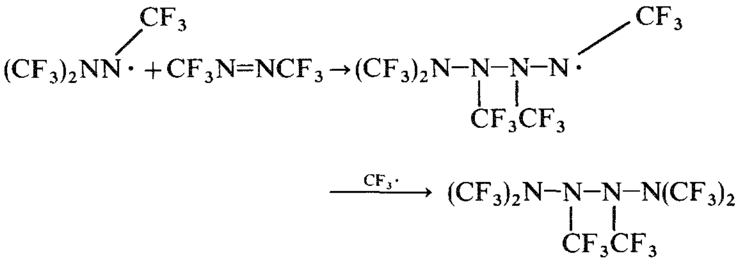


$$(CF_3)_2N\overset{CF_3}{N}\cdot + CF_3\cdot \rightarrow (CF_3)_2NN(CF_3)_2$$



$$2(CF_3)_2N\overset{CF_3}{N}\cdot \rightarrow (CF_3)_2NN(CF_3)N(CF_3)N(CF_3)_2$$

An alternate route to the tetrazane, however, could be the reaction of the hydrazo radical with the starting material which would in turn react with the $CF_3\cdot$ radical.



$$(CF_3)_2N\overset{CF_3}{N}\cdot + CF_3N{=}NCF_3 \rightarrow (CF_3)_2N{-}\underset{CF_3}{N}{-}\underset{CF_3}{N}{-}\overset{CF_3}{N}\cdot$$

$$\xrightarrow{CF_3\cdot} (CF_3)_2N{-}\underset{CF_3}{N}{-}\underset{CF_3}{N}{-}N(CF_3)_2$$

AgF_2 reacts with $CF_3N{=}CF_2$ at room temperature to give both the azomethine dimer, $(CF_3)_2NCF{=}NCF_3$, and the substituted hydrazine, $(CF_3)_2NN(CF_3)_2$ [268]. At higher temperatures, both $CF_3N{=}CF_2$ and $(CF_3)_2NCF{=}NCF_3$ are converted to $(CF_3)_2NF$ but the hydrazine derivative does not react further.

The irradiation of an equimolar mixture of CF_3I and CF_3NO under various conditions gives $(CF_3)_2NOCF_3$ (50%), *O*-nitrosobis(trifluoromethyl)hydroxylamine $(CF_3)_2NONO$ (23%) and other higher boiling products [269]. Use of a 2:1 ratio of reactants forms $(CF_3)_2NOCF_3$ in 90% yield as well as other gaseous products, such as C_2F_6, COF_2, CO_2 and SiF_4 [270]. Intense irradiation of $(CF_3)_2NOCF_3$ gives $(CF_3)_2NON(CF_3)_2$ (73%), while weaker irradiation leads to $(CF_3)_2NN(CF_3)_2$ (~80%). The formation of these products has been explained by initial cleavage of the N–O bond in the hydroxylamine to give the $(CF_3)_2N\cdot$ and $CF_3O\cdot$ radicals. Reaction of $(CF_3)_2N\cdot$ with tris(trifluoromethyl)hydroxylamine leads to the formation of hydrazines, e.g.

$$CF_3I \text{ or } CF_3NO \xrightarrow{h\nu} CF_3\cdot$$

$$(CF_3)_2NOCF_3 \xrightarrow{h\nu} (CF_3)_2N\cdot + CF_3O\cdot$$

$$2(CF_3)_2N\cdot \rightarrow (CF_3)_2NN(CF_3)_2$$

$$(CF_3)_2N\cdot + CF_3NO \rightarrow (CF_3)_2NN(CF_3)O\cdot \xrightarrow{CF_3\cdot} (CF_3)_2NN(CF_3)OCF_3$$

$$(CF_3)_2NN(CF_3)O\cdot \xrightarrow{NO\cdot} (CF_3)_2NN(CF_3)ONO$$

$$\begin{tikzcd}
 & {} \arrow[r, "h\nu"] & (CF_3)_2N\dot{N}(CF_3)+NO_2 \arrow[dl] \arrow[dr, "CF_3\cdot"] & \\
 & {\begin{matrix}(CF_3)_2NN(CF_3)N(CF_3)N(CF_3)_2\\(95\%)\end{matrix}} & & (CF_3)_2NN(CF_3)_2
\end{tikzcd}$$

Irradiation of mercury bis(trifluoromethyl)amide, $Hg[N(CF_3)_2]_2$ forms $(CF_3)_2NN(CF_3)_2$, again probably via a free radical mechanism [271]. Reactions of *N*-bromobis(trifluoromethyl)amine with hexafluorocyclobutene and octafluorobut-2-ene at 100°, 96 h and 100°, 48 h, respectively, lead to olefin dibromides and tetrakis(trifluoromethyl)hydrazine [272].

N-Bromobis(trifluoromethyl)amine undergoes addition reactions with an excess of cyanogen chloride in a sealed vessel under UV irradiation to give bis(trifluoromethyl)aminocarbylamine chloride, $(CF_3)_2NNCCl_2$, in >40% yield. The other major product is $(CF_3)_2NN(CF_3)_2$ [273]. Bis(trifluoromethyl)aminocarbylamine chloride reacts with mercury fluoride at 140°C, to form di[tris(trifluoromethyl)hydrazyl]mercury, $[(CF_3)_2NN(CF_3)]_2Hg$. This parallels the addition of HgF_2 to perfluoro-2-azopropene [274] to form di(bis(trifluoromethyl)amino)mercury, and to SF_5NCF_2 [275] to give di(*N*-trifluoromethyl-*N*-pentafluorosulfuramino)mercury. Di(tris-(trifluoromethyl)hydrazyl)mercury reacts with bromine at room temperature, to give a mixture of *N*-bromo(tristrifluoromethyl)hydrazine and perfluorohexamethyltetrazane, previously reported to be formed in the photolysis of hexafluoroazomethane [267,276].

N,*N*-Dimethylformamide on fluorination with F_2/He at ~275° gives $(CF_3)_2NN(CF_3)_2$ (~3.4%) [277]. Irradiation of $(CF_3)_2NBr$ in a sealed quartz ampoule for 5 days with a mercury lamp gave $(CF_3)_2NN(CF_3)_2$ [278]. Photolytic or thermal decomposition (350–500°) of perfluoroazoalkanes leads to the generation of free radicals $R_f\cdot$. These can be coupled to give R_f–R_f or added to the parent molecule to give tetrasubstituted hydrazines [279].

Hydrogen fluoride adds to $SF_5N{=}CF_2$ to give an amine, F_5SNHCF_3, which on treatment with silver(II) fluoride at 100°C forms a substituted hydrazine, which is stable hydrolytically [275].

$$2AgF_2 + 2F_5SNHCF_3 \rightarrow F_5S(CF_3)NN(CF_3)SF_5 + 2AgF + 2HF$$

Direct fluorination of 2-fluoropyridine with F_2/N_2 at 150–160°C gives a mixture of various fluorinated compounds including $(CF_3)_2NN(CF_3)_2$ [280]. When an equimolar mixture of $CF_3(FCO)NCl$ or $(FCO)_2NCl$ and $(CF_3)_2NCl$ is allowed to mix by diffusion and is then photolyzed at 2537 Å for 1 h at 30°C, a mixture of substituted hydrazines along with a substantial amount of $(CF_3)_2NN(CF_3)_2$ is obtained [191]. The methods of preparing $(CF_3)_2NN(CF_3)_2$ are numerous and include fluorination of $(CF_3)_3N$ with CoF_3 at 250°C [281], and reaction of $(CF_3)_2NCl$ with Hg [282]. Pyrolysis of $CF_3N{=}NCF_3$ at 325°C for 8 h yields $(CF_3)_2NN(CF_3)_2$ [283]. Reaction of $CF_3N{=}CF_2$ with various metal fluorides [268] and $(CF_3)_2NC(O)F$ with AgF_2 [284] give the hydrazine derivative. Irradiation of an equimolar mixture of *N*-chlorobis(trifluoromethyl)amine and methane sealed in a quartz ampoule for 20 h yields a mixture of $(CF_3)_2NN(CF_3)_2$, HCl, SiF_4 and $(CF_3)_2NH$ [285]. Reaction of bis(trifluoromethyl)nitroxide radical with white phosphorus at −50°C gives a mixture of products including $(CF_3)_2NN(CF_3)_2$ [286]. Disulfur decafluoride reacts with $(CF_3)_2NO$ at 150°C to give $(CF_3)_2NOSF_5$ in quantitative yield which on pyrolysis at 350°C affords CF_4, C_2F_6, SOF_4, $(CF_3)_2NNO$ and $(CF_3)_2NN(CF_3)_2$. The latter is a liquid that boils at 32°C (density 1.2408 g cm^{-3}) and which is thermally very stable. Its stability is even more remarkable when it is considered that it is among the most crowded of the derivatives and must suffer substantial repulsions between its bulky CF_3 groups. Structural parameters have been determined by electron diffraction [287]. A detailed vibrational study of this molecule was carried out in all phases [283,288] with the conclusion that the $(CF_3)_4N_2$ molecule exists in the C_2 *gauche* conformation.

(ii) N,N,N′,N′-substituted hydrazines $(R_f)_2NN(R_f)_2$ ($R_f = CF_3$, *FCO*)

Fluorinated *N*-chloramines are obtained using various techniques, e.g. from proton abstraction reactions of fluorinated amines with ClF [289] or chlorine [275,290,291] in the presence of alkali metal fluorides or by the reaction of ClF with fluoroalkylamines [289,292,293] and fluoroalkyl or acyl isocyanates [294]. The polar character of the $\gt N^{-\delta}\text{–}Cl^{+\delta}$ bond is supported by the formation of elemental chlorine when *N*-chloramines are treated with compounds which contain negative chlorine [274,294]. In addition to metathetical reactions [273,278], under appropriate thermal or photolytic conditions, chloramines give rise to hydrazines [278,289]. Photolysis of various combinations of $(CF_3)_2NCl$, $CF_3(FCO)NCl$ and $(FCO)_2NCl$ generate a new series of substituted hydrazines, $(CF_3)_{4-n}(FCO)_nN_2$ ($n = 0$–4) [191]. Photolysis is carried out at 30°C for 1 h using a low-pressure lamp at 2537 Å.

$$R_fR_f'NCl + R_f''R_f'''NCl \xrightarrow[\text{gas, 1 h}]{2537\ \text{Å}} (R_fR_f'N)_2 + R_fR_f'NNR_f''R_f''' + (R_f''R_f'''N)_2 + Cl_2$$

(R_f, R_f', R_f'', $R_f''' =$ any combination of CF_3 and/or FCO)

Physical properties, IR, ^{19}F NMR and mass spectra of these substituted hydrazines are known [191]. The ^{19}F NMR spectra of the hydrazines are temperature-dependent, which implies conformer effects. The spectra indicate multiple conformer changes over the range of −70 to 70°C. From 70 to 120°C, various conformer effects seem to disappear or are minimized. The changes may involve hindered bond rotation about the N–N bond [287,288,295,296], inversion at the nitrogen atom [297,298], and the resonance effects of the non-bonded electrons of the nitrogen interacting with the fluoroformyl group resulting in hindered bond rotation about the carbonyl nitrogen bond [298,299]. The number and location of the FCO group(s) seem to determine the complexity of the variable temperature spectra, e.g. $(CF_3)_4N_2$ yields the simplest spectrum and $CF_3(FCO)NNCF_3(FCO)$ has the most complex spectrum of the hydrazine series.

The synthesis of bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$, [300,301] by the reaction of NH_3 with $(CF_3)_2SF_2$ in the presence of a primary amine occurs in 50–60% yield. The lithiated salt $LiN{=}S(CF_3)_2$ behaves as a useful transfer reagent for the $(CF_3)_2S{=}N$ moiety [301,302]. In the reaction of $(CF_3)_2S{=}NH$ with ClF in the presence of CsF, the *N*-chloro imide [303] is formed which upon photolysis gives a substituted azine. It is a colorless liquid which is stable in Pyrex glass for indefinite periods. The infrared, ^{19}F NMR and mass spectra are known.

$$(CF_3)_2SF_2 + NH_3 \xrightarrow{PhCH_2NH_2} (CF_3)_2S{=}NH$$

$$(CF_3)_2S{=}NH + ClF \xrightarrow[CsF]{-78\ \text{to}\ 25^\circ} (CF_3)_2S{=}NCl$$

(70%)

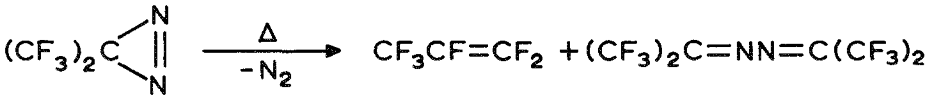
$$(CF_3)_2S{=}NCl \xrightarrow[\text{Pyrex}]{h\nu} (CF_3)_2S{=}N{-}N{=}S(CF_3)_2 + Cl_2$$

(50%)

Studies of the reactions of trifluoroacetyl halides with amines [304] or substituted hydrazines [305,306] show that formation of the trifluoroacetamide derivative with concomitant loss of HX is typical behavior. In contrast to trifluoroacetyl chloride, hexafluoroacetylacetone has been reacted with ammonia, primary amides, and hydrazine monohydrate to eliminate water and form imines, which may be cyclic [307]. However, the trifluoroacetyl derivative of *N*,*N*-dimethylhydrazine which forms by the reaction of the latter with CF_3COCl in the presence of CsF or Et_3N, at 25° is isolable [308]. This product is a white crystalline solid, m.p. 85–87°C.

$$CF_3COCl + (CH_3)_2NNH_2 \xrightarrow{Et_3N} (CH_3)_2NNHC(O)CF_3$$

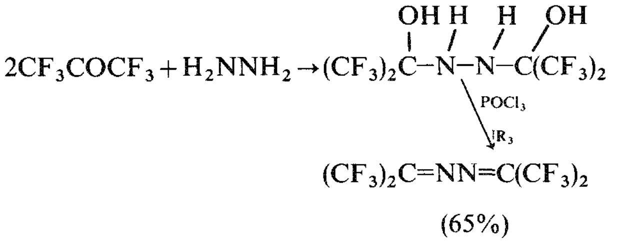
Pyrolysis of bis(trifluoromethyl)diazirine in quartz at 300°C (helium flow system) gives hexafluoroacetone azine [309] and hexafluoropropene as major products.



Not unexpectedly, the proton of $(CF_3)_2C{=}NH$ is acidic. On treatment with CH_3Li, it gives $(CF_3)_2C{=}NLi$, which on bromination forms the *N*-bromo compound, $(CF_3)_2C{=}NBr$. On photolysis, the *N*-bromo compound loses Br_2 to give the azine (94%) [298].

$$2(CF_3)_2C{=}NBr \xrightarrow{h\nu} (CF_3)_2C{=}NN{=}C(CF_3)_2 + Br_2$$

A simple synthesis of hexafluoroacetone azine is the direct treatment of hydrazine or hydrazine hydrate with an excess of hexafluoroacetone [310].



$$2CF_3COCF_3 + H_2NNH_2 \rightarrow (CF_3)_2\overset{OH}{C}{-}\overset{H}{N}{-}\overset{H}{N}{-}\overset{OH}{C}(CF_3)_2 \xrightarrow[NR_3]{POCl_3} (CF_3)_2C{=}NN{=}C(CF_3)_2$$

(65%)

Hexafluoroacetone azine is a colorless liquid which boils at 67–67.5° [311]. Reactions of $(CF_3)_2C{=}NN{=}C(CF_3)_2$ with alkanes [312,313], with alkenes [314–322], with alkynes [322,323], with nitriles [324], with silanes [312] and with phosphines [310,325] have been described and the products characterized.

Perfluoroazopropene can be dimerized in the presence of CsF to give

$(CF_3)_2NCF{=}NCF_3$, which on further treatment with ClF at −78°C for 14 h results in a 75% yield of $(CF_3)_2NCF_2N(Cl)CF_3$. This chloramine on photolysis provides a diazane, $[(CF_3)_2NCF_2(CF_3)N-]_2$ in 80% yield. It is a colorless liquid that has been characterized by infrared, ^{19}F NMR and mass spectra [326].

(iii) Triazanes and tetrazanes

Triazane, $H_2NN(H)NH_2$, with a completely reduced acyclic three-nitrogen chain, is the hypothetical parent of this class. Most known triazanes contain both acyl and alkyl or aryl substituents together with one or more hyrogen atoms, and are moderately stable. Stability seems to be conferred by the simultaneous presence on the triazane chain of an electron-releasing and an electron-withdrawing group [327]. Benson [327] has mentioned some organic (non-fluorinated) substituted catenated nitrogen compounds having as many as eight nitrogen atoms. Among fluorinated highly catenated nitrogen compounds, only triazanes and tetrazanes are known and will be described here.

1,1,3-Trifluoro-2,3-bis(perfluoroalkyl)triazanes, $F_2NNR_fNFR_f'$ (**I**), in which $R_f = R_f'$ or $R_f \neq R_f'$ and are perfluoroalkyl, ω-hydroxyperfluoroalkyl, or ω-chloroperfluoroalkyl of up to 19 carbon atoms, were prepared by subjecting a mixture of N_2F_4 and azo compound, $R_fN{=}NR_f'$ (**II**) to photolysis. Fluorinated triazanes (**I**) are useful as catalysts for the polymerization of ethylenic compounds and as energy-rich sources in propulsion systems [328]. Ultraviolet irradiation of an equimolar mixture of hexafluoroazomethane and N_2F_4 at 25°C for 1.25 h gave 1,1,3-trifluoro-2,3-bis(trifluoromethyl)triazane, $F_2NN(CF_3)N(CF_3)F$ (**III**). Similarly, irradiation of a mixture of decafluoroazoethane and N_2F_4 gave the corresponding perfluoroethyl derivative (**IV**) in 36% yield [299].

The mechanism of the reaction involves photolytic decomposition of N_2F_4 via an excited difluoramino radical [329] to give a fluorine radical which subsequently adds to the azo bond. No products corresponding to the direct addition of N_2F_4 to the azo group have been observed. These triazanes are stable materials; **III** boils at 19°C and **IV**, a yellow liquid, boils at 77°C. They can be stored indefinitely at −78°C. Thermal cleavage of the reaction products gives the starting materials.

(a) N-Nitroso[tris(trifluoromethyl)]hydrazine, $(CF_3)_2NN(CF_3)NO$

Bis(trifluoromethyl)aminocarbylamine chloride, $(CF_3)_2NN{=}CCl_2$, reacts with mercuric fluoride in a sealed ampoule at 140°C to give a volatile solid, di[tris(trifluoromethyl)hydrazyl]mercury, $[(CF_3)_2NN(CF_3)]_2Hg$, [273]. The latter with nitrosyl chloride at room temperature gives a yellow liquid (b.p. 30°C) identified as $(CF_3)_2NN(CF_3)NO$ in almost quantitative yield. The infrared spectrum of the vapor showed a band at 1630 cm^{-1} attributed to $\nu(N{=}O)$. These reactions show the similarity of the trifluoromethyl and bis(trifluoromethyl)amino groups, since the properties and reactions of tris(trifluoromethyl)hydrazyl compounds resemble those of the corresponding bis(trifluoromethyl)amino compounds [273].

(b) N-Nitro[tris(trifluoromethyl)]hydrazine, $(CF_3)_2NN(CF_3)NO_2$

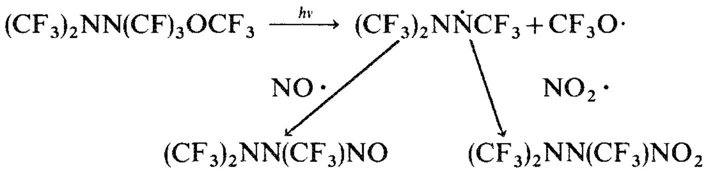
The irradiation of an equimolar mixture of trifluoroiodomethane and trifluoronitrosomethane gave tris(trifluoromethyl)hydroxylamine, $(CF_3)_2NOCF_3$ in excellent yield [270]. The formation of *N*-nitroso[tris(trifluoromethyl)]hydrazine (described above) and *N*-nitro[tris(trifluoromethyl)]hydrazine has been explained based on the reaction mechanism:

$$(CF_3)_2NOCF_3 \xrightarrow{h\nu} (CF_3)_2N\cdot + \cdot OCF_3$$

$$CF_3NO \xrightarrow{h\nu} (CF_3)_2NONO \xrightarrow{h\nu} (CF_3)_2N\cdot + NO_2\cdot$$

$$CF_3NO \text{ or } CF_3I \xrightarrow{h\nu} CF_3\cdot + NO\cdot$$

$$(CF_3)_2N\cdot + CF_3NO \rightarrow (CF_3)_2NN(CF_3)O\cdot \xrightarrow{CF_3\cdot} (CF_3)_2NN(CF_3)OCF_3$$



$$(CF_3)_2NN(CF)_3OCF_3 \xrightarrow{h\nu} (CF_3)_2N\dot{N}CF_3 + CF_3O\cdot$$

$$(CF_3)_2N\dot{N}CF_3 \xrightarrow{NO\cdot} (CF_3)_2NN(CF_3)NO \qquad (CF_3)_2N\dot{N}CF_3 \xrightarrow{NO_2\cdot} (CF_3)_2NN(CF_3)NO_2$$

Attack of the $(CF_3)_2N\cdot$ radical on the nitrogen of nitrosotrifluoromethane is expected by analogy with $CF_3\cdot$ radical attack on trifluoronitrosomethane [282,331]. The nitro analogue, $(CF_3)_2NN(CF_3)NO_2$, is a colorless liquid with ν_{NO_2} assigned to an infrared band at 1672 cm^{-1} [330].

(c) Hexakis(trifluoromethyl)tetrazane, $(CF_3)_2NN(CF_3)N(CF_3)N(CF_3)_2$

Hexafluoroazomethane, $CF_3N{=}NCF_3$, on photolysis gives hexakis(trifluoromethyl)tetrazane [267,276]. The mechanism of the reaction has already been described in an earlier section. Di[tris(trifluoromethyl)hydrazyl]mercury, $[(CF_3)_2NN(CF_3)]_2Hg$, reacted at room temperature with bromine, gives a mixture of *N*-bromo[tris(trifluoromethyl)]hydrazine and the perfluorohexamethyltetrazane [273]. When the *N*-bromo compound is exposed to daylight, it disproportionates to the tetrazane and bromine in a short time [273]. Irradiation of perfluoro(methoxytrimethyl)hydrazine, $(CF_3)_2NN(CF_3)OCF_3$, gives the tetrazane in ~95% yield [270]. Hexakis(trifluoromethyl)tetrazane is a slightly volatile colorless liquid which boils at 103°C and is stable thermally. Although the mass spectrum of the tetrazane did not show the molecular ion peak, a mass fragment corresponding to $[(CF_3)_4N_3^+]$ was observed [331].

(d) Polyfluoro- and (perfluoroalkyl)tetrazanes

The chemistry of nitrogen halogen bonds has been a subject of study for over three decades, but the reactivity of these bonds has only rarely been utilized in the preparation of fluorinated, highly catenated nitrogen-containing compounds. Both fluorinated and non-fluorinated olefins can be inserted into nitrogen–halogen bonds, e.g. hexafluoropropene or ethylene into the nitrogen–halogen bond of bromo- or iodobis(trifluoromethyl)amine [272,274,278,332,333] or olefins into chlorobis(trifluoromethyl)amine [334,335]. Recently, stepwise insertions of $CF_2{=}CFX$ ($X = Cl$, F) into the N–Cl bonds of dichloro(perfluoroalkyl)amines [336] were examined. Insertion of cyanogen chloride and/or trifluoroacetonitrile into N–Cl bonds, e.g. in chlorobis(trifluoromethyl)amine [273] and into sulfur–chlorine bonds, e.g. SF_5Cl [275] and CF_3SF_4Cl [337] via photolysis provides interesting reaction intermediates.

Insertion of ClCN and CF_3CN into the nitrogen–chlorine bonds of bis(polyfluoroalkyl)- or bis(perfluoroalkyl)chloroamines, followed by the facile addition of chlorine monofluoride to the carbon–nitrogen double bond and subsequent photolysis of the resulting nitrogen–chlorine bonds give rise to tetrazanes that are highly stable and insensitive to water, air, heat and shock [338]. These compounds are stable fluids with densities of $\sim 2\ \mathrm{g\ cm^{-3}}$. For example, when mixtures of *N*-chloro compounds, $CF_3N(Cl)CF_2CXClF$ ($X = Cl$, F) or $CF_3(C_2F_5)NCl$, and RCN, ($R = Cl$, CF_3) are photolyzed for 6–8 h at room temperature, the insertion of $-C{\equiv}N$ into the N–Cl bond occurs readily to form carbimides in high yields.

$$R_f(CF_3)NCl + RC{\equiv}N \xrightarrow{h\nu} R_f(CF_3)NN{=}CClR$$

$R_f = CCl_2FCF_2$, $R = Cl$ (**I**) $\qquad$ $R_f = CF_3CF_2$, $R = Cl$ (**III**)

$R_f = CClF_2CF_2$, $R = Cl$ (**II**) $\qquad$ $R_f = CF_3CF_2$, $R = CF_3$ (**IV**)

In the case of compounds **I**–**III**, addition of ClF at 25°C results both in the addition of ClF and partial fluorination.

$$\mathbf{I} \xrightarrow[25^\circ C]{ClF} CF_3(CCl_2FCF_2)NN(Cl)CClF_2$$

$$\mathbf{II} \xrightarrow[25^\circ C]{ClF} CF_3(CClF_2CF_2)NN(Cl)CClF_2$$

$$\mathbf{III} \xrightarrow[25^\circ C]{ClF} \underset{\mathbf{V}}{CF_3(CF_3CF_2)NN(Cl)CClF_2}$$

With **IV**, ClF adds to the double bond without concomitant fluorination to form $CF_3(CF_2CF_3)NN(Cl)CClFCF_3$ (**VI**). Subsequent photolysis of **V** results in the formation of a stable tetrazane, **VII**

$$\mathrm{V} \xrightarrow{h\nu} [CF_3(CF_3CF_2)NN(CClF_2)]_2 + Cl_2$$

$$\mathbf{VII}\ (90\%)$$

The photolysis of **VI** causes the loss of chlorine to form a new perfluorinated carbimide, **VIII**. However, ClF does react readily with **VIII** to give $CF_3(CF_3CF_2)NN(Cl)CF_2CF_3$ which, when photolyzed, results in the totally fluorinated tetrazane, **IX**.

$$\mathrm{VI} \xrightarrow[-Cl_2]{h\nu} CF_3(CF_3CF_2)NN{=}CFCF_3$$

$$\mathbf{VIII}$$

$$\mathrm{VIII} + ClF \rightarrow CF_3(CF_3CF_2)NN(Cl)CF_2CF_3 \xrightarrow{h\nu} [CF_3(CF_3CF_2)NN(CF_2CF_3)]_2$$

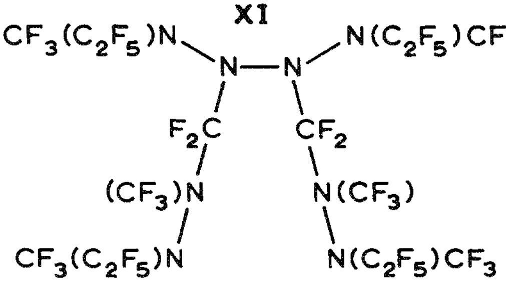
$$\mathbf{IX}\quad (90\%)$$

Compounds **III** and **IV** were reacted with CsF to replace chlorine atoms with fluorine. Simple fluorination of **IV** gave $CF_3(C_2F_5)NN{=}CFCF_3$ (**VIII**). However, with **III**, fluorination first occurred to form $CF_3(C_2F_5)NN{=}CF_2$ with dimerization occurring by the same route as has been suggested for $(CF_3)_2NN{=}CF_2$ [267] to give $CF_3(C_2F_5)NN(CF_3)CF{=}NN(C_2F_5)CF_3$ (**X**). When reacted with ClF, **X** was converted to **XI** which, on photolysis, produces another complex tetrazane **XII**.

$$\mathrm{X} + ClF \longrightarrow CF_3(C_2F_5)NN(CF_3)CF_2N(Cl)N(C_2F_5)CF_3$$

$$\mathbf{XI}$$

$$\mathrm{XI} \xrightarrow{h\nu}$$



XII (93%)

Each of these compounds is characterized by IR, NMR and mass spectral measurements [338]. Mass spectra are particularly helpful in the elucidation of the structures of these tetrazanes.

In view of the fact that the formation of tetrazanes is based on a radical mechanism, it is possible to insert olefins into the N-2–N-3 bond of tetrazanes under quite mild conditions. The tetrazane, $[CF_3(C_2F_5)NN(C_2F_5)]_2$, when heated at 100–110°C with the polyfluorolefins $CF_2{=}CFCl$, $CFCl{=}CFCl$, $CF_2{=}CH_2$, $CF_2{=}CFH$ forms $CF_3(C_2F_5)NN(C_2F_5)CX_2CY_2N(C_2F_5)N(C_2F_5)CF_3$ [339]. These adducts are colorless liquids obtained in 30–40% yield. The spectral data of these compounds, as well as confirming elemental analyses, are known [339].

Insertion of nitriles into the N–Cl bonds of chlorotris(perfluoroalkyl)hydrazines gives highly fluorinated three nitrogen compounds in low yield.

$$CF_3(C_2F_5)NN(Cl)C_2F_5 + CF_3CN \xrightarrow[6\text{–}10\,h]{h\nu}$$

$$CF_3(C_2F_5)NN(C_2F_5)N{=}C(Cl)CF_3 + [CF_3(C_2F_5)NN(C_2F_5)]_2$$

XIII (5–10%) (60–70%)

XIII is a viscous, water-white, slightly volatile liquid, stable at room temperature for long periods. While addition of ClF to the double bond of **XIII** leads to fragmentation.

XIII reacts with lithium polyfluoroalkoxides to give stable compounds.

$$\mathbf{XIII} + LiOR_f \xrightarrow{-196\text{ C to RT}} CF_3(C_2F_5)NN{=}C(OR_f)CF_3 + LiCl$$

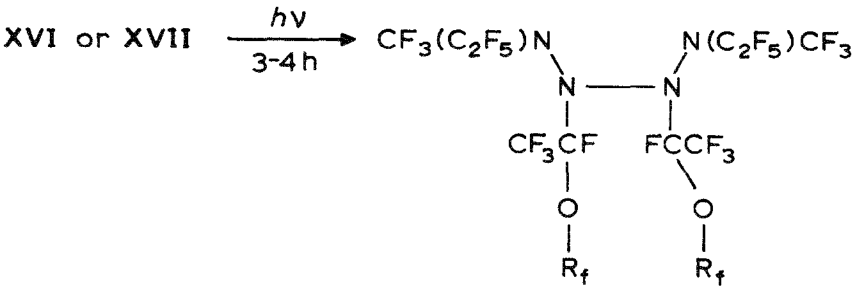
$(R_f = CH_2CF_3$ (**XIV**), $R_f = C(CF_3)_2H$ (**XV**))

When compounds **XIV** and **XV** are combined with ClF at −78°C for 10–12 h, addition across the carbon–nitrogen double bond occurs smoothly.

$$\mathbf{XIV}\text{ or }\mathbf{XV} + ClF \xrightarrow[10\text{–}12\,h]{-196\text{ to }-78^\circ C} CF_3(C_2F_5)NN(Cl)CF(OR_f)CF_3$$

$(R_f = CH_2CF_3$ (**XVI**), $R_f = C(CF_3)_2H$ (**XVII**))

Both **XVI** and **XVII** are viscous liquids that are stable indefinitely at room temperature. On photolysis, two new tetrazanes with polyfluoroether functionalities are formed.



$R_f = CH_2CF_3$ **XVIII**, $R_f = C(CF_3)_2H$ **XIX**

80% 75%

Compound **XVIII** is a colorless, involatile liquid that is stable at 60°C for at least 11 h but undergoes significant decomposition at 80°C in a short time. Compound

XIX is a colorless, involatile liquid that is considerably decomposed after 8 h at 60°C. At 25°C the densities of **XVIII** and **XIX** are 2.1 and 2.2 g cm^{-3}, respectively.

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