FLUORINATED PEROXIDES

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I. Introduction

Syntheses studies which produced fluorinated carbon-containing peroxides were greatly accelerated by interest in obtaining new high-energy oxidizers in the years following the launching of the satellite Sputnik. A large number of new compounds were obtained which were prepared by low yield methods and which were chemically poorly characterized. We have included peroxides of this type only where the presence of fluorine would be expected to have some effect on the oxygen–oxygen bond energy and, thus, on the reaction chemistry of these compounds. Based on the patent literature, some use is made of these peroxides as polymerization catalysts. During this same period, considerable additional information was obtained about compounds which contain only oxygen and fluorine, the oxygen fluorides. However, there are several good, recent reviews (*141*, *163a*, *221*, *237*, *238*) on this subject and, as a result, we have limited discussion of these highly interesting and sometimes controversial compounds. Also included are fluorinated polyoxides, i.e., compounds which contain more than two catenated oxygen atoms, even if their chemistry may not be strictly that of bona fide peroxides. Although fewer inorganic peroxides are known, some of them have been thoroughly studied. Six reviews include briefly some of the fluorosulfur peroxides (*35*, *37*, *99*, *188*, *196*, *251*). All these compounds are formally derivatives of either bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, or bis(pentafluorosulfur)peroxide, $S_2F_{10}O_2$.

We have summarized in appropriate tables available spectral data which we feel will be particularly useful to the synthetic chemist. The literature has been covered through December 1972 with an occasional additional reference which appeared early in 1973. The intent of this review is to give an overall view, accompanied by pertinent references, of the fluorinated peroxides known at this time and to point out areas where additional work is needed or new frontiers which are available for exploration.

II. Oxygen Fluorides

In the past decade the oxygen fluorides have been the subject of much interest and of several reviews (*141*, *163a*, *221*, *237*, *238*). In this review only oxygen fluorides containing more than one oxygen atom, i.e., peroxides or polyoxides, will be considered. All these oxygen fluorides are thermally unstable and ultimately decompose to oxygen and fluorine.

A. DIOXYGEN DIFLUORIDE, O_2F_2

The synthesis of the various oxygen fluorides has been accomplished by flow reactions via electric discharge methods at low temperatures and low reactant pressures. The first member of this group is dioxygen difluoride, O_2F_2, which was synthesized in 1933 by Ruff and Menzel (*199*, *200*). The present method of preparing O_2F_2 is essentially the same. The

$$O_2 + F_2 \xrightarrow[-183°C]{\text{discharge}} O_2F_2$$

reactant ratio, temperature, pressure, and electrical power are important in determining the products formed (*141*). For O_2F_2, the O_2/F_2 ratio is 1 with a pressure of 7–17 mm Hg and a discharge of 25–30 mA and 2.1–2.4 kV. Other preparative methods have also been developed to synthesize O_2F_2, including the low temperature discharge or photolysis reactions of liquid and gaseous O_2/F_2 mixtures (*8*, *142*), of OF_2/O_2 (*8*, *226*) or of F_2/O_3 (*137*) and, most recently, from the radiolysis of liquid O_2/F_2 mixtures (*110*). Streng and Streng (*226*) found that a 44–65 W discharge in a 2:1 OF_2/O_2 mixture at –183° and a reactant pressure of 1–10 mm resulted in a good synthesis for O_2F_2. Kirshenbaum (*137*) prepared O_2F_2 from the photolysis of approximately 2:1 mixture of O_3 and F_2 at –150° using 3650 Å radiation, but did not find any O_2F_2 when the reaction was attempted at –78°.

The most recent synthesis of O_2F_2 by Goetschel *et al.* (*110*) results in the purest O_2F_2 samples reported. Mixtures of liquid oxygen and fluorine contained in a stainless steel reactor were irradiated with 3 MeV bremsstrahlung through a sapphire window for 1–4 hr at –196°. Then, after removing excess reactants, the impurities were removed by warming the sample to –78°. The physical constants for O_2F_2 have been tabulated (*238*) and therefore will not be considered in detail. While initial reports described the compound as an orange solid melting to a red liquid at –164°, Goetschel *et al.* characterized O_2F_2 as a yellow solid and liquid with a melting point of −154°. O_2F_2 decomposes to oxygen and fluorine and at −160° this decomposition occurs at the approximate rate of 4% per day (*211*).

The chemistry of O_2F_2 is *not* the chemistry of the FO radical since the O–O bond dissociation energy is about six times that of the O–F bond energy (103.5 vs. 18 kcal/mole) (*150*). The reactions of O_2F_2 have been summarized in the previous reviews (*141*, *221*, *238*) and only a few general reaction types are considered here. The oxygen fluorides are all strong oxidizing agents and even at low temperatures solvents are often required to moderate their reactions.

In the presence of fluoride ion acceptors, the general reaction of O_2F_2 is to form dioxygenyl salts (*141*).

$$O_2F_2 + AF_n \rightarrow O_2^+AF_{n+1}^- + 1/2F_2$$
$$AF_n = BF_3, PF_5, AsF_5, SbF_5, MoF_6\,(\mathit{18}), WF_6\,(\mathit{18})$$

In addition, a bis(dioxygenyl) salt (*18*), $(O_2)_2SnF_6$, has been reported from the reaction of O_2F_2 and SnF_4; but this reaction, like those with MoF_6 snd WF_6, is of low yield and poor reproducibility.

The reactions of O_2F_2 with chlorine and bromine derivatives generally result in the formation of higher halogen fluorides. Chlorine derivatives are normally oxidized to ClF_3, which does not react with O_2F_2, while with sufficient O_2F_2, bromine derivatives generate BrF_5. With many chlorine-containing molecules a violet solid (*224*), O_2ClF_3, is formed under appropriate conditions. Streng (*222*) also reported similar intermediates with some bromine derivatives and SF_4. The reactions of O_2F_2 with sulfur, sulfur oxides (*141*), sulfur oxy acids, or sulfur oxide fluorides (*211*) result in the formation of SF_6 and various sulfur oxide fluorides. With nitrogen-containing molecules, similar oxidation products are found including nitrogen oxides and nitrogen oxide fluorides.

Reactions which demonstrate that the chemistry of O_2F_2 is due to O–F bond cleavage are somewhat lacking, undoubtedly owing to the extremely vigorous reactions that occur. The reaction of O_2F_2 with C_2F_4 results in decomposition products even when moderated by liquid argon. Solomon and co-workers (*210*, *212*) were able to demonstrate OOF transfer with C_3F_6 and SO_2. In the O_2F_2/SO_2 reaction they were also able to show this transfer by utilizing ^{17}O-labeled reactants and ^{17}O NMR spectral studies on the FSO_2OOF formed. With ^{17}O-labeled O_2F_2, the FSO_2OOF contained labeled oxygen in the OOF group, whereas with ^{17}O-labeled SO_2 none was found in this function. Another experiment (*131*), using ^{18}F tracer techniques in the O_2F_2/BF_3 reaction, has been interpreted also as demonstrating the existence of an $\cdot$OOF intermediate.

B. POLYOXYGEN DIFLUORIDES, O_nF_2 ($n = 3$–6)

1. O_3F_2

The original synthesis for "O_3F_2" involving photolytic and electric discharge reactions with O_2/F_2 or OF_2/O_2 mixtures was reported a number of years ago by Aoyama and Sakuraba (*7*, *8*). Krishenbaum and Grosse (*138*) also report "O_3F_2" as the product formed from the reaction of a 3:2 mixture of O_2 and F_2 at −196° and a discharge of 20–25 mA and 2.0–2.2 kV. More recently Streng and Streng (*226*) have claimed "O_3F_2" also results from the reaction of a 1:1 mixture of $OF_2\cdot$ and O_2 at −184° using a discharge of 40–60 W.

The actual existence of "O_3F_2" as a discrete, isolable entity has been the subject of considerable controversy over the past years. The predominant opinion is that this oxygen fluoride does not exist under the conditions reported for its preparation. Alternative explanations of the nature of the isolated product have been postulated and reviewed (*238*). The most widely accepted explanation for O_3F_2 is that it is a mixture of O_2F_2 and O_4F_2 (or $\cdot OOF$) and this has been strongly supported by ^{19}F and ^{17}O NMR data obtained by Solomon and co-workers (*215*, *216*). Briefly, these studies showed three ^{17}O resonances: a larger one corresponding to O_2F_2 and two of equal intensity assigned to the two oxygen environments in O_4F_2. The ^{19}F NMR spectrum showed two resonances for O_2F_2 and O_4F_2 which were difficult to separate in neat samples but clearly separated in an OF_2 solution. As stated by these workers, this does not preclude the possibility of preparing O_3F_2 under conditions that would generate oxygen atoms which require a higher energy than that used in the reported preparations. The possible matrix isolation of O_3F_2 has been mentioned briefly by Arkell (*9*) as an intermediate in the formation of $^{16}OF_2$ from $^{18}OF_2$ in an ^{16}O matrix. Unfortunately, no additional support could be offered for this intermediate.

$$^{18}OF_2 + {}^{16}O_2 \leftrightarrows F^{18}O^{16}O^{16}OF \rightarrow {}^{16}OF_2 + {}^{16}O^{18}O$$

2. O_4F_2

The synthesis of O_4F_2 was initially achieved from an electrical discharge of an oxygen–fluorine mixture (*113*, *223*). The reaction conditions were considerably milder than for the preparation of O_2F_2 (4.6 mA, 840–1500 V, 6 W at −213° to −196°). Streng and Streng (*226*) isolated O_4F_2 from the reaction of an OF_2/O_2 mixture using a 9–11 W discharge at −196°; Goetschel *et al.* (*110*) report O_4F_2 from their radiolysis experiments.

Much of the characterization of O_4F_2 with regard to physical properties has been carried out by Streng (*223*) who also gives an excellent description of the discharge equipment used. The stability of O_4F_2 is considerably less than O_2F_2 and it decomposes at −183° with a half-life of 16 days at this temperature. The solid and liquid are red-brown in color and the melting point was determined as $-191° \pm 2°$. Several groups have measured the ESR spectrum (*238*) of O_4F_2 and found very strong signals which were assigned to the $\cdot OOF$ radical arising from the $O_4F_2 \rightleftharpoons 2O_2F$ equilibrium. The magnitude for the equilibrium constant has been estimated to be 8×10^{-5} in solid CF_3Cl (*110*, *130*) (−196°), while in very dilute CF_4 solutions (−160° to −180°) no dimer was present (*88*).

Relatively little reaction chemistry has been attempted with O_4F_2. Streng (*223*) reported the initial reactions of O_4F_2 of which none demonstrated O_2F radical reactions. A mixture of O_4F_2 and O_3 in CF_2H_2 at −157° resulted in an explosion, whereas with N_2F_4 in an OF_2 solution at −196°, fluorination and decomposition to NF_3 and O_2F_2 occurred. Xenon was fluorinated to various xenon fluorides. Solomon and co-workers have demonstrated the transfer of O_2F groups from O_4F_2 in the following reactions (*131*, *209*).

$$O_4F_2 + BF_3 \xrightarrow{-138°} O_2BF_4 + F_2$$

$$O_4F_2 + SO_2 \rightarrow \underset{(32\%)}{FSO_2OOF} + \underset{(54\%)}{SO_2F_2}$$

In comparison, with the O_2F_2/SO_2 reaction the formation of FSO_2OOF from O_4F_2 occurs at a lower temperature, more rapidly, and in a much better yield (32 vs. 5%).

3. O_5F_2 *and* O_6F_2

The last of the catenated oxygen fluorides to be reported are O_5F_2 and O_6F_2 (*225*). Their preparation again resulted from the very mild electric discharge reaction of O_2/F_2 mixtures. The oxygen and fluorine ratios were adjusted to the required stoichiometry, the reactor cooled to between −213° and −196°, and a discharge of 4–6 W utilized. The O_5F_2 has been characterized as a red-brown liquid at −183°, where it decomposes, while O_6F_2 was described as being crystalline with a metallic luster at −213° and decomposing at −196°. 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.

Solomon and co-workers (*215*) have presented a straightforward argument for the failure to isolate O_3F_2. The isolation of O_3F_2 would require the formation of oxygen atoms or ozone and under the mild reaction conditions employed for its preparation, sufficient energy (119 kcal/mole) is not present to form these atoms and relatively little O_3 is formed. This argument when applied to O_5F_2 casts doubt on its existence since the preparative conditions which are cited are even milder than for O_3F_2. Clearly, further work, especially with regard to spectral measurements, would prove invaluable in confirming the existence of O_5F_2 under these conditions.

C. POLYOXYGEN FLUORIDE RADICALS, O_nF ($n = 2, 3, 4, 6$)

At the present time, four polyoxygen fluoride radicals have been postulated, namely, $\cdot O_2F$, $\cdot O_3F$, $\cdot O_4F$, and $\cdot O_6F$. Of these radicals only $\cdot O_2F$ has been definitively characterized by detailed matrix ESR and infrared spectral techniques. The data concerning this radical has recently been reviewed by Turner (*238*).

The possibility of the other polyoxygen fluoride radicals has also been mentioned. Arkell (*9*) suggested that the weak bands appearing at 1503 and 1512 cm^{-1} in the O_2F infrared spectrum may be due to O_3F and O_4F radicals. Goetschel *et al.* (*110*) have suggested also from decomposition studies of O_2BF_4 at $-33°$ and $-140°$ that the unstable compounds, $O_4^+BF_4^-$ and $O_6^+BF_4^-$, were also present. They suggest that these salts could result from the reaction of O_4F and O_6F radicals with BF_3. These polyoxygen monofluoride radicals must, at least at this time, be considered as speculative, and more definite work must be carried out to confirm the existence of O_3F, O_4F, and O_6F.

If the O_3F radical is proved to exist, then the possibility of the preparation of O_3F_2 through simple fluorination would be greatly enhanced and may well lead to additional speculation. Before extrapolation is attempted, it must be remembered that O_3F is postulated in a matrix system at 4°K and Arkell (*9*) has suggested O_3F_2 under these conditions and not under the conditions used to generate O_3F_2 from discharge reactions.

III. Bis(fluorosulfuryl) Peroxide, FSO_2OOSO_2F (Peroxodisulfuryl Difluoride)

A. PREPARATION AND PROPERTIES

Bis(fluorosulfuryl) peroxide is readily prepared in good yield (>90%) and in relatively large quantities by the flow reaction of fluorine with an excess of sulfur trioxide in the presence of a AgF_2 catalyst at 160° (*71*, *205*). Although first reported in 1955 (*249*), based on accepted physical properties, $S_2O_6F_2$ was probably first synthesized as a side product in the preparation of fluorine fluorosulfate (*73*). Caution should always be exercised when preparing $S_2O_6F_2$ since small amounts of FSO_3F, which is reported to be explosive (*36*), often are formed. Small amounts of bis(fluorosulfuryl) peroxide are conveniently prepared by the fluorination of SO_3 in a static, noncatalytic system at 170° with pyrosulfuryl fluoride as the major impurity, accompanied by only traces of FSO_3F (*197*). $S_2O_6F_2$ also results from the low-temperature electrolysis of a solution of an alkali metal fluorosulfate in fluorosulfuric acid (*70*).

When $Ni(SO_3F)_2$ or $Cu(SO_3F)_2$ is exposed to a stream of fluorine at 200°, $S_2O_6F_2$, FSO_3F, and SO_2F_2 are the main products formed. Fluorine fluorosulfate admitted to a static reactor containing $Ni(SO_3F)_2$ was converted essentially quantitatively to $S_2O_6F_2$ after 30 min. Thermolysis (*71*) or photolysis (*59*) of a mixture of SO_3F_2 and SO_3 yields $S_2O_6F_2$ as the only product. This reaction involves the initial formation and subsequent combination of fluorosulfate radicals as is the case when fluorine and sulfur trioxide are photolyzed at 365 nm (*217*) between 18° and 40°.

$$F_2 + h\nu \rightleftharpoons 2F\cdot$$

$$F\cdot + SO_3 \rightarrow FSO_3\cdot$$

$$2FSO_3\cdot \rightleftharpoons S_2O_6F_2$$

In a recent review, Cady (*37*) has summarized some of the kinetics studies carried out and reaction mechanisms suggested by Professor H. J. Schumacher and co-workers at the Universidad Nacional de La Plata in Argentina where most effort has been expended in attempting to understand the formation of $S_2O_6F_2$ from gas phase reactants.

Some less practical, but chemically interesting, routes to $S_2O_6F_2$ which involve the xenon fluorides have been reported. In 1963 while attempting to oxidize xenon with FSO_3F at 170°, Cady *et al.* (*93*) found $S_2O_6F_2$, in addition to XeF_2 and traces of XeF_4. Fluorosulfuric acid reacts readily with the xenon fluorides to form fluorosulfates which decompose to give $S_2O_6F_2$.

$$XeF_2 + HOSO_2F \xrightarrow{-75^\circ} FXeSO_3F \xrightarrow{25^\circ} Xe + XeF_2 + S_2O_6F_2$$

$$Xe(SO_3F)_2 \xrightarrow{25^\circ} Xe + S_2O_6F_2 \quad (\textit{24, 77, 249a})$$

$$XeF_4 + 4HOSO_2F \longrightarrow Xe(SO_3F)_2 + HF + S_2O_6F_2 \quad (\textit{78})$$

$$XeF_6 + 2HOSO_2F \longrightarrow F_5Xe(SO_3F) \xrightarrow{80^\circ} Xe + XeF_6 + S_2O_6F_2 \quad (\textit{78})$$

$$XeF_6 + SO_3 \xrightarrow{70^\circ} S_2O_6F_2 + Xe \quad (\textit{78})$$

As will be seen below, the chemistry of $S_2O_6F_2$ is essentially that of the fluorosulfate radical,  $F\overset{O}{\underset{O}{S}}O$. Although $S_2O_6F_2$ is a colorless gas, liquid, (b.p. 67.1°), or solid (m.p. −55.4°), when the gas is heated to about 100°, a yellow-brown color is produced which on cooling disappears. The infrared spectrum (at 25°) of the gas remains unchanged after dissociation and recombination.

Equilibrium constants for the reaction

$$S_2O_6F_2 \leftrightharpoons 2SO_3F$$

between 450° and 600°K as determined from temperature–pressure measurements may be calculated from the equation $\log K_p = 7.981 - 4.785 \times 10^3 T^{-1}$ (*72*). This method gives an enthalpy change of 22.0 kcal/mole, whereas a less dependable spectrophotometric method based on the temperature dependence of the absorption of the fluorosulfate radical at 474 nm gives an enthalpy change of 23.3 kcal/mole. Schumacher also using temperature–pressure measurements reported $\Delta H =$ 21.8 kcal/mole (*46*). Electron spin resonance studies of the $S_2O_6F_2$–SO_3F equilibrium in gas and liquid phases and in solution confirm the production of only a single kind of species ($OSO_2F\cdot$) (*163, 167, 168, 218, 219*). The resonance consists of a single very broad line with $g = 2.0108$ and $\Delta H_{ms} \sim 25$ G (17°) increasing to $\Delta H_{ms} = 48$ G (180°), which accompanied by greater peak height denotes an increase in radical concentration (*167*). The average value obtained for the enthalpy of cleavage is 22.4 ± 0.9 kcal/mole.

The visible spectrum of SO_3F has been examined by Dudley (*72*), Schumacher (*46*), and most extensively by King (*133–135*) who has found and interpreted these regions of absorption: 3600–5500, 5700–10,000, and 10,000–20,000 Å. The Raman spectrum (*180*) indicates a staggered nonplanar configuration with C_2 symmetry for $S_2O_6F_2$ with the O–O stretch assigned to a band at 801 cm^{-1}. Principal bands in the infrared spectrum (*71, 180*) include 1498vs, 1248vs, 1162m, 878m, 847vs, 795m, 752s, and 524s cm^{-1}. A single resonance is observed at -40.4ϕ in the ^{19}F NMR spectrum (*92, 125*). When the ^{19}F NMR spectrum of $S_2O_6F_2$ was recorded, no satellite due to fluorine on ^{33}S was observed, although spin-spin coupling between the nonequivalent fluorine atoms on ^{32}S and ^{34}S were clearly noticeable and gave rise to a quartet, $[\Delta\delta(^{34}S - {}^{32}S) = 0.0487]$ $J_{^{34}SF-^{32}SF} = 3.23$ Hz (*220*). Over the temperature range 35.5°–45.9°, the density of liquid $S_2O_6F_2$ may be calculated using the equation $d = 2.3959 - 2.434 \times 10^{-3}\, T$ ($d_{35.5} = 1.6450$ gm/cm^3).

Vapor pressure information over the range of 9°–68° may be obtained from

$$\log P_{\mathrm{mm}} = 5.49916 - \frac{1.2925 \times 10^2}{T} - \frac{2.5921 \times 10^5}{T^2}$$

B. Reactions of $S_2O_6F_2$

Of all the fluorinated peroxides, bis(fluorosulfuryl) peroxide has been studied the most extensively and has the most varied and interesting chemistry. The low oxygen–oxygen bond energy (22 kcal) and the high stability of the $\cdot SO_3F$ radical contribute to its reactivity and great versatility. Extreme caution should be exercised when using $S_2O_6F_2$ as a reagent owing to its enthusiastic participation in reactions especially with organic materials.

1. *With Halogens and Other Elements*

In a flow system at 250°, F_2/N_2 converts $S_2O_6F_2$ essentially quantitatively to $FOSO_2F$ (*71, 191*). The kinetics of this reaction have been studied in a static system in the temperature range 230°–250°. Formation of F_2SO_3 occurs in a bimolecular reaction between $FSO_3\cdot$ and F_2 (*48*). For the photolytically induced reaction, the reaction rate is proportional to the intensity of the absorbed light and independent of the ($S_2O_6F_2$) and total pressure (*96, 202*).

Chlorine is the only halogen with which reaction occurs with difficulty

$$Cl_2 + S_2O_6F_2 \xrightarrow[5\ \text{days}]{125^\circ} ClOSO_2F \qquad (\mathit{101, 244})$$

and even this reaction proceeds to completion at 25° if the contact time is several weeks. With bromine

$$Br_2 + 3S_2O_6F_2 \xrightarrow{25^\circ} 2Br(OSO_2F)_3 \qquad (\mathit{192})$$

$$Br(OSO_2F)_3 + Br_2 \xrightarrow{25^\circ} 3BrOSO_2F \qquad (\mathit{17, 192})$$

while in solutions of $BrOSO_2F$ in $HOSO_2F$, there is no evidence for formation of either Br^+ or Br_2^+ (*17*) much evidence exists for a variety of complex iodine-containing cations when iodine and $S_2O_6F_2$ are combined in different molar quantities in fluorosulfuric acid. Roberts and Cady (*192*) report the formation of the solid $I(SO_3F)_3$ when the neat reactants are combined in an $I_2/S_2O_6F_2$ ratio of 1 : 3. Equimolar amounts of iodine and $S_2O_6F_2$, allowed to stand at 25° for 8 hr and then heated for 1 hr at 60°, gave the black diamagnetic $IOSO_2F$ (m.p. 51.5°) (*15*). If the molar ratio of $I_2/S_2O_6F_2$ exceeds 3 and the mixture is heated to 85°, a dark brown solid formed which analyzes to be I_3SO_3F and melts at 92° with decomposition to give iodine. These latter two compounds apparently contain I_2^+ (*104*) and I_3^+ (*15*), respectively, when dissolved in HSO_3F. It is also possible to produce I_7SO_3F (*54*).

Bis(fluorosulfuryl) peroxide behaves as a nonelectrolyte in HSO_3F (*107*), but conducting solutions form when I_2 and $S_2O_6F_2$ are mixed in HSO_3F. Results of NMR, freezing point, and conductivity measurements on 1:7 and 1:3 $I_2/S_2O_6F_2$ in HSO_3F show that $I(SO_3F)_3$ is the highest fluorosulfate formed in solution in HSO_3F (*103*). Further studies including cryoscopic, conductometric, spectroscopic, and magnetic susceptibility measurements on the I_2–$S_2O_6F_2$–HSO_3F system have produced interesting results.

$$I_2 + 7S_2O_6F_2 \rightarrow 2I(SO_3F)_3 + 4S_2O_6F_2 \qquad (\mathit{103})$$

$$I_2 + 3S_2O_6F_2 \rightarrow 2I(SO_3F)_3 \qquad (\mathit{102, 103})$$

(yellow solution)

$$5I_2 + 5S_2O_6F_2 \rightarrow 4I_2^+ + 4SO_3F^- + 2I(SO_3F)_3 \qquad (\mathit{102})$$

$\downarrow -86°$ (blue solution

I_4^{2+} (*105*)

$$2I_2 + S_2O_6F_2 \rightarrow 2I_2^+ + 2SO_3F^- \qquad (\mathit{102, 104})$$

$$3I_2 + S_2O_6F_2 \rightarrow 2I_3^+ + 2SO_3F^-$$

(blue solution)

$$5I_2 + S_2O_6F_2 \rightarrow 2I_5^+ + 2SO_3F^-$$

A neat reaction between S and $S_2O_6F_2$ produces $S_2O_5F_2$ and SO_2 which subsequently reacts with $S_2O_6F_2$ to give $S_3O_8F_2$ (*204*). Interesting complex cations are formed when $S_2O_6F_2$ oxidizes sulfur in HSO_3F at 0°.

$$2S_8 + S_2O_6F_2 \xrightarrow[0°]{HSO_3F} S_{16}{}^{2+} + 2SO_3F^- \qquad (\mathit{23, 107})$$

(red solution)

$$S_8 + S_2O_6F_2 \xrightarrow[0°]{HSO_3F} S_8{}^{2+} + 2SO_3F^-$$

(unstable blue solution)

Fluorosulfuric acid dissolves elemental selenium to form a green solution. Bis(fluorosulfuryl) peroxide oxidizes selenium in HSO_3F to give green, yellow, and finally colorless solutions as the quantity of

$$4Se + S_2O_6F_2 \rightarrow Se_4^{2+} + 2SO_3F^- \qquad (\mathit{19})$$

$S_2O_6F_2$ is increased (*20*). The yellow species is Se_4^{2+}, which may be reduced to the green Se_8^{2+} by the addition of elemental Se.

$$\underset{\text{(green solution)}}{Se_4^{2+} + 4Se \rightarrow Se_8^{2+}}$$

Tellurium can be oxidized by $S_2O_6F_2$ in HSO_3F at −23° to the yellow Te_n^{n+} ($n = 4, 6$, or 8) (*21, 22*), which precipitates from solution on addition of SO_2 at −78° as a bright yellow solid of composition $TeSO_3F$ stable only at −75° and below. In SO_2, at −63° to −23°, $S_2O_6F_2$ oxidizes Te to form a dark red amorphous solid which analyzes to be $Te_4(SO_3F)_2$.

Antimony is also oxidized by $S_2O_6F_2$ in HSO_3F, e.g.,

$$2Sb_4 + S_2O_6F_2 \rightarrow Sb_8^{2+} + 2SO_3F^- \quad (172)$$
(blue solution)

$$Sb_4 + S_2O_6F_2 \rightarrow Sb_4^{2+} + 2SO_3F^-$$
(yellow solution)

Thermolysis with Xe gives no reaction other than the decomposition of $S_2O_6F_2$ to O_2 and SO_2F_2 (*93*).

Other elements which are readily oxidized in neat reactions with $S_2O_6F_2$ include Hg (*193*), Mo (*204*), Re (*139*), Nb (*139*) to give $Hg(OSO_2F)_2$, $MoO_2(SO_3F)_2$, $ReO_3(SO_3F)$, $ReO_2(SO_3F)_3$, and $NbO(SO_3F)_3$. Invariably the metal exhibits its highest oxidation state in the compound formed.

2. *Reactions with Oxides*

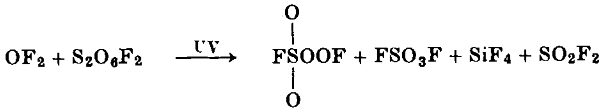
In most cases these reactions are accompanied by the release of oxygen and the formation of element–fluorosulfate bonds. However, if oxidation of the central element is possible, oxidation as well as fluorosulfation, accompanied by $S_2O_5F_2$ formation, may occur.

a. Metal Oxides. Only the oxides of neodymium, samarium, and europium give solid compounds of the type $MO(SO_3F)$ with $S_2O_6F_2$ (*128*). Oxides of the other lanthanide elements appear not to react.

$$Ag_2O + S_2O_6F_2 \xrightarrow{25^\circ} Ag_2O(SO_3F)_2 \quad (67)$$

$$HgO + S_2O_6F_2 \xrightarrow{150^\circ} Hg(OSO_2F)_2 + O_2 + S_2O_5F_2 \quad (204)$$

b. Nonmetallic Oxides. With O_2F_2, reaction occurs slowly only above −63° to produce SO_2F_2 (*211*).



$$OF_2 + S_2O_6F_2 \xrightarrow{UV} FS(O_2)OF + FSO_3F + SiF_4 + SO_2F_2$$ (*48, 92*)

$$2ClO_2 + S_2O_6F_2 \xrightarrow[fast]{-40°} 2(ClO_2)OSO_2F$$ (*42*)

$$I_2O_5 + S_2O_6F_2 \xrightarrow[2\ hr]{65°} 2IO_2SO_3F + 0.5O_2$$ (*16, 41*)

$$SO_2 + S_2O_6F_2 \xrightarrow[N_2\ flow]{200°} S_3O_8F_2$$ (*191*)

The kinetics of this reaction have been studied in a static system between 20° and 50° (*47, 49*).

$$SeO_2 + S_2O_6F_2 \xrightarrow[10\ hr]{50°} SeO(SO_3F)_2 + 1/2O_2$$ (*40*)

$$N_2O + S_2O_6F_2 \xrightarrow{60°} \text{No reaction}$$ (*179*)

$$2NO + S_2O_6F_2 \xrightarrow{25°} 2NOSO_3F$$ (*179, 193, 246*)

$$N_2O_3 + S_2O_6F_2 \xrightarrow[phase]{condensed} NOSO_3F + NO_2SO_3F + O_2 + S_2O_5F_2$$ (*179*)

$$N_2O_4 + \text{excess } S_2O_6F_2 \xrightarrow[phase]{condensed} NO_2SO_3F + S_2O_5F_2 + O_2$$ (*179, 247*)

$$N_2O_5 + S_2O_6F_2 \xrightarrow[phase]{condensed} NO_2SO_3F + O_2$$ (*179*)

$$CO + S_2O_6F_2 \xrightarrow{25°} CO_2 + S_2O_5F_2$$ (*95, 97, 204*)

The velocity of CO_2 formation is greater in the presence of oxygen than direct oxidation of CO in oxygen-free systems (*95*).

Each mole of $S_2O_6F_2$ releases 0.5 mole of oxygen from H_2O and forms fluorosulfuric acid. The reaction is highly exothermic.

3. *Reactions with Halogen-Containing Compounds*

Typically these reactions involve oxidation of the halogen to free halogen (Cl_2, Br_2) and replacement by fluorosulfate, oxidation of the halogen by the formation of complex anions (Br, I), addition to the central atom with halogen unaffected (F), or oxygenation.

$$KICl_4 + 2S_2O_6F_2 \xrightarrow[24\ hr]{70°} 2Cl_2 + KI(SO_3F)_4$$ (*42*)

$$KBrO_3 + 2S_2O_6F_2 \xrightarrow{0°} K[Br(OSO_2F)_4] + 1.5O_2$$ (*42*)

$$KClO_3 + S_2O_6F_2 \longrightarrow KSO_3F + (ClO_2)OSO_2F + 0.5O_2$$ (*43*)

$$KI + 2S_2O_6F_2 \longrightarrow K[I(SO_3F)_4]$$ (*146*)

With aqueous KI each mole of $S_2O_6F_2$ liberates a mole of iodine.

$$KBr + 2S_2O_6F_2 \xrightarrow{50^\circ} K[Br(OSO_2F)_4] \quad (\mathit{146})$$

$$2KCl + S_2O_6F_2 \xrightarrow{25^\circ} 2KOSO_2F + Cl_2 \quad (\mathit{204})$$

$$2ICl + 3S_2O_6F_2 \longrightarrow 2I(SO_3F)_3 + Cl_2$$

$$CsBr + S_2O_6F_2 \xrightarrow{Br_2} CsBr(OSO_2F)_2 \quad (\mathit{55})$$

$$CsBr + 2S_2O_6F_2 \xrightarrow{Br_2} CsBr(OSO_2F)_4$$

$$SOF_2 + S_2O_6F_2 \longrightarrow SO_2F_2 + S_2O_5F_2 \quad (\mathit{204})$$

$$SF_4 + S_2O_6F_2 \xrightarrow{128^\circ} \underset{(\mathit{cis})}{SF_4(OSO_2F)_2} \quad (\mathit{46, 49, 204})$$

$$SOClF + S_2O_6F_2 \xrightarrow{25^\circ} S_2O_5F_2 + Cl_2 \quad (\mathit{204})$$

$$2SeOCl_2 + S_2O_6F_2 \xrightarrow{25^\circ} SeOCl(OSO_2F) + Cl_2 \quad (\mathit{39})$$

$$SeOCl_2 + \text{excess } S_2O_6F_2 \xrightarrow{25^\circ} SeO(SO_3F)_2 + Cl_2 \quad (\mathit{40})$$

$$CrO_2Cl_2 + S_2O_6F_2 \xrightarrow{25^\circ} CrO_2(SO_3F)_2 \quad (\mathit{146, 195})$$

$$N_2F_4 + S_2O_6F_2 \longrightarrow 2NF_2OSO_2F \quad (\mathit{147, 245})$$

$$2NOCl + S_2O_6F_2 \xrightarrow[\text{phase}]{\text{condensed}} 2NOSO_3F + Cl_2 \quad (\mathit{179})$$

$$2NO_2Cl + S_2O_6F_2 \xrightarrow[\text{phase}]{\text{condensed}} 2NO_2SO_3F + Cl_2$$

$$OPBr_3 + 6S_2O_6F_2 \longrightarrow OP(OSO_2F)_3 + 3Br(SO_3F)_3 \quad (\mathit{65})$$

$$SPF_2Br + S_2O_6F_2 \xrightarrow{-45^\circ} SPF_2(OSO_2F) + Br_2 \quad (\mathit{144})$$

$$PF_3 + S_2O_6F_2 \longrightarrow OPF_3 + S_2O_5F_2 \quad (\mathit{204})$$

$$SbCl_5 + 2.5S_2O_6F_2 \longrightarrow x/2Cl_2 + SbCl_{5-x}(SO_3F)_x \quad (x \geqq 4) \quad (\mathit{166})$$

$$VOCl_3 + \text{excess } S_2O_6F_2 \xrightarrow{60^\circ} VO(SO_3F)_3 + ClOSO_2F \quad (\mathit{139})$$

$$NbCl_5 + \text{excess } S_2O_6F_2 \xrightarrow{60^\circ} NbO(SO_3F)_3 + S_2O_5F_2 + ClOSO_2F$$

$$TaCl_5 + \text{excess } S_2O_6F_2 \xrightarrow{60^\circ} TaO(SO_3F)_3 + S_2O_5F_2 + ClOSO_2F$$

$$CCl_4 + S_2O_6F_2 \longrightarrow S_2O_5F_2 + COCl_2 + Cl_2 \quad (\mathit{204})$$

$$COCl_2 + S_2O_6F_2 \xrightarrow{UV} CO_2 + Cl_2 + S_2O_5F_2$$

$$CBr_2F_2 + S_2O_6F_2 \longrightarrow F_2C(OSO_2F)_2 + Br_2 + S_2O_5F_2 + COF_2 + Cl_2 \quad (\mathit{145})$$

$$CBr_3F + S_2O_6F_2 \longrightarrow FC(OSO_2F)_3 + FC(O)OSO_2F + Br_2 + S_2O_5F_2 + CO_2$$

$$CBr_4 + S_2O_6F_2 \longrightarrow OC(OSO_2F)_2$$

$$CF_3C(O)Br + S_2O_6F_2 \xrightarrow[N_2]{3^\circ} CF_3C(O)OSO_2F + CF_3SO_3F + CO_2 + S_2O_5F_2 + Br_2 \quad (\mathit{60})$$

$$CF_3Cl + S_2O_6F_2 \xrightarrow[150^\circ]{300\text{ atm}} CF_3SO_3F + ClSO_3F \quad (\mathit{186})$$

$$CF_3Br + S_2O_6F_2 \xrightarrow{25^\circ} CF_3SO_3F + BrSO_3F + Br_2$$

$$C_3H_7Br + S_2O_6F_2 \xrightarrow[CFCl_3,\ 4\ hr]{-25^\circ \text{ to } 0^\circ} C_3H_7SO_3F + BrSO_3F \quad (154)$$

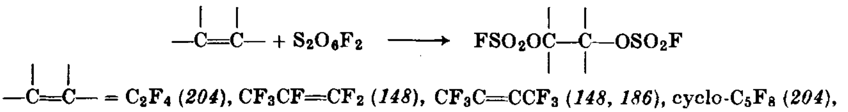
$$SnCl_4 + S_2O_6F_2 \xrightarrow{25^\circ} SnCl(SO_3F)_3 \quad (146)$$

$$SnCl_4 + S_2O_6F_2 \xrightarrow{120^\circ} Sn(SO_3F)_4 + 2Cl_2 \quad (254)$$

$$GaCl_3 + S_2O_6F_2 \longrightarrow Ga(SO_3F)_3 \quad (220a)$$

4. *Reactions with Olefins and Nitriles*

As is to be expected of reactive free radicals, $FSO_3\cdot$ adds enthusiastically to unsaturated molecules and in many cases the reaction to be controlled requires a diluent, such as nitrogen, or an inert solvent, such as CCl_3F, or lower temperatures.



$$-C{=}C- + S_2O_6F_2 \longrightarrow FSO_2OC{-}C{-}OSO_2F$$

$-C{=}C- = C_2F_4$ *(204)*, $CF_3CF{=}CF_2$ *(148)*, $CF_3C{\equiv}CCF_3$ *(148, 186)*, cyclo-C_5F_8 *(204)*, cyclo-C_4F_6 *(148)*, $ClCF{=}CF_2$ *(186)*, $H_2C{=}CHF$ *(186)*, $H_2C{=}CHCl$ *(186)*, $Cl_2C{=}CHCl$ *(154)*

$$XC{\equiv}N + S_2O_6F_2 \xrightarrow{\Delta} XC(OSO_2F)_2N(OSO_2F)_2 \quad (203)$$

$X = Cl, CF_3$

With the exception of the vinyl addition products, the reaction products are stable and have been characterized.

It has been reported that $S_2O_6F_2$ will not saturate $C_2F_5N{=}CF_2$ (*161*). Similar results are observed with $CF_3N{=}CF_2$ (*136*). However, with nitriles reaction does occur to give the saturated products in high yield.

5. *Hydrogen Abstraction Reactions*

Under moderating conditions of solvent and lower temperatures, it is possible to abstract hydrogen with $S_2O_6F_2$ from organic compounds to form fluorosulfuric acid and organic fluorosulfates. However, it should be remembered that any reaction involving $S_2O_6F_2$ is potentially hazardous and neat reactions with organics tend to be very rapid and typically explosive.

Merrill (*154*) has studied the reactions of $S_2O_6F_2$ with organic acids and benzene and has isolated alkyl or aryl fluorosulfates in good yields.

$$C_3F_7CO_2H + S_2O_6F_2 \xrightarrow[\text{neat}]{25^\circ} CO_2 + C_3F_7SO_3F + HSO_3F$$

$$RCO_2H + S_2O_6F_2 \xrightarrow[\text{CFCl}_3\text{, 3 hr}]{-24^\circ \text{ to } -10^\circ} CO_2 + RSO_3F$$

$$R = CH_3, C_2H_5$$

$$C_6H_6 + S_2O_6F_2 \xrightarrow[\text{CFCl}_3]{-45^\circ} C_6H_5SO_3F + HSO_3F$$

Perfluoroalkanes and perfluoro alcohols are converted quantitatively.

$$CF_3H + S_2O_6F_2 \rightarrow CF_3OSO_2F + HSO_3F \qquad \textit{(136, 140a)}$$

$$(CF_3)_2CHOH + S_2O_6F_2 \rightarrow 2HSO_3F + (CF_3)_2C{=}O \qquad \textit{(181)}$$

Organic acid anhydrides also react readily.

$$(R_fCO)_2O + S_2O_6F_2 \rightarrow CO_2 + R_fOSO_2F + R_fC(O)OSO_2F \qquad \textit{(64)}$$

$$R_f = CF_3, ClCF_2, C_2F_5, C_3F_7, CF_2$$

However, with $(CHF_2CO)_2O$ only CHF_2OSO_2F was reported (*108*).

6. *Miscellaneous Reactions*

There are few, if any, types of compounds which have not been reacted with $S_2O_6F_2$. Some reactions which do not fit into the above categories are listed below.

a. Carbonyls and Carbonates.

$$Mo(CO)_6 + S_2O_6F_2 \rightarrow S_2O_5F_2 + MoO_2(SO_3F)_2 + CO_2 \qquad \textit{(204)}$$

$$W(CO)_6 + S_2O_6F_2 \rightarrow S_2O_5F_2 + WO(SO_3F)_4 + CO_2 \qquad \textit{(67a)}$$

With carbonates, oxidation of the metal may occur,

$$2M_x(CO_3)_y + S_2O_6F_2 \rightarrow 2MO(SO_3F) + 2CO_2$$

M = Te(I) (*67*), Mn(II) (*67*), Co(II) (*67*), Ni(II) (*67*), La(III) (*128*), Pr(III) (*128*), Nd(III) (*128*)

$$Ce_2(CO_3)_3 + S_2O_6F_2 \rightarrow CeO(SO_3F)_2 + CO_2 \qquad \textit{(128)}$$

$$Ag_2CO_3 + S_2O_6F_2 \rightarrow Ag_2O(SO_3F)_2 + CO_2 \qquad \textit{(67)}$$

or in some cases, may not.

$$M_2(CO_3)_3 + S_2O_6F_2 \rightarrow M(SO_3F)_3 + CO_2 \qquad \textit{(128)}$$

M = Sc, Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

b. Nitrites, Nitrates, and Peroxodisulfates.

$$KNO_3 + \text{excess } S_2O_6F_2 \xrightarrow[\text{phase}]{\text{condensed}} KSO_3F + NO_2SO_3F + O_2 \qquad \textit{(179)}$$

$$NaNO_2 + \text{excess } S_2O_6F_2 \xrightarrow{65^\circ} NaSO_3F + NO_2SO_3F + S_2O_5F_2 + O_2$$

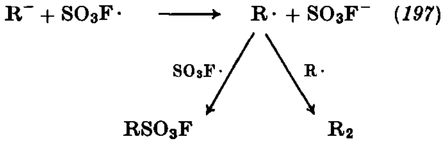
CF_3OSO_2F and CF_3OSO_2F plus $ONSO_3F$ are the only reported products with $(CF_3)_2NO$ and CF_3NO, respectively (*108*).

$$M_2[O_3SOOSO_3] + S_2O_6F_2 \xrightarrow{25^\circ} 2M(O_3SOSO_2F) + O_2$$

$$2M(O_3SOSO_2F) \xrightarrow[\text{slow}]{25^\circ} 2MSO_3F + 2SO_3 \quad (66)$$

$$M = K, Na, \text{ or } NH_4$$

c. *Complex Anions Giving Covalent Compounds.*



$$R^- = CF_3O^-, N(SO_2F)_2^-, C(NO_2)_2CN^-, CF_3CO_2^-, (CF_3)_2CFO^-, SF_5O^-$$

IV. Peroxide Derivatives of $S_2O_6F_2$

A. Pentafluorosulfur(fluorosulfuryl) Peroxide, SF_5OOSO_2F

When equimolar quantities of SF_5OOSF_5 and FSO_2OOSO_2F are photolyzed, equal amounts of SF_5OOSO_2F, SF_5OOSF_5, and FSO_2OOSO_2F are found (*157*). Separation of SF_5OOSO_2F from the residual $S_2O_6F_2$ is easily carried out by reacting the latter with iodine. Low yields of SF_5OOSO_2F are also obtained when SF_5OF and SO_3 are heated at 210°. Thionyl tetrafluoride was oxidized with $S_2O_6F_2$ in the presence of excess KF to SF_5OOSO_2F (40%). The yields are moderate owing to a side reaction of the excess fluoride ion with the product (*197*). SF_5OOSO_2F boils at 54.1° and its vapor pressure is given by $\log P_{\text{mm}} = 5.58822 - 281.402/T - 198,002/T^2$. The heat of vaporization is 7.2 kcal/mole and the Trouton constant is 21.9 eu. The infrared spectrum includes bands at 1494s, 1247s, 936vs, 910s, 883s, 848vs, 796ms, and 740 m cm^{-1}.

B. Perfluoroalkyl(fluorosulfuryl) Peroxides, R_fOOSO_2F

1. *Trifluoromethyl(fluorosulfuryl) Peroxide,* CF_3OOSO_2F

Fluoroxytrifluoromethane reacts with sulfur trioxide in the temperature range 245° to 260° to form trifluoromethyl(fluorosulfuryl) peroxide, CF_3OOSO_2F, a substance which melts at −117° and boils at 12.9° (*240*).

Thermal decomposition of CF_3OOSO_2F gives COF_2, O_2, and SO_2F_2. Vapor pressure data are given for the temperature range −40.1° to 12.9°.

When carbonyl fluoride and $S_2O_6F_2$ were condensed onto dried, powdered KF and allowed to stand at 25° for 2 hr, CF_3OOSO_2F (50% yield) was formed. The yield is reduced because of fluoride ion attack at the sulfur of the fluorosulfate group of either reactant or product to produce SO_2F_2.

$$CF_3OOSO_2F + CsF \xrightarrow[2\text{ hr}]{25^\circ} O_2 + SO_2F_2 + CsOCF_3 \quad (\mathit{197})$$

$$CsOCF_3 + F_2 \xrightarrow[2\text{ hr}]{-78^\circ} CsF + FOCF_3$$

$$CF_3OOSO_2F + CsF + CF_3OF \xrightarrow[3\text{ hr}]{25^\circ} SO_2F_2 + CF_3OOOCF_3$$

The heat of vaporization is 6.6 kcal/mole, the Trouton constant is 23.1, and the liquid density at 25° is 1.56 gm/ml. The principal peaks in the infrared spectrum are 1490s, 1300s, 1250s, 1190s, 927m, 855s, 805s, and 680m cm^{-1}. NMR resonances occur at $\delta_{CF_3} = 68.3\phi$ and $\delta_{S-F} = -37.9\phi$ (*197*).

CF_3OOSO_2F was found to react at room temperature with aqueous iodide solutions to produce free iodine, but not to react readily with water or concentrated sulfuric acid. The reaction with aqueous sodium hydroxide was slow, but complete within a few hours at 100°, according to the equation.

$$CF_3OOSO_2F + 8OH^- \rightarrow SO_4^{2-} + CO_3^{2-} + 4F^- + 0.5O_2 + 4H_2O$$

2. *Perfluoroisopropyl(fluorosulfuryl) Peroxide*, $(CF_3)_2CFOOSO_2F$; *Perfluoro-t-butyl(fluorosulfuryl) Peroxide*, $(CF_3)_3COOSO_2F$; *and 2-Methylhexafluoroisopropyl(fluorosulfuryl) Peroxide*, $(CF_3)_2CH_3COOSO_2F$

In the presence of dried and powdered KF, $(CF_3)_2C{=}O$ and $S_2O_6F_2$ reacted at 0° to give the rather unstable $(CF_3)_2CFOOSO_2F$ (32% yield). The peroxide decomposes on standing in glass at 25°. The principal bands in the infrared spectrum include 1492ms, 1312s, 1258s, 1196mw, 1162m, 1106ms, 1016ms, 860vs, 806mw, 776ms, and 735m cm^{-1}. ^{19}F NMR resonance bands occur at $\delta_{CF_3} = 76.2\phi$, $\delta_{CF} = 137.5\phi$, $\delta_{SF} = 38.2\phi$; $J_{SF-CF} = 8$ Hz (*197*).

Two additional perfluoroalcoholates, $(CF_3)_3COK$ and $(CF_3)_2CH_3CONa$, yield $(CF_3)_3COOSO_2F$ and $CH_3(CF_3)_2COOSO_2F$ with $S_2O_6F_2$, respectively. The former compound has ^{19}F NMR resonances at 69.2 and -38.0ϕ and an extrapolated boiling point of 95° (*181*).

V. Bis(pentafluorosulfur) Peroxide, SF_5OOSF_5

PREPARATION, PROPERTIES, AND REACTIONS

The fortuitous presence of molecular oxygen in the fluorine used in the fluorination of sulfur resulted in the first preparation of bis(pentafluorosulfur) peroxide in low yield (*119*). Since that time, this peroxide has been prepared via a number of routes, most of which are only modestly productive. Merrill and Cady (*155*) reacted pentafluorosulfur hypofluorite (three parts) with sulfinyl fluoride (one part) under a variety of conditions in both static and flow systems, e.g.,

Flow a.

$$SF_5OF + SOF_2 \xrightarrow[\text{AgF}_2\text{ catalytic reactor, 190°–233°}]{N_2} 2SOF_4$$

$$SF_5OF + SOF_4 \xrightarrow[\text{AgF}_2\text{ catalytic reactor, 190°–233°}]{N_2} \underset{(2\text{–}5\%)}{SF_5OOSF_5}$$

Static b.

$$SF_5OF + SOF_2 \xrightarrow{\text{AgF}_2\text{ catalytic reactor, 225°}} \text{recycle after 20 min contact time and separation of } SF_5OOSF_5\ (21\%)$$

Static c.

$$SF_5OF + SOF_2 \xrightarrow[\text{high pressure, 100°, 16 hr}]{\text{Cu vessel}} \underset{(20\%)}{SF_5OOSF_5}$$

Static d.

$$SF_5OF + SOF_2 \xrightarrow[\text{high pressure, 168°, 12 hr}]{\text{Cu vessel}} \underset{(33\%)}{SF_5OOSF_5}$$

In other gas phase reactions, pentafluorosulfur hypofluorite was also thermolyzed with SOF_4 at 190°, in the presence of AgF_2, to give a 2% yield of SF_5OOSF_5 and with SF_4 (*252*) at 140° to give SF_6, SOF_4, SF_5OOSF_5, and SF_5OSF_5 (7 : 3 : 2 : 1). However, when the latter reaction is carried out in the liquid phase (*170*) at 75° for 12 hr, the ratio of SF_5OOSF_5/SF_5OSF_5 is 1.2/1.3, while the other products are qualitatively the same with the exception of the formation of $SF_5OSF_4OSF_5$ (one part), their relative amounts are somewhat different. The yield of SF_5OOSF_5 is slightly greater if oxygen is heated with the SF_5OF–SF_4 mixture.

Photolysis of SF_5OF (*155*) at 1 atm for 3 hr with a 350-W ultraviolet lamp results in a mixture of sulfur fluorides and sulfur oxyfluorides, but SF_5OOSF_5 is obtained in yields greater than 25%. Longer irradiation does not increase the yield of peroxide since SF_5OOSF_5 is itself slowly decomposed by ultraviolet radiation. Cady and Merrill conclude that, although none of the preparative methods described by them give high yields of bis(pentafluorosulfur) peroxide, it is likely that the yields could be increased by removing the product as it is formed and by continuing the preparative reaction until the reactants have been consumed.

That this is the case was demonstrated by Witucki (*253*), who showed that yields of 90% (70% conversion) SF_5OOSF_5 are possible when the photochemical reaction of SF_5Cl and O_2 (diluted with N_2) in a circulating system is utilized and the SF_5OOSF_5 is continuously removed as it is formed. This yield is in contrast with that reported by Roberts (*189*), who photolyzed a 3 : 1 mixture of SF_5Cl–O_2 through quartz for 6 hr and obtained a 25% yield of SF_5OOSF_5 based on the liquid left after shaking the reaction mixture with 20% NaOH. Optimum conditions for the circulating method are a 3 : 1 ratio of SF_5Cl/O_2, a 40-hr reaction time, and a SF_5OOSF_5 trapping temperature of $-80°$. When the proposed reaction mechanisms in static (thermal or photolytic) and flow-removal systems are compared, it is likely that the $SF_5O\cdot$ radical coming from degradation of the peroxide, if the molecule remains in the reaction zone, reacts with other free radicals irreversibly, thus increasing the possibility for recombination and reducing the overall yield of SF_5OOSF_5 (*253*), e.g.,

Static

$$\begin{aligned} SF_5\cdot + O_2 &\rightleftharpoons SF_5OO\cdot \\ SF_5OO\cdot + SF_5Cl &\rightarrow (SF_5O)_2 + Cl\cdot \\ Cl\cdot + SF_5Cl &\rightleftharpoons SF_5\cdot + Cl_2 \\ (SF_5O)_2 &\rightleftharpoons 2SF_5O\cdot \\ SF_5O\cdot + SF_5\cdot &\rightarrow SF_5OSF_5 \end{aligned}$$

Flow-removal

$$\begin{aligned} SF_5\cdot + O_2 &\leftrightarrows SF_5OO\cdot \\ SF_5OO\cdot + SF_5Cl &\leftrightarrows (SF_5O)_2 + Cl\cdot \\ Cl\cdot + SF_5Cl &\leftrightarrows Cl_2 + SF_5\cdot \end{aligned}$$

Photolysis of SF_5OCl (*202b*) or of a mixture of SF_5OF and Cl_2 gives SF_5OOSF_5 (*55a*).

Bis(pentafluorosulfur) peroxide is stable as a colorless liquid in glass for at least 2 years at 25° (*119*) and is thermally stable to 200° (*155*), at which temperature a positive deviation from perfect gas behavior occurs and after heating to 338° to constant pressure, the decomposition products are SF_6, SO_2F_2, SOF_4, and O_2. In another decomposition study, the temperature was held at 521° for 12 hr with only SO_2F_2 and SF_6 observed in an infrared spectrum of the product mixture. SO_2F_2 must be formed at the expense of the SOF_4, i.e.,

$$2SOF_4 \rightarrow SF_6 + SO_2F_2$$

The peroxide is relatively unattacked by 5 *N* NaOH after 7 days at 100°. This stability is reminiscent of organic peroxides with large substituent groups such as di-*t*-butyl peroxide. Similarly, after 48 hr at 100°, a solution of iodide ion is only slightly affected; however, after 1 week at 100° the reaction is complete to give two equivalents of iodine per mole of $S_2O_2F_{10}$. This peroxide is a liquid of high density (1.968 gm/ml at 20°) which melts at –95.4° and boils at 49.4°. From available vapor pressure data over the temperature range of –50.3° to 50.3°, the heat of vaporization is 7.45 kcal/mole and a Trouton constant of 23.1 eu. The infrared spectrum in the NaCl region includes bands at 944s, 913s, 857s, 734m and 694w cm^{-1}. The mass spectrum does not contain a molecule ion and the highest *m*/*e* is a peak of low intensity assigned to SF_5^+. Other peaks include SOF^+, SF_2^+, SOF_2^+, SF_3^+, and SOF_3^+ in order of decreasing intensity.

An electron diffraction study (*119*) indicates a peroxide structure very similar in configuration to that of H_2O_2 with SF_5 groups replacing the hydrogen atoms. The SF_5 groups are octahedral, as in SF_6, with the S–F bond length 1.56 ± 0.02 Å. The length of the S–O bond is 1.66 ± 0.05 Å and that of the O–O bond, 1.47 ± 0.03 Å. The angles S–O–O and S–O–O–S are, respectively, 105° ± 3° and 107° ± 5° compared to 101.5° and 106° for H_2O_2. The distance of closest approach of the fluorine atoms on opposing (SF_5O) groups is about 2.4–2.5 Å, a value which is in agreement with that found for S_2F_{10} (*118*). On the basis of reports by Evans (*87*) and Walsh (*248*), who calculate the dissociation energy of the O–O bond to be about 56 kcal/mole, there should be a general increase in stability of $S_2O_2F_{10}$ over H_2O_2 owing to a more extensive transfer of charge to the oxygen atoms.

While several ^{19}F NMR studies of the compounds which contain the SF_5 moiety have been reported (*114*, *115*, *156*, *158*), the most definitive study (*89*) on SF_5OOSF_5 concluded that the through-space effect in F–F couplings is most likely. SF_5OOSF_5 is a $AB_4B_4'A'$ system with $\phi_A^* = -57.70$ MHz and $\phi_B^* = -56.53$ MHz with the latter assigned to the equatorial fluorine. The following couplings are reported:

$$J_{AB} = \pm 152.3 \pm 0.5 \text{ Hz}$$
$$J_{AB'} = J_{AA'} = 0.0 \pm 0.2 \text{ Hz}$$
$$J_{BB'} = \mp 4.3 \pm 0.2 \text{ Hz}$$

The chemical inertness of SF_5OOSF_5 compared to FSO_2OOSO_2F is well demonstrated, both by the dearth of reports of successful reactions and by the low yields of predicted products when reactions do occur. Yields are also decreased by decomposition of the peroxide to SF_6, SOF_4, and O_2. A summary of reactions is given in Table I. Side reactions which involve oxygenation or fluorination or both often occur (e.g., with CF_2Cl_2, C_2F_4, SO_2, SF_4, and NO). In some instances these side reactions are so extensive that none of the desired product is detected (e.g., with CF_2Cl_2, C_2F_4, and NO). Where oxygenation occurs, e.g., reaction with C_2F_4, CF_2Cl_2, and SF_4, bis(pentafluorosulfur) oxide appears as a product arising as a result of the reduction of an $SF_5O\cdot$ radical to $SF_5\cdot$, followed by combination of the $SF_5\cdot$ radical with $SF_5O\cdot$.

TABLE I

REACTIONS OF $S_2O_2F_{10}$

Reactant	Conditions	Products[a]	Refs.
C_6H_6	150°	$C_6H_5OSF_5$ (50%)	*45*
$C_6H_5CH_3$	90° (CCl_3F)	*p*-$CH_3C_6H_4OSF_5$	*45*
C_6H_5Cl	150°	*p*-$ClC_6H_4OSF_5$ + *o*-$ClC_6H_4OSF_5$ (10:1)	*45*
I_2	Δ	N.R.	*157*
SF_4	UV (liquid)	*cis*-$(SF_5O)_2SF_4$ (70%)	*157*
SF_4	210°	SOF_4 + SF_5OSF_5	*157*
$S_2O_6F_2$	UV, 4 days	SF_5OOSO_2F	*157*
NO	UV	N.R.	*157*
SO_2	2537 Å	SF_5OSO_2F (45%)	*80, 157*
SO_2	225°	SF_5OSO_2F + $(SF_5)_2SO_4$	*157, 169*
CF_3OOCF_3	UV, 7 days	SF_5OOCF_3	*157*
C_2F_4	UV	COF_2 + $CF_3C(O)F$ + $S_2O_2F_{10}$ (decomposition products)	*157*
C_3F_6	150° or UV	$F_5SO(C_3F_6)_nOSF_5$ ($n = 2, 3,$ or 4)	*44*
CF_2Cl_2	UV	COF_2 + SF_5OSF_5 + Cl_2 (main products)	*157*

[a] N.R., No reaction.

VI. Peroxide Derivatives of $S_2O_2F_{10}$

A. PENTAFLUOROSULFUR(FLUOROCARBONYL) PEROXIDE, $SF_5OOC(O)F$

Equimolar mixtures of SF_5OOSF_5 and $F(O)COOC(O)F$ when photolyzed for 2 hr gave conversions to $SF_5OOC(O)F$ of about 50% based on SF_5OOSF_5 consumed (*57*). Large quantities of CO_2, COF_2, SiF_4, SF_6,

SO_2F_2, and SOF_4 are formed in the reaction. The compound has an approximate boiling point of 25°. It is stable at room temperature, but attacks Hg and oxidizes aqueous iodide solutions readily. Hydrolysis in aqueous base occurs easily.

$$SF_5OOC(O)F + 10OH^- \rightarrow 6F^- + SO_4^{2-} + CO_3^{2-} + 5H_2O + 0.5O_2$$

The ^{19}F NMR spectrum contains the usual complex region at $\phi - 57.7$ (S–F), and at $\phi - 56.3$ (SF_4) ($J_{SF-SF_4} = 156$ Hz) observed in compounds with the SF_5 moiety. The resonance assigned to the C(O)F occurs at $+34.4\phi$ ($J_{SF_4-CF} = 3$ Hz). Principal bands in the infrared spectrum are found at 1922vs, 1239ms, 1196vvs, 998w, 937vvs, 889vvs, 751m, 692w, 611s, and 569w cm^{-1}.

B. PENTAFLUOROSULFUR(TRIFLUOROMETHYL) PEROXIDE, SF_5OOCF_3

Photolysis through quartz for 7 days of equimolar amounts of SF_5OOSF_5 and CF_3OOCF_3 resulted in formation of the mixed peroxide, SF_5OOCF_3 (*157*). Equal amounts of the three peroxides were in the reaction vessel. Thermolysis of SF_5OF and COF_2 at 210° gave a low yield of SF_5OOCF_3. This colorless liquid boils at 7.7° and melts at −136°. Vapor pressure can be calculated from the equation

$$\log P_{mm} = 7.11733 - \frac{1020.00}{T} - \frac{47{,}780.2}{T^2}$$

The heat of vaporization is 6.4 kcal/mole and Trouton constant is 22.8 eu. At 20°, the density is 1.760 gm/ml. The principal peaks in the infrared spectrum are at 1493m, 1291vs, 1248vs, 1207vs, 963s, 931vs, 880vs and 748m cm^{-1}.

C. PENTAFLUOROSULFUR(TETRAFLUOROPENTAFLUOROSULFOXYSULFUR) PEROXIDE, $SF_5OSF_4OOSF_5$, AND BIS(TETRAFLUOROPENTAFLUOROSULFOXYSULFUR) PEROXIDE, $SF_5OSF_4OOSF_4OSF_5$.

A large number of products, including SF_6, SF_4, SOF_4, SF_5OSF_5, $SF_5OSF_4OSF_5$, and three peroxides, SF_5OOSF_5 (0.031 mole), $SF_5OSF_4OOSF_5$ (0.047 mole), and $SF_5OSF_4OOSF_4OSF_5$, are formed when SF_5OF (0.207 mole), SF_4 and O_2 are heated at 75° for 12 hr (*170*). When the reaction is over the temperature range 0°–90°, the proportion of $SF_5OSF_4OOSF_4OSF_5$ in the product decreases with increasing temperature, while that of SF_5OOSF_5 increases. The proportion of $SF_5OSF_4OOSF_5$ increases sharply from 0° to 20°, but thereafter slowly declines. These results may be attributed to decreasing stability of the compounds with increasing chain length. The decomposition which occurs at the higher temperature follows the reaction scheme

$$\begin{tikzcd}
SF_5OSF_4OOSF_4OSF_5 \arrow[r] & SF_5OSF_4OOSF_5 + SOF_4 \arrow[d] \\
& SF_5OOSF_5 + SOF_4
\end{tikzcd}$$

Pyrolysis at 300° for 12 hr of 9 mmoles of $SF_5OSF_4OOSF_4OSF_5$ gave SOF_4 (26 mmoles) and $S_2O_2F_{10}$ (5 mmoles). This symmetric peroxide boils at 59° (20 mm) and its vapor pressure can be obtained from $\log P_{mm} = 8.709 - 2479/T$. From this equation, the normal boiling point is 152°; the heat of vaporization is 11.3 kcal/mole and the Trouton constant is 26.7 eu. The principal bands in the infrared spectrum are at 959vs, 944vs, 873m, 848vs, 820w, 803vs, 610–594d,vs, and 550–543d,vs cm^{-1}.

Pyrolysis of $SF_5OSF_4OOSF_5$ also gives SOF_4 and $S_2O_2F_{10}$. It boils at 99°. The infrared spectrum consists of bands at 960vs, 945vs, 875s, 849s, 798vs, 721m, 597s, 589s, and 548s cm^{-1}. Both $SF_5OSF_4OOSF_4OSF_5$ and $SF_5OSF_4OOSF_5$ when refluxed with benzene gave, in addition to SOF_4, $C_6H_5OSF_5$ and $C_6H_5OSF_4OSF_5$. Sulfur dioxide reacts with $SF_5OSF_4OOSF_5$ in the liquid phase at 125° to give $SF_5OSO_2OSF_4OSF_5$ (*169*). No compound corresponding to $(SF_5OSF_4)_2SO_4$ was formed between SO_2 and the symmetric peroxide $(SF_5OSF_4)_2O_2$ at temperatures up to 125°, at which temperature the latter began to decompose appreciably. $SF_5(OSF_4)_2OOSF_5$ has also been reported (*171*).

D. PENTAFLUOROSULFUR(TETRAFLUOROTRIFLUOROMETHOXYSULFUR) PEROXIDE, $CF_3OSF_4OOSF_5$, AND BIS(TETRAFLUOROTRIFLUOROMETHYOXYSULFUR) PEROXIDE, $CF_3OSF_4OOSF_4OCF_3$

When trifluoromethyl hypofluorite and sulfur tetrafluoride are heated to 75° for 10 hr, the main product is CF_3OSF_5. However, when the latter two are heated in the presence of oxygen under analogous conditions, as with SF_5OF, a number of products are obtained including four peroxides SF_5OOSF_5, $SF_5OSF_4OOSF_4OSF_5$ (trace), $CF_3OSF_4OOSF_4OCF_3$, and $CF_3OSF_4OOSF_5$. $CF_3OSF_4OOSF_4OCF_3$ boils at 102° and its infrared spectrum has principal bands at 1279vs, 1244vs, 1198vs, 1181vs, 984s, 935s, 922s, 854vs, 846vs, and 837vs cm^{-1}. $CF_3OSF_4OOSF_5$ boils at 125° and has principal infrared bands at 1279vs, 1245vs, 1190vs, 985s, 942vs, 927s, 903s, 869s, 840vs, 797vs and 546s cm^{-1}. These compounds are stable to 5 *M* KOH under reflux.

Pass and Roberts (*170*) have proposed a plausible mechanism for the formation of the more complex peroxides in the presence of oxygen, thus

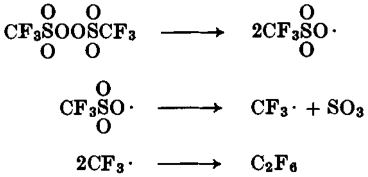
$$\begin{aligned}
ROF + SF_4 &\rightarrow SF_5\cdot + RO\cdot \\
R = SF_5,\ CF_3 & \\
RO\cdot + SF_4 &\rightarrow ROSF_4\cdot \\
(\text{or } RO\cdot + SF_4 &\rightarrow R\cdot + SF_4O) \\
ROSF_4\cdot + O_2 &\rightarrow ROSF_4OO\cdot \\
SF_5\cdot + O_2 &\rightarrow SF_5OO\cdot \\
SF_5\cdot + ROSF_4OO\cdot &\rightarrow ROSF_4OOSF_5 \\
(\text{or } SF_5OO\cdot + ROSF_4\cdot &\rightarrow ROSF_4OOSF_5) \\
ROSF_4\cdot + ROSF_4OO\cdot &\rightarrow ROSF_4OOSF_4OR
\end{aligned}$$

accounting for formation of $SF_5OSF_4OOSF_5$, $CF_3OSF_4OOSF_5$, $SF_5OSF_4OOSF_4OSF_5$, and $CF_3OSF_4OOSF_4OCF_3$.

VII. Other Inorganic Peroxides

A. BIS(TRIFLUOROMETHYLSULFURYL) PEROXIDE, $(CF_3SO_2)_2O_2$

Although the substitution of CF_3 groups for fluorine atoms most often results in increased stability, such is not the case for $(CF_3SO_2)_2O_2$. Just as $S_2O_6F_2$ forms upon electrolysis of HSO_3F, so $CF_3SO_2OOSO_2CF_3$ can be prepared by the electrolysis at −23° of trifluoromethanesulfuric acid which contains a small amount of sodium trifluoromethanesulfonate to increase the conductivity (*165*). Hydrogen is generated at the cathode. No oxygen is observed at the anode and colorless $CF_3SO_2OOSO_2CF_3$ is among the products found there. When a cold sample of this liquid compound was allowed to warm up, it decomposed suddenly—with evolution of heat at 10°. Decomposition products found were perfluoroethane, sulfur trioxide, and the ester, trifluoromethyl trifluoromethanesulfonate, $CF_3SO_3CF_3$, as well as small amounts of COF_2, SO_2, $(CF_3SO_2)_2O$, and CF_3SO_2OH. The ester is resistant to hydrolysis by water, but does hydrolyze at 100° in 0.1 *N* NaOH. An explanation of the products may be

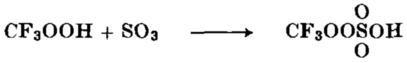


$$\begin{aligned}
CF_3\overset{O}{\underset{O}{S}}OO\overset{O}{\underset{O}{S}}CF_3 &\longrightarrow 2CF_3\overset{O}{\underset{O}{S}}O\cdot \\
CF_3\overset{O}{\underset{O}{S}}O\cdot &\longrightarrow CF_3\cdot + SO_3 \\
2CF_3\cdot &\longrightarrow C_2F_6
\end{aligned}$$

It is not possible to obtain pure $CF_3\underset{O}{\overset{O}{S}}OO\underset{O}{\overset{O}{S}}CF_3$, but chemical analyses were carried out by determining the amounts of decomposition products that were produced from a weighed sample of $CF_3SO_2OOSO_2CF_3$ contaminated with small amounts of CF_3SO_3H. These analyses show that the explosive material is $(CF_3SO_3)_n$, but that n does not necessarily equal 2. However, the existence of the peroxide as a low-temperature species can be strongly argued based on physical properties and most conclusively on ^{19}F NMR studies, i.e., on cold solutions which show a peak at 72.36 ppm (ext. CCl_3F) assigned to $(CF_3SO_3)_2$ plus peaks at 54.66 and 75.30 ppm for $(CF_3)_2SO_3$ and at 77.19 ppm for CF_3SO_3H. Upon warming to 25°, the peroxide peak disappeared, the ester peaks grew and a new peak at 89.06 ppm (C_2F_6) appeared. Impure samples of $(CF_3SO_3)_2$ immediately liberate iodine from cold KI solution.

B. HYDROXOSULFURYL(TRIFLUOROMETHYL) PEROXIDE, $HOSO_2OOCF_3$

Advantage is taken of the ease of insertion of SO_3 into the O–H bond of CF_3OOH to prepare quantitatively another mixed carbon–sulfur peroxide (*29, 124*).



$$CF_3OOH + SO_3 \longrightarrow CF_3OO\underset{O}{\overset{O}{S}}OH$$

It exhibits a vapor pressure of less than 3 Torr at 25°, but apparently undergoes dissociation at this temperature when being transferred. Thermal decomposition gives equimolar amounts of COF_2 and $HOSO_2F$ and one-half that molar amount of oxygen. It is a colorless shock-insensitive material which melts over the range −46.2° to −45.0°. The ^{19}F and ^{1}H NMR spectra consist of single resonances at $\phi^*67.3$ and $\delta 10.35$, respectively. Principal infrared bands occur at 1482w, 1444m, 1399w, 1382w, 1292m, 1256s, 1197m, 940m, 876w, 789m, 678vw, and 560w cm^{-1}.

C. TRIFLUOROMETHYL(TRIFLUOROMETHOXOSULFURYL) PEROXIDE, $CF_3OOSO_2OCF_3$

At 75° the reaction of sulfur trioxide and bis(trifluoromethyl) trioxide produces $CF_3OOSO_2OCF_3$ in 50% yield (*124*). It is a colorless liquid that boils at 46.2° and has a density as defined by $d_t = 1.6844 - 0.002891t$. Vapor pressure data may be obtained from

$$\log P_{\mathrm{mm}} = 6.89575 - \frac{1001.8}{T} - \frac{89{,}500}{T^2}$$

and from the P–T curve, $\Delta H_{\mathrm{vap}} = 7.1$ kcal/mole and $\Delta S_{\mathrm{vap}} = 22.4$ eu. Two quartets ($J = 0.9$ Hz) observed at 56.5 and 68.4ϕ^* are assigned to CF_3OS and CF_3OOS, respectively. Principal bands in the infrared spectrum occur at 1492s, 1294sh, 1282vs, 1263vs, 1248vs, 1190vvs, 1142vvs, 962s, 802s, 782sh, 615sh, 581m, and 543w cm^{-1}.

D. Nitryl(trifluoromethyl) Peroxide, O_2NOOCF_3

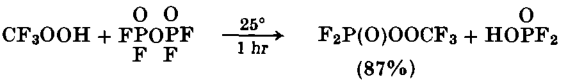
The first nitrogen peroxide which contains fluorine was synthesized in 95% yield by Hohorst and DesMarteau (*29*, *124*).

$$CF_3OOH + N_2O_5 \xrightarrow{-78^\circ} CF_3OONO_2 + HNO_3$$

It is a shock-sensitive compound which boils at 0.7° and whose vapor pressure curve is defined by $\log P_{\mathrm{mm}} = 7.6063 - 1294.1/T$ ($\Delta H_{\mathrm{vap}} = 5.9$ kcal/mole, $\Delta S_{\mathrm{vap}} = 21.6$ eu). Liquid density as a function of temperature is given by $d_t = 1.5308 - 0.00263t$. A single ^{19}F NMR resonance occurs at $\phi^*72.56$. Principal infrared bands occur at 1828w, 1758vs, 1760sh, 1730sh, 1620sh, 1580sh, 1552sh, 1535sh, 1407sh, 1298vs, 1242vs, 1187vs, 1047w, 951m, 780s, 703w, 667w, 598w, 557w, and 486w cm^{-1}.

E. Difluorophosphoryl(trifluoromethyl) Peroxide, $F_2P(O)OOCF_3$

The first fluorine-containing phosphorus peroxide has also been obtained from the reaction of the nucleophile CF_3OOH with the acid anhydride, $P_2O_3F_4$ (*27*, *29*).



$$CF_3OOH + \underset{F\quad F}{\overset{O\quad O}{FPOPF}} \xrightarrow[1\,hr]{25^\circ} \underset{(87\%)}{F_2P(O)OOCF_3} + \overset{\qquad O}{HOPF_2}$$

$F_2P(O)OOCF_3$ undergoes slow decomposition at 25° after 57 days when present entirely as a gas to give COF_2, POF_3, and O_2. However, a sample of liquid, in equilibrium with vapor, was completely decomposed after 9 days at 25°. It melts at $-88.6° \pm 0.3°$, boils at 15.5°, and its vapor pressure may be calculated from $\log P_{mm} = 8.677 - 1672.8/T$ (−32.4° to 7.4°), while the enthalpy and entropy of vaporization are 7.7 kcal/mole and 26.5 eu (*27*).

The ^{19}F NMR spectrum consists of a set of quartets centered at ϕ*88.3 ($J_{P-F} = 1109$ Hz, and $J_{F-F} = 2.6$ Hz) assigned to the fluorines bonded to phosphorus and two overlapping triplets at ϕ*69.8 ($J_{P-CF_3} = 1.3$ Hz) assigned to fluorines bonded to carbon. Principal bands in the infrared spectrum occur at 1395s, 1289vs, 1255vs, 1205vs, 970s, 915s, 865m, 827m, 675vw, 595vw, and 500s cm^{-1}.

Photolysis of $F_2P(O)OOCF_3$ at 2537 Å did not provide a route to the symmetric phosphorus peroxide, but only decomposition and rearrangement products, including POF_3, COF_2, $HOPOF_2$, $P_2O_3F_4$, CF_3OOCF_3, CF_3OOOCF_3, and O_2, were produced (*27*).

Some reaction chemistry of $F_2P(O)OOCF_3$ was examined and details of the results are included in Table II (*27*). Two unstable fluorophosphorus peroxides, difluoromonophosphoric acid (OPF_2OOH) and monofluoroperoxomonophosphoric acid ($OPF_2(OH)OOH$), resulted from solvolysis of $P_2O_3F_4$ and $OPCl_2F$ with H_2O_2, respectively (*89a*).

TABLE II

REACTIONS OF $F_2P(O)OOCF_3$ AT 24°

Reactant	Time (days)	Products[a]
H_2S	1	CF_3OOH, COF_2, POF_3, S, $HOPOF_2$, O_2
HCl	14	CF_3OOH, HCl, COF_2, POF_3, Cl_2
$CF_3C(O)OH$	1	N.R.
Cl_2	2	N.R.
CF_3OF ($h\nu$)	1	COF_2, POF_3, CF_3OOOCF_3
$CF_2(OF)_2$	0.2	$CF_2(OF)_2$, COF_2, POF_3, O_2
SF_5OF	2	SF_5OF, COF_2, POF_3, O_2
$S_2O_6F_2$	1	$S_2O_6F_2$, COF_2, POF_3, O_2
C_2F_4	3	C_2F_4, $F_2P(O)OOCF_3$, white solid

[a] N.R., No reaction.

F. BIS(PENTAFLUOROSELENIUM) PEROXIDE, $F_5SeOOSeF_5$

An area where more work is needed and which may give rise to some surprises is that involving selenium compounds. Since fluorination of $KSeO_2F$ gives not only SeF_5OF (14% yield) but also the only Group VIa bis(hypofluorite), $SeF_4(OF)_2$ (16% yield) (*206*), it is likely that additional, more complex selenium peroxides will be discovered.

Flow fluorination of selenium dioxide at 60°–90° with F_2/N_2 yields $F_5SeOOSeF_5$ in addition to SeF_6 and $SeOF_6$ plus a higher boiling compound which contains three selenium atoms per molecule (*160*). The yield of $Se_2O_2F_{10}$ can be greatly increased by inserting a roll of silver-plated copper screening on the downstream side of the heated portion of the nickel tube reactor in which the boat containing SeO_2 is placed. This catalyst, which is useful in many fluorination reactions, is also helpful here. In a run with the reactor at about 110°, an 8-gm sample of SeO_2 was treated for 1.5 hr with a mixture of F_2/N_2 (1:1) flowing at a rate of 6 liters/hr. About 1.6 gm of $Se_2O_2F_{10}$ and little $SeOF_2$ were obtained. Products observed are temperature dependent. Although this "catalytic" method is preferred, $SeOCl_2$ may be fluorinated first at 50° and subsequently at 75° with F_2/N_2 (8:2 liters/hr) to give $Se_2O_2F_{10}$ as the second most abundant product. Again, little $Se_2O_2F_{10}$ is obtained without the presence of the silver-plated copper screening. The fluorination of $(F_5SeO)_2Hg$ gives $Se_2O_2F_{10}$, also (*202c*).

Bis(pentafluoroselenium) peroxide is nearly inert toward water and concentrated solutions of sulfuric acid or sodium hydroxide. As is true for its sulfur analog, $(SeF_5O)_2$ reacts very slowly with a solution of potassium iodide. Anhydrous calcium chloride does not react and sulfur reacts only on warming. With organics, such as benzene, α-naphthalene, and pyridine, reaction occurs very quickly to give strongly colored products. With $S_2O_6F_2$, photolysis gives SeF_5OSO_2F (*186a*).

Again, as is typical of other peroxides, $Se_2O_2F_{10}$ reacts with fluorine on heating in an empty tube flow reaction.

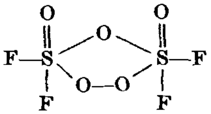
$$Se_2O_2F_{10} + F_2 \xrightarrow{70^\circ} \underset{(78\%)}{SeF_6} + \underset{(18\%)}{SeF_5OF}$$

In a copper tube heated to 200°, decomposition of $Se_2O_2F_{10}$ to SeF_6 and other unidentified products occurs. On standing in a copper tube at 25° for 1 month, none of the $Se_2O_2F_{10}$ remained, while other samples which were stored in Pyrex vessels showed little or no decomposition after 3 months. These relative stabilities suggest that SeF_5OOSeF_5 is unstable to attack by metal fluorides.

Bis(pentafluoroselenium) peroxide melts at −62.8° and boils at 76.2°, and vapor pressure data for the temperature range 28.7°–75.9° are available (*206*). Its mass spectrum contains peaks assigned to SeF_5^+, SeF_4^+, $SeOF_3^+$, $SeOF_2^+$, SeF_2^+, $SeOF^+$, SeF^+, and Se^+. The infrared spectrum of $Se_2O_2F_{10}$ contains bands at 1405w, 1295w, 858m, 842s, 775vs, 762vs, 737vs, and 722s cm^{-1}. At low resolution, the ^{19}F NMR spectrum consists of a single peak, but at higher resolution evidence for much more complex interactions is obtained which must arise from the presence of ^{77}Se as well as from the likelihood that the apical and equatorial fluorine atoms are not equivalent. A band in the Raman spectrum at 897 cm^{-1} is assigned to the —O–O— stretching vibration (*202c*).

G. μ-OXO-μ-PEROXOBIS(DIFLUOROSULFATE), $S_2O_2F_4$

When a 1:1 mixture of SOF_2 and oxygen was subjected to electric discharge at –50° to –60°, a liquid was formed which on distillation gave unreacted starting materials, sulfuryl fluoride, bis(fluorosulfuryl) peroxide (?), and $S_2O_5F_4$ (*249*). Above –20°, $S_2O_5F_4$ decomposes to SO_2F_2 and O_2. It has a melting point of –95° and oxidizes I^- to I_2. The postulated structure is



H. HYDRO(PENTAFLUOROSULFUR) PEROXIDE, SF_5OOH

Stoichiometric amounts of water hydrolyze $F_5SOOC(O)F$ to a stable, colorless liquid, SF_5OOH (*63a*), which boils at 0° (150 Torr) and freezes at 55.6°. Thermal decomposition at 85° in a Monel vessel produced OSF_4, O_2, and HF. The infrared spectrum contains bands at 3560m, 1385s, 920vs, 725w, and 610s cm^{-1}. A strong Raman band at 735 cm^{-1} is assigned to the —O–O— stretching mode.

VIII. Fluoroperoxides

A. FLUORO(FLUOROSULFURYL) PEROXIDE, FSO_2OOF

The only confirmed inorganic -OOF compound is fluoro(fluorosulfuryl) peroxide which can be thought of as a formal derivative of FOOF. Unfortunately, the reaction chemistry of this compound has not been elucidated, but from ESR studies it is established that upon photolysis, $FSO_2\cdot$ and $\cdot OOF$ radicals (*163*) are formed predominantly which is entirely analogous to

$$FOOF \rightarrow \cdot F + \cdot OOF \qquad (130)$$

Fluoro(fluorosulfuryl) peroxide is readily synthesized by the photolysis of oxygen difluoride in 6:1 molar excess over sulfur trixoide using radiation energies lower than 365 nm to prevent activation of any molecules other than OF_2 (*92*, *98*). If the energy of radiation exceeds this, only a trace of FSO_2OOF is isolated with the predominant products being $S_2O_5F_2$ and SO_2F_2. These products, plus oxygen, are identical to the products obtained when FSO_2OOF is photolyzed through Pyrex with a high-pressure mercury vapor lamp. Two conflicting reports indicate $SO_2F_2/S_2O_5F_2$ ratios of 0.5 (*92*) and 8 (*211*). The latter seems to be the more realistic, although the former workers found the same decomposition product ratio when FSO_2OOF was mixed with N_2O_4 and allowed to stand at 25° overnight. The N_2O_4 was recovered essentially quantitatively.

The reaction of OF_2 with SO_3 to form FSO_2OOF involves the transfer of the OF radical as is shown by ^{17}O NMR studies (*213*). Photolysis of $^{17}OF_2$ with SO_3, OF_2 with $S^{17}O_3$, and $^{17}OF_2$ with $S^{17}O_3$ gives $FSO_2O^{17}OF$, $FS^{17}O_2{}^{17}OOF$, and $FS^{17}O_2{}^{17}O^{17}OF$, respectively. The ^{17}O nuclear magnetic resonance spectra of $FSO_2O^{17}OF$ and $FS^{17}O_2{}^{17}O^{17}OF$ consist of a doublet at −669 MHz (relative to H_2O) with $J_{^{17}O-F} > 430$ Hz. The latter as well as $FS^{17}O_2{}^{17}OOF$ have doublets at −152 MHz with $J_{O-F} = \sim 31$ Hz and a singlet at −365 MHz.

Sulfur dioxide reacts with either O_2F_2 or O_4F_2 to form FSO_2OOF in 5 and 32% yields in CF_3Cl solvent at −183° (*208*). Similar ^{17}O NMR studies of the $O_2F_2 + SO_2$ reaction show that FSO_2OOF is formed via an $\cdot OOF$ intermediate (*212*).

Small amounts of FSO_2OOF are also obtained when O_2F_2 and H_2SO_5 are mixed at −100° (*211*).

$$\underset{(21\text{ mmoles})}{O_2F_2} + \underset{(13\text{ mmoles})}{H_2SO_5} \rightarrow \underset{(0.9\text{ mmoles})}{FSO_2OF} + \underset{(0.5\text{ mmoles})}{FSO_2OOF} + \underbrace{S_3O_8F_2 + \text{higher polymers}}_{(1.23\text{ gm})} + \underset{(6\text{ mmoles})}{SiF_4}$$

Fluoro(fluorosulfuryl) peroxide is a pale yellow-green liquid which boils at 0° and is thermally stable to 50° (*98*). The liquid obeys the vapor pressure equation $\log P_{mm} = 6.781 - 1063T^{-1}$. The gas phase infrared spectrum in the sodium chloride region contains bands at 1493, 1250 (S=O asymmetric and symmetric stretches), 855, 787, and 725 cm^{-1}. The ^{19}F NMR consists of two doublets (relative to CCl_3F) at −291 and −43 ppm ($J_{F-F} = 10.5$ Hz), both of which occur in regions typical of $-OOF$ and $F\overset{O}{\underset{O}{S}}O-$ groups.

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.

$$\underset{(25.5\text{ ml})}{FSO_2OOF} + \underset{(16.8\text{ ml})}{SO_2} \xrightarrow[1\text{ hr}]{25^\circ} \underset{(18.4\text{ ml})}{SO_2F_2} + \underset{(5.8\text{ ml})}{S_2O_5F_2} + \underset{(10.0\text{ ml})}{O_2}$$

Whereas

$$\underset{(3.2\text{ mmoles})}{FSO_2OF} + \underset{(3.1\text{ mmoles})}{SO_2} \xrightarrow[6\text{ days}]{25^\circ} \underset{(1.3\text{ mmoles})}{S_2O_5F_2}$$

While at 195°, the insertion is quantitative (*194*).

A molecule ion is not observed in the mass spectrum (*92*) with *m/e* 99 (SO_3F^+) the highest mass fragment observed. Other fragments include SO_2F^+, SO_3^+, FSO^+, SO_2^+, SF^+, SO^+, and OF^+. This mode of fragmentation indicates an initial fracture of the oxygen–oxygen bond or at least does not suggest that breaking of the sulfur–oxygen single bond occurs to any extent which electron paramagnetic resonance indicates to be the major decomposition route upon interaction with ultraviolet radiation in a CCl_3F matrix (*154*). (No evidence is found for OF, FSO_2O, or FSO_2OO radicals.)

B. FLUORO(FLUOROHALOGEN)- AND FLUORO(PENTAFLUOROSULFUR) PEROXIDES

While FSO_2OOF appears to be perfectly stable at 25°, other compounds which have been synthesized from O_2F_2 and which formally may be dioxygen fluorides are only stable at or below 195°K and have not been studied extensively. Reactions of O_2F_2 become increasingly exothermic proceeding from ClF to BrF_3 to SF_4, and as a consequence more difficult to control, so that the highly colored product, O_2MF_x formed in each case is more difficult to obtain (*221*, *222*, *224*).

1. *Fluoro[difluorochlorine(III)] Peroxide, ClF_2OOF*

If O_2F_2 and ClF are mixed above 140°K, the reaction is violent, with ClF abstracting fluorine from O_2F_2 to form ClF_3 and O_2. However, if the reaction is moderated by using lower temperatures (119°–130°K) and slow addition of ClF, a violet compound is formed.

$$O_2F_2 + ClF \xrightarrow{119^\circ\text{–}130^\circ\text{K}} O_2ClF_3$$

Although a solvent such as C_3F_8 improves the yield, the stability of O_2ClF_3 in solution is low. The pure solid compound was reported to be thermally stable at temperatures up to 195°K for 2 years. Its synthesis was realized in systems where it was possible to generate ClF *in situ*, e.g., with Cl_2 or HCl at 130°K, or when chlorine trifluoride was photolyzed at 2537 Å and 195°K under 2 atm of oxygen.

O_2ClF_3 is soluble in ClF at 125°K, O_2F_2 at 140°K, and ClF_3 at 190°K. It is readily soluble in anhydrous HF at 190°K to give deep violet solutions, which decolorize rapidly with decomposition to O_2 and ClF_3. It is a nonelectrolyte in this solvent which precludes the existence of $(O_2ClF_2)^+F^-$ (*224*). Turner (*239*) has suggested, based on the fact that O_2F_2 behaves as $\cdot F + \cdot OOF$ and not as $2 \cdot OF$ (*127, 143*), that ClF_2OOF is to be preferred to $ClF(OF)_2$ as a structure. Supporting this are the visible and the infrared spectra obtained at 77°K which indicate the presence of an O–O group (*94*). Unfortunately, no ^{19}F NMR data have appeared for the resonance position of the fluorine bonded to oxygen since this would be definitive.

Reaction between O_2F_2 and excess ClF produces a blue compound which also contains an O–O group based on infrared and visible spectral studies. An oxygen-sensitive equilibrium exists between the blue and violet compounds in ClF_3 solution which suggests that the blue compound could be $F_2ClOOClF_2$ (*94*).

O_2ClF_3 is a powerful oxidizing agent whose low temperature reactions with NH_3, C_2H_6, C_2H_4, C_6H_6, H_2O, H_2, and CH_4 are rapid, with the exception of the latter two, where no reaction occurs up to 120°K, and produce white solids and a variety of small gaseous molecules (*221, 222, 224*).

2. *Fluoro[tetrafluorobromine(V)] Peroxide, BrF_4OOF*

Although O_2BrF_5 can result from reaction of O_2F_2 with BrF_3 at 130°K, the favored reaction is one to give BrF_5 and O_2, and the violet intermediate O_2BrF_5 is not always observed. Again it is reported to be possible to obtain O_2BrF_5 with O_2F_2 and a molecule which permits *in situ* generation of BrF_3, such as HBr. O_2BrF_5 begins to decompose at 150°K and production of BrF_5 and O_2 is complete at 170°K (*221, 222*).

3. *Fluoro(pentafluorosulfur) Peroxide, SF_5OOF*

Although the purple-violet O_2SF_6 (SF_5OOF) is reported to be generated sometimes from the reaction of O_2F_2 with SF_4 at 130°K with ClO_3F as diluent, little real evidence for its existence is available. Decomposition to O_2 and SF_6 occurs in the 150°–170°K range (*221, 222*), but additional work is needed.

C. FLUORO(PERFLUOROALKYL) PEROXIDES, R_fOOF

The fluoro(perfluoroalkyl) peroxides represent a very interesting class of compounds in that they contain the novel OOF group. The compounds with this group are limited to CF_3OOF, C_2F_5OOF, *n*-C_3F_7OOF, and *i*-C_3F_7OOF. The small number is indicative of the synthetic difficulties in introducing the OOF function rather than a lack of interest.

The first report of a fluoro(perfluoroalkyl) peroxide was by Thompson (*232*) in 1967. Fluoro(trifluoromethyl) peroxide, CF_3OOF, and fluoro(pentafluoroethyl) peroxide, C_2F_5OOF, were found to be relatively minor products arising from the flow fluorination of sodium trifluoroacetate.

$$CF_3CO_2Na + F_2/N_2 \rightarrow CF_3OOF + \underset{(1\text{-}5\%)}{C_2F_5OOF}$$

The synthesis of C_2F_5OOF has not been improved to date, but alternative higher yield syntheses for CF_3OOF have been developed.

In the synthesis of bis(trifluoromethyl) trioxide Anderson and Fox (*1*) postulated CF_3OOF as an intermediate in the reaction of OF_2 with $CsOCF_3$ but were unable to detect the fluoroperoxide. Solomon and co-workers (*214*) in studying the mechanism of the $OF_2/CsOCF_3$ reaction by ^{17}O labeling successfully developed the first practical synthetic route to CF_3OOF. By using a 4:1 mixture of OF_2 to $CsOCF_3$ (COF_2 free), the reaction yielded the intermediate peroxide.

$$OF_2 + CsOCF_3 \xrightarrow[\text{72 hr}]{\text{room temp.}} CF_3OOF + CF_3OOOCF_3$$

CF_3OOF was formed in a three-fold excess over the trioxide and the mixture was conveniently separated by fractional condensation.

In an attempt to generate higher members of the R_fOOF family the reaction of OF_2 and $CsOC_2F_5$ was investigated (*207*), but only $CF_3OOC_2F_5$, CF_3OOOCF_3, and $C_2F_5OOOC_2F_5$ were isolated. The formation of $C_2F_5OOOC_2F_5$ suggests that C_2F_5OOF was present and reacted in a manner analogous to CF_3OOF, namely,

$$C_2F_5OOF + C_2F_5OCs \rightarrow C_2F_5OOOC_2F_5$$

or

$$C_2F_5OOF + CF_3C(O)F \rightarrow C_2F_5OOOC_2F_5$$

Solomon suggests that mild reaction conditions (23°, 16 hr) may lead to the isolation of the fluoroperoxide.

Another method for the synthesis of CF_3OOF was developed by DesMarteau (*63*), who discovered that the direct reaction of CF_3OOH and fluorine resulted in CF_3OOF in moderate yield.

$$CF_3OOH + F_2 \xrightarrow{CsF} \underset{(25\text{–}35\%)}{CF_3OOF}$$

The maximum yields were obtained under various conditions [F_2/CF_3OOH, time (hr), temp. (°C): 1, 14, −111° to −18°; 2, 2, −196° to −78°; 2, 5, −78°; or 0.5, 19, −78°]. Owing to the more involved preparation of CF_3OOH, the synthesis of CF_3OOF developed by Solomon is probably the more convenient method.

The most direct synthesis of fluoroperoxides is one which involves the transfer of the OOF function in reactions of O_2F_2. The instability and high reactivity of O_2F_2 has led to mixed results. Holzmann and Cohen (*126*) found that only CF_3OOCF_3 and decomposition products were isolated from the low-temperature reaction of O_2F_2 and C_2F_4 even when diluted with helium or liquid argon. However, Solomon *et al.* (*210*) were successful in transferring the OOF group with C_3F_6 by using a solvent

$$C_3F_6 + O_2F_2 \xrightarrow{CClF_3,\ -183^\circ} C_3F_7OOF$$

Both isomers, fluoro(heptafluoropropyl) peroxide and fluoro(heptafluoroisopropyl) peroxide, were isolated in a combined yield of ~20%. Unfortunately, the authors were unable to separate the isomers and characterization had to be accomplished on the mixture. The relative amounts of both isomers were determined by ^{19}F NMR to be 3:1 heptafluoroisopropyl to heptafluoropropyl peroxide.

Although moderate yields of the fluoroperoxides were obtained by using $CClF_3$ as a solvent, the utilization of O_2F_2 to synthesize these peroxides must be approached with caution. With very reactive perfluoroolefins the reaction proceeds vigorously even at −196° and fragmentation occurs. Also, Solomon and co-workers found, in addition to cleavage products (C_2F_6, C_3F_8, COF_2, CF_3OOF, and $SiF_4 \sim 5\%$), there was a major fraction which was thermally and shock sensitive. This fraction did not show any ^{19}F NMR resonances for OF or OOF functions and the explosive decomposition gave fluorocarbonyl derivatives indicating an unknown oxygenated fluoroalkyl compound was present.

The characterization of these fluoroperoxide derivatives with respect to physical constants is limited to CF_3OOF. The difficulty in separating the fluoro(heptafluoropropyl) peroxide isomers prevented their complete characterization and no mention was made of their stability. DesMarteau has characterized CF_3OOF in detail, including vapor pressure and density determinations. This fluoroperoxide was found to have a melting point below −196° and had a normal boiling point of −69.4°. No decomposition of CF_3OOF in glass was noted after 4 days at 25°. In metal vessels a rapid initial decomposition to CF_4 and O_2 occurred (10% in 1 hr), then only slow decomposition after 24 hr indicating that storage of the peroxide in metal would require passivated vessels. Complete decomposition even in passivated vessels was accomplished at 95° over a 4-hr period, but no tendency toward explosive decompositions was observed.

D. CHLORO(TRIFLUOROMETHYL) PEROXIDE, CF_3OOCl

Fox and co-workers (*184*, *185*) were able to synthesize the first chloroperoxy compound in a low-temperature reaction utilizing the acidic character of CF_3OOH and the polar nature of ClF.

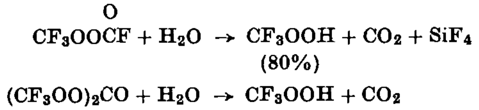
$$CF_3OOH + ClF \xrightarrow{-111^\circ} CF_3OOCl + HF$$

Chloro(trifluoromethyl) peroxide is a unique compound in that it contains not only the peroxide but also the hypochlorite function. A comparison of the chemistry of this compound with typical hypochlorite insertion reactions (*6*, *151*, *255*, *256*), e.g., SO_2 and CO, demonstrated that it is not analogous to the R_fOCl derivatives. Also, CF_3OOCl explosively initiated the polymerization of C_2F_4 and photolytically decomposed to give CF_3OOCF_3, ClO_2, and O_2. Both results can be explained by peroxide cleavage.

As in the case of CF_3OOH, this compound is stable at 25° and can be stored in glass or Kel-F vessels, although rapid decomposition occurs at 100° in glass yielding COF_2, SiF_4, CO_2, and $FClO_2$. Chloro(trifluoromethyl) peroxide melts to a pale yellow liquid at −132° and, from the vapor pressure curve of $\log P_{mm} = 7.742 - 1221/T$, a boiling point of −22° was determined. The Trouton constant is 22.2 eu.

E. HYDRO(PERFLUOROALKYL) PEROXIDES, CF_3OOH AND $(CF_3)_2C(OOH)OH$

The first member of this class of compounds, trifluoromethylhydroperoxide, was prepared by Talbott (*229*) by the hydrolysis of fluoroformyl(trifluoromethyl) peroxide or bis(trifluoromethylperoxy) carbonate. The synthetic utility of this preparation was limited owing to the relatively poor yield of the peroxyester precursors, but recent improved syntheses for $CF_3OO\overset{O}{C}F$ by DesMarteau (*61*) and Anderson and Fox (*2*) have enabled CF_3OOH to be prepared more readily.



$$CF_3OO\overset{O}{C}F + H_2O \rightarrow \underset{(80\%)}{CF_3OOH} + CO_2 + SiF_4$$

$$(CF_3OO)_2CO + H_2O \rightarrow CF_3OOH + CO_2$$

Due to the attack of HF on glass, the hydrolysis of the peroxyfluoroformate requires less than stoichiometric amounts of water, but when trace amounts of water were used, the bis(peroxy)carbonate was isolated rather than the hydroperoxide (*229*). Both liquid and vapor phase hydrolyses have resulted in the formation of CF_3OOH, but DesMarteau *et al.* (*28*) reported that in comparative reactions, the use of excess water and a liquid phase afforded better yields and more facile product separation.

The interaction of hydrogen peroxide and hexafluoroacetone was found to result in the formation of 2-hydroperoxyhexafluoropropan-2-ol, which is the only other hydro(perfluoroalkyl) peroxide now known (*52*, *182*).

$$(CF_3)_2CO + 90\%\ H_2O_2 \rightarrow (CF_3)_2C(OOH)OH$$

In contrast with CF_3OOH, at 25° $(CF_3)_2C(OOH)OH$ undergoes a slow decomposition to yield CF_3OOH as a major product and this decomposition has been reported as an alternative route to CF_3OOH (*183*).

$$(CF_3)_2C(OOH)OH \rightarrow \underset{\text{(major products)}}{CF_3OOH \quad + CO_2 + O_2}$$

Repeated fractionation of the mixture is required to obtain good yields of CF_3OOH. Attempts were made to accelerate the decomposition thermally, photolytically, and chemically without success.

The determination of the physical properties of $(CF_3)_2C(OOH)OH$ is hindered by its instability, but CF_3OOH is more completely characterized (*28*). Hydro(trifluoromethyl) peroxide is stable for months when stored in glass vessels at 25°, but it decomposes at 150° to COF_2, SiF_4, and O_2. In prefluorinated stainless steel vessels the decomposition to COF_2, O_2, and HF is evident at 25°. This decomposition is catalyzed by HF, whereas the presence of active metal fluorides results in the formation of O_2, CF_3O^- salts, and small amounts of CF_3OOOCF_3. The compound melts to a colorless liquid at −75° to −74° and boils at 11.5° with vapor pressure curves of $\log P_{\text{mm}} = 8.5568 - 1614.5/T$ (−25° to 11.5°) and

TABLE III

SPECTRAL PROPERTIES OF FC(O)OOC(O)F AND R_fOOX PEROXIDES

Peroxide	Infrared spectrum (cm^{-1})	Ref.	^{19}F NMR (ppm)[a]	Ref.	*J* Values (Hz)	Raman (cm^{-1})	Ref.
FC(O)OOC(O)F A	1934vs, 1905vs, 1899vs, 1221s, 954s, 912s, 749s	*10*	A 34.4	*90*	—	—	—
CF_3OOH A B	3580m, 1382m, 1268s, 1238vs, 1140w, 945m, 862w, 675m, 613w	*28*	A 72.3 B ^1H δ − 9.2	*28*	—	870	*181*
CF_3OOCl A	1275s, 1235s, 1207s, 891m, 813m	*184*	A 69.9	*184*	—	943	*181*
$(CF_3)_2C(OOH)OH$ A	3600m, 1250s, 1175s, 1060br, 970s, 735br	*181*	A 79.1	*181*	—	—	—
CF_3OOF A B	1300vs, 1270vs, 1190vs, 950s, 870w, br, 755s, 685w, 620m, 585m, 510m	*63*	A 68.9(d)[c] B −292(q)	*63*	$J_{AB} = 5.0$	883	—
CF_3CF_2OOF A B C	1387w, 1263m, 1244s, 1179m, 1074s, 752m	*231*	A 84.1(q) B 97.4(d, q) C −291.6(t, q)	*231*	$J_{AB} = J_{AC} = 1.8$ $J_{BC} = 15.6$	—	—

[a] Relative to $CFCl_3$.

[b] Peroxide stetching frequency.

[c] d, Doublet; t, triplet; q, quartet.

$\log P_{\mathrm{mm}} = 9.4176 - 7303.9/T - 1{,}106{,}340/T^2$ (−47° to −25°). A Trouton constant of 26.0 eu demonstrates considerable association in the liquid phase. Aqueous solutions of CF_3OOH are stable and oxidize iodide ion. Titration of an aqueous solution with base gives a pK_a value of approximately 6.4, which indicates that CF_3OOH is considerably more acidic than H_2O_2 ($pK_a = 11.85$). Neutralized solutions of CF_3OOH maintain their oxidizing potential indicating that the CF_3OO^- anion is stable in aqueous solution. Spectral data for the R_fOOX peroxides, in addition to FC(O)OOC(O)F, are summarized in Table III.

IX. Bis(perfluoroalkyl) Peroxides

A. PREPARATION AND PROPERTIES

The perfluoroalkyl peroxides represent the first and largest class of fluorinated peroxides known at this time. Bis(trifluoromethyl) peroxide was first synthesized by Swarts (*227*) in 1933 by the electrolysis of trifluoroacetate solutions. The low yield and lack of purity of the product formed by this method precludes its use as a synthetic route, but since then, other methods have been developed.

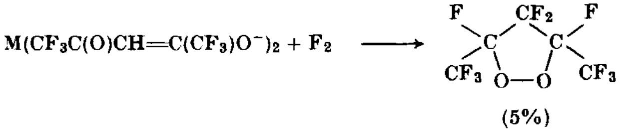
Historically, the first useful synthetic route to bis(perfluoroalkyl) peroxides was through various fluorination reactions. Porter and Cady (*173–176*) found that mixtures of CF_3OF and COF_2 heated to 290° in a nickel vessel resulted in the formation of CF_3OOCF_3. They were also able to prepare this compound by the fluorination (*173, 175, 176*) of CO and found that the reaction was facilitated by the presence of metal fluoride catalysts. Thus, in a reactor which contained silver fluorides coated on copper ribbon, the reaction proceeded at room temperature, although maximum yields were obtained at 180°. In the absence of any

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

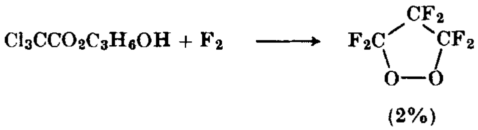
catalytic metal fluoride, the best yield was 20% at 300°–400°. A comparative study of catalytic fluorinations by Wechsberg and Cady (*250*) indicated that AgF_2 functions as a catalyst in the fluorination of COF_2 to CF_3OOCF_3 by fluorine, but that it does not function as a catalyst in the fluorination of COF_2 to CF_3OOCF_3 by CF_3OF. The authors therefore suggested the possibility of an intermediate of the type $Ag(OCF_3)_2$ formed by the fluorination of COF_2 by AgF_2. The subsequent fluorination of this intermediate could result in the release and coupling of the CF_3O groups.

The formation of CF_3OOCF_3 from the COF_2/CF_3OF system has been developed to produce relatively large amounts of this peroxide. Roberts (*190*) has successfully prepared in a high yield approximately 100 gm of CF_3OOCF_3 (93%) from a single reaction by using a nickel-lined autoclave and a temperature of 265°. In other peroxide preparations, the fluorination of metal oxalates at 85°–90° was found by Morrow (*162*) to give CF_3OOCF_3 as the major product. Bis(pentafluoroethyl) peroxide has been reported by Thompson (*232*) to be a component from the reaction of fluorine with salts of trifluoroacetic acid. The use of fluorinating agents other than fluorine has also been employed. Holzmann and Cohen (*126*) found CF_3OOCF_3 as one of the products from the reaction of O_2F_2 and C_2F_4. In another excellent large-scale synthesis, Ellingboe and McClelland (*79*) used ClF_3 and COF_2 with alkali metal fluorides or alkali metal hydrogen fluorides and a temperature of 250° to produce approximately 42 gm of bis(trifluoromethyl) peroxide in a 92% yield.

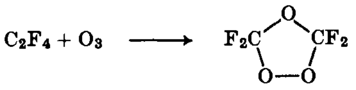
Fluorination reactions have also led to the isolation of some fluorinated cyclic peroxides in low yields. Talbott (*228*) prepared the cis and trans isomers of 3,4,4,5-tetrafluoro-3,5-bis(trifluoromethyl)-1,2-dioxolane by the fluorination of copper(II) or nickel(II) hexafluoroacetylacetonate.



At the completion of the reaction the cis/trans ratio was >2, but owing to the greater stability of the trans isomer, NMR characterization of both isomers was possible. The hexafluoro-1,2-dioxolane was prepared in low yield by Prager (*177*) by the fluorination of 1-hydroxy-3-trichloroacetoxypropane.



Another cyclic peroxide, tetrafluoro-1,2,4-trioxolane, was prepared by Gozzo and Camaggi (*112a*) from the reaction of ozone and C_2F_4.



Fluorinated alkyl peroxides have been prepared by the photolysis of fluorinated hypochlorites; e.g., Schack and Maya (*202a*) photolyzed trifluoromethyl hypochlorite to synthesize bis(trifluoromethyl) peroxide in high yield, but on a small scale.

$$CF_3OCl \xrightarrow[100\ W]{Pyrex} \underset{(90\%)}{CF_3OOCF_3}$$

However, an attempt to prepare bis(pentafluoroethyl) peroxide via the photolysis of C_2F_5OCl only resulted in the isolation of CF_3Cl and COF_2. Fox and co-workers were also able to prepare additional peroxides via the photolysis of hypochlorites (*182*). Thus, the photolysis of $CH_3C(CF_3)_2OCl$ at 25° and the photolysis of $(CF_3)_3COCl$ at low temperature resulted in the corresponding peroxides in good yield.

$$CH_3C(CF_3)_2OCl \xrightarrow[quartz]{550\ W} \underset{(90\%)}{CH_3C(CF_3)_2OOC(CF_3)_2CH_3}$$

$$(CF_3)_3COCl \xrightarrow[\substack{40\ W\\ quartz}]{-78^\circ} \underset{(30\%)}{(CF_3)_3COOC(CF_3)_3}$$

The reaction temperature and lamp power utilized were functions of the stability of the hypochlorite. Also, this reaction was determined not to be a general reaction for all hypochlorites. Although the substitution of a CH_3 group for a CF_3 group in the perfluoro-*t*-butyl case resulted in peroxide formation, the substitution of a hydrogen atom for a CF_3 group resulted in photolytic decomposition giving $(CF_3)_2CO$, CF_3Cl, and $COCl_2$. The extreme hydrolytic sensitivity of these fluorinated hypochlorites also led to the isolation of the corresponding fluorinated alcohols.

A third method for the synthesis of perfluoroalkyl peroxides which utilizes ClF_3 was developed by Fox *et al.* (*111*, *112*, *182*). The overall reaction involves the oxidation of fluorinated alcohols to peroxides in high yields.

$$\underset{R = CF_3,\ C_2F_5,\ CH_3}{RC(CF_3)_2OH + ClF_3} \longrightarrow \underset{(40\text{–}80\%)}{RC(CF_3)_2OOC(CF_3)_2R}$$

The completely fluorinated peroxides can be prepared at room temperature, but the partially fluorinated peroxide was prepared at −78° in lower yield. The reaction is believed to give initially the unstable corresponding bis(alkoxy)chlorine(III) fluoride which decomposes to give the peroxide by coupling of $RC(CF_3)_2O$ radicals and reduction of the trivalent chlorine to ClF.

$$R_fOH + ClF_3 \rightarrow [(R_fO)_2ClF] + HF$$
$$[(R_fO)_2ClF] \rightarrow R_fOOR_f + ClF$$

From low temperature ^{19}F NMR work the authors found some evidence which suggests the presence of the unstable bis(alkoxy)chlorine(III) fluoride, but were unable to isolate the intermediate. As might be expected, this reaction is limited not only by the necessity of having a stable fluorinated alcohol but also to a system reasonably free from competing oxidizable functions. In cases where the R group was CCl_3, CCl_2F, or $CClF_2$ explosions occurred unless the reaction was moderated, but in cases where the reaction was moderated, only decomposition products were isolated. Also, when hydrogen atoms were substituted for CF_3 groups, isolation of the corresponding peroxides was not possible. The reactions of ClF_3 with pentafluorophenol and inorganic OH functions was attempted, but no peroxide was isolated. In the case of $(CF_3)_2NOH$ only the stable $(CF_3)_2NO$ radical was found, while with FSO_2OH the acid anhydride, $S_2O_5F_2$, was isolated. With pentafluorophenol, mass spectral analysis indicated the formation of chlorofluorinated aromatics but no peroxide.

The preparation of bis(pentafluorophenyl) peroxide has been achieved by the reaction of xenon difluoride and pentafluorophenol (*164*). The

$$XeF_2 + C_6F_5OH \xrightarrow{MeCN} Xe + HF + C_6F_5OOC_6F_5$$

reaction undoubtedly involves the xenon(II) pentafluorophenolate which decomposes to give the peroxide and xenon. The use of XeF_2 to prepare additional peroxides has not been exploited and in comparing the reactions of C_6F_5OH with ClF_3 and XeF_2, the latter must be a milder oxidant which indicates further work on the oxidative synthesis of peroxides from XeF_2 would be lucrative.

The synthesis of peroxides utilizing xenon is not restricted to the above type of reaction. Cady and co-workers (*93*) found a convenient synthesis of CF_3OOCF_3 by the fluorination of xenon with trifluoro(fluoroxy)methane. As with the photolysis of hypochlorites, this would

$$CF_3OF + Xe \rightarrow XeF_2 + CF_3OOCF_3$$

not be expected to be a general reaction for fluoroxy compounds and decomposition would be anticipated with the higher members of the fluoroxy derivatives.

Although there are several compounds to represent the bis(fluoroalkyl) peroxide family, there are only a few compounds which are mixed fluoroalkyl peroxides, i.e., R_fOOR_f'. There are no general methods for synthesizing these compounds, as in the case of bis(fluoroalkyl) peroxides, and this has greatly curtailed their investigation. The attempted preparation of the mixed peroxides by the photolysis of a mixture of hypochlorites or by the reaction of a mixture of fluoro alcohols with ClF_3 or XeF_2 has not been reported, but, these methods would have to involve the fortuitous coupling of R_fO and $R_f'O$ radicals generated from photolysis of their hypochlorites or decomposition of the mixed alkoxy chlorine(III) fluoride or xenon alcoholate. Therefore, as a synthetic route to mixed fluoroalkyl peroxides, these methods probably would be characterized by low yields. Unfortunately, the mixed peroxides which have been isolated resulted from fluorination reactions which are also of low yield. Thompson (*232*) reported the first mixed fluoroalkyl peroxide, pentafluoroethyl(trifluoromethyl) peroxide, as a component from the fluorination of trifluoroacetate salts.

$$CF_3CO_2M + F_2 \rightarrow CF_3OOC_2F_5$$

As anticipated, several products result from the reaction and this peroxide is a minor component. Fox and co-workers (*182*) found that the reaction of OF_2 with perfluoro-*t*-butyl alcoholates also generated a mixed peroxide rather than the trioxide.

$$OF_2 + (CF_3)_3CONa \rightarrow \underset{(8\%)}{CF_3OOC(CF_3)_3}$$

The major products were the esters $[(CF_3)_3CO]_2CO$ (60%) and $CF_3CO_2C(CF_3)_3$ (30%). The use of the lithium salt gave a slightly better yield, but the reaction was marked by more frequent detonations heard within the Hoke bomb reactor. In a similar reaction Solomon (*207*) identified $CF_3OOC_2F_5$ from the reaction of OF_2 and C_2F_5OCs, but no yield was indicated. These two peroxides apparently are the only reported unsymmetrical fluoroalkyl peroxides.

The available physical properties for the fluoroalkyl peroxides are summarized in Table IV. In general, these peroxides are stable at room temperature, although both *cis*- and *trans*-3,5-bis(trifluoromethyl)-3,4,4,5-tetrafluoro-1,2-dioxolane are reported to decompose in Pyrex glass in 10 days and 12 weeks, respectively. The major product from this

TABLE IV

PHYSICAL PROPERTIES OF R_fOOR_f

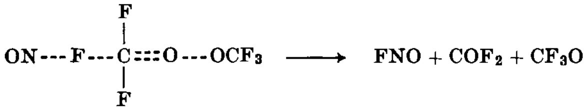
R	CF_3	$(CF_3)_3C$	$CH_3C(CF_3)_2$	$C_2F_5C(CF_3)_2$
Melting point (°C)	—	12	2	18
Boiling point (°C)	−37	98.6	109	148 (est.)
$\log P_{\mathrm{mm}}$	—	$8.178 - \frac{1969}{T}$	$8.571 - \frac{2174}{T}$	—
ΔH_{vap}(kcal/mole)	—	9.02	9.57	—

decomposition is $CF_3C(O)F$ with smaller amounts of $CF_3CO_2CF_2H$ and SiF_4. When water is not excluded, the decomposition rates were about the same. In comparison, hexafluoro-1,2-dioxolane is reported to be very stable during storage and was purified from $FOCF_2CF_2C(O)F$ by water washing. The half-lives of bis(perfluoro-*t*-butyl) peroxide and bis(2-methylhexafluoroisopropyl) peroxide were determined to be 7.9 (fluorobenzene) and 5.6 hr (toluene), respectively. The decomposition products consisted of C_2F_6 and $(CF_3)_2CO$ from the *t*-butyl peroxide, while the isopropyl peroxide resulted in C_2F_6 and the mixed ketone $CF_3C(O)CH_3$.

B. REACTIONS

Most of the reaction chemistry of these peroxides has been investigated through bis(trifluoromethyl) peroxide. Porter and Cady (*173*) found that CF_3OOCF_3 did not react readily with aqueous iodide and irradiation of the solution was needed to enhance the reaction rate. Synthetic reactions involving CF_3OOCF_3 have been studied to a small extent by other groups. Fox *et al.* (*91*) found the oxygen–oxygen bond to be relatively strong in comparing the reaction conditions needed in the CF_3OOCF_3/N_2F_4 reaction to prepare CF_3ONF_2. In this case, a reaction temperature of 130° was required for 10 days while $FC(O)ONF_2$ was prepared from $F(O)COOC(O)F$ at 25°. Roberts (*190*) found that the CF_3O group was transferred in the reaction of CF_3OOCF_3 with C_3F_6 to give ethers of the $CF_3O(C_3F_6)_nOCF_3$ type (where $n = 2$, 3, or 4). Some evidence, but no definitive proof, was presented for $CF_3OC_3F_6OCF_3$. Varetti and Aymonino (*241*) have utilized this peroxide to prepare $(CF_3O)_2CO$ from photolytic reactions with $CF_3C(O)F$ and also isolated $CF_3O_2CCO_2CF_3$ from the reaction (*242*) with CO. Also, Duncan and Cady (*74*) found that the peroxide oxidized SF_4 to bis(trifluoromethoxy)-tetrafluorosulfur(VI), $(CF_3O)_2SF_4$, in a 10% yield from the photolysis of equimolar amounts of CF_3OOCF_3 and SF_4.

Bis(trifluoromethyl) peroxide has been reported to function as a fumigant (*100*) and has also been used as a polymerization catalyst (*58*, *75*). Kinetic studies have been undertaken with regard to the CF_3OOCF_3/NO reaction (*121*, *123*). The data encompass a temperature range of 25°–177° and include a large span of the bimolecular rate constant with relatively good agreement between the studies. Hogue and Levy (*123*) postulate the following concerted mechanism involving the attack of the fluorine by NO and concomitant bond weakening throughout the molecule.



$$\mathrm{ON{-}{-}{-}F{-}{-}{-}\overset{F}{\underset{F}{C}}{:::}O{-}{-}{-}OCF_3 \longrightarrow FNO + COF_2 + CF_3O}$$

$$\mathrm{CF_3O + NO \longrightarrow FNO + COF_2}$$

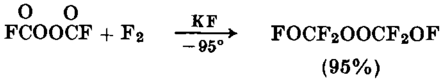
The arguments for this mechanism are based on the activation energy and reactivity of NO with nonfluorinated peroxides. A thermal decomposition study was reported (*132a*). The spectral data for the fluoroalkyl peroxides are found in Table V.

X. Fluoroxy-Containing Peroxides

MONO- AND BIS(FLUOROXYPERFLUOROALKYL) PEROXIDES

The fluoroxy-containing perfluoroalkyl peroxides represent a novel class of compounds in that they contain not only the peroxide function but also the OF group. Their preparation is rather straightforward and has been accomplished by typical fluoroxy-forming reactions. The patent literature (*178*, *230*, *235*, *236*) offers other methods of preparation, but the yields are not reported and mixtures obtained generally require gas chromatographic separations. The products can best be described as resulting from fragmentation–recombination reactions which preclude the controlled synthesis of individual members.

The use of alkali metal fluorides to catalyze the fluorination of perfluoroacyl fluorides has been shown to yield fluoroxyperfluoroalkanes in essentially quantitative yield (*198*). Lustig and Ruff (*149*) extended this method to include a peroxyperfluoroacyl derivative, FC(O)OOC(O)F, and isolated bis(difluorofluoroxymethyl) peroxide. The alkali metal

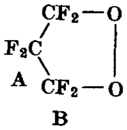
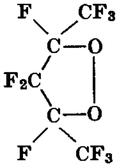
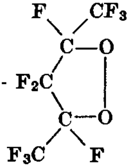


$$\mathrm{F\overset{O}{C}OO\overset{O}{C}F + F_2 \xrightarrow[-95^\circ]{KF} \underset{(95\%)}{FOCF_2OOCF_2OF}}$$

TABLE V

SPECTRAL PROPERTIES OF FLUOROALKYL PEROXIDES

Peroxide	Infrared spectra (cm^{-1})	Ref.	^{19}F NMR (ppm)^a	Ref.	J Value (Hz)	Raman (cm^{-1})^b	Ref.
$(CF_3O)_2$ A	1287vs, 1265vs, 1240vs, 1191sh, 1166vs, 1125s, 1065m, 975w, 890m, 713m, 673w, 627s, 610sh, 558w, 490m, 445sh	*76*	A 69.0	*232*	—	886	*181*
$(CF_3)_3COOCF_3$ A B	1300vs, 1270s, 1250s, 1217s, 1120s, 1020s, 985s, 732s	*181*	A 69.8(q)^c B 68.7(dec)	*181*	$J_{AB} = 1.12$	—	—
$[(CF_3)_3CO]_2$ A	1290s, 1235w, 1110s, 1008s, 988s, 775w, 740w,sh, 733s	*181*	A 70.0	*181*	—	781	*181*
$[CF_3CF_2C(CF_3)_2O]_2$ A B C	1345m, 1295vs, 1270vs, 1255vs, 1235s, 1200m, 1100s, 1090m, 990m, 980m, 930m, 905s, 770m, 745s, 733m	*181*	A 80.2(hept) B 115.4(hept) C 67.1(mult)	*181*	$J_{AC} = 8.3$ $J_{BC} = 12$	—	—
$[CH_3C(CF_3)_2O]_2$ A B	1460m, 1398m, 1300s, 1234vs, 1217vs, 1162m, 1134s, 1086s, 955m, 930m, 875m, 760m, 705s	*181*	A ^{1}H δ1.0 B 74.6	*181*	—	774	*181*
$CF_3OOCF_2CF_3$ A B C	1379w, 1292s, 1247s, 1209m, 1171s, 1085s	*233a*	A 68.7(t) B 95.7 C 83.2(t)	*232*	$J_{AB} = 4.3$ $J_{BC} = 1.5$	—	—

	1393w, 1340s, 1239s, 1140s, 1085s, 1028w, 980m, 711m	*177*	A 125.0(p) B 96.6(t)	*177*	$J_{AB} = 3.3$	—	—
cis- 	—	—	A 110 } 126 } AB spectrum B 128.5 C 75.7	*228*	—	—	—
trans- 	—	—	A 114 B 135 C 76.7	*228*	—	—	—

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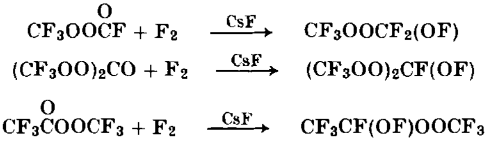
[a] Relative to $CFCl_3$.

[b] Peroxide stretching frequency.

[c] t, Triplet; q, quartet; p, pentet; hept, heptet; dec, dectet; mult, multiplet.

fluoride-catalyzed fluorination of perfluoroacyl peroxides offers the best method for preparing fluoroxy-containing peroxides and has also been employed by Talbott (*229*) and DesMarteau and co-workers (*28*) to prepare additional members of this family. In each case, the yields are reasonably high and the isolation of the desired product is straightforward.



$$\mathrm{CF_3OO\overset{O}{C}F + F_2 \xrightarrow{CsF} CF_3OOCF_2(OF)}$$
$$\mathrm{(CF_3OO)_2CO + F_2 \xrightarrow{CsF} (CF_3OO)_2CF(OF)}$$
$$\mathrm{CF_3\overset{O}{C}OOCF_3 + F_2 \xrightarrow{CsF} CF_3CF(OF)OOCF_3}$$

Although the preparative methods in the patent literature are not recommended as general synthetic routes for these compounds, several fluoroxy-containing peroxides have been prepared only by these methods. The fluorination of sodium trifluoroacetate (*236*) resulted in the isolation of each of the other members of this class. In addition, the more readily prepared CF_3OOCF_2OF and $CF_3OOCF(OF)CF_3$ and the fluoroxyperfluoroalkanes, C_2F_5OF, $CF_3CF(OF)_2$ and $CF_2(OF)_2$, were isolated also.

$$\mathrm{CF_3CO_2Na + F_2/N_2 \rightarrow C_2F_5OOCF_2OF + C_2F_5OOCF(OF)CF_3 + FOCF_2OOCF(OF)CF_3 + CF_3CF(OF)OOCF(OF)CF_3}$$

Based on previous work, if the corresponding perfluoroacyl derivatives ($\mathrm{C_2F_5OO\overset{O}{C}F}$, $\mathrm{C_2F_5OO\overset{O}{C}CF_3}$ and $\mathrm{F\overset{O}{C}OO\overset{O}{C}CF_3}$) are synthesized, the metal fluoride-catalyzed fluorination of these compounds would provide a much more direct route to these less accessable fluoroxy-containing peroxides.

The characterization of these compounds has not been done. They have been reported to be essentially unchanged after storage at room temperature for several months. Although Lustig and Ruff reported explosions while working with $FOCF_2OOCF_2OF$, Talbott found that CF_3OOCF_2OF was stable for 1.3 hr at 195° in stainless steel cylinders and was unaffected by large excesses of fluorine after 1 hr at 150°. The infrared and ^{19}F NMR spectra for these peroxides are found in Table VI.

XI. Perfluoroacyl-Containing Peroxides

A. PEROXYTRIFLUOROACETIC ACID

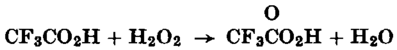
Fluorinated peroxides containing the carbonyl function can be divided into three groups: peroxyperfluoroacyl acids, bis(perfluoroacyl)

TABLE VI: Spectral Properties of Fluoroxy-Containing Peroxides

Peroxide	Infrared spectrum (cm^{-1})	Ref.	^{19}F NMR (ppm)[a]	Ref.	J Values (Hz)
$(FOCF_2O)_2$ A B	1258vs, 1193vs, 1143vs, 939m, 869w	*149*	A −158.6(t)[b] B 80.9(d)	*149*	$J_{AB} = 36$
CF_3OOCF_2OF A B C	1285s, 1255s, 1217sh, 1200m, 1153s, 937vw	*229*	A 69.0(d, t) B 80.6(d, q) C −156.7(t, unres)	*229*	$J_{AB} = 3.4$ $J_{BC} = 35.1$ $J_{AC} = 1.4$
$(CF_3OO)_2CF(OF)$ A B C	1297vs, 1271vs, 1250vs, 1163s, 1130vs, 942w,br	*229*	A 68.7 B 90.6 C −168	*229*	$J_{AB} = 3.5$ $J_{BC} = 25$ $J_{AC} < 3$
$CF_3OOCF(OF)CF_3$ A B C D	1345m, 1295s, 1240s, 1190s, 1085s, 1020w, 930w, 895w, 743m, 690w, 613w, 570w, 540w	*28*	A 69.0(d, d) B 110(d, q) C −139(d, d, q) D 78.8(d)	*28*	$J_{AB} = 5.3$ $J_{BC} = 37.0$ $J_{AC} = 1.7$ $J_{CD} = 12.5$
$CF_3CF(OF)OOCF_2OF$ A B C D E	—		A 78 B 110 C −148 D 80 E −157	*236*	
$[CF_3CF(OF)O]_2$ A B C	—		A 78 B 110 C −149	*236*	
$CF_3CF_2OOCF_2OF$ A B C D	—		A 83 B 95 C 80 D −157	*236*	
$CF_3CF_2OOCF(OF)CF_3$ A B C D E	—		A 83 B 95 C 110 D −148 E 78	*236*	

[a] Relative to $CFCl_3$. [b] d, Doublet; t, triplet; q, quartet; unres, unresolved.

peroxides, and peroxy esters. The peroxyperfluoroacyl acids are limited primarily to peroxytrifluoroacetic acid and will therefore only be considered briefly. The method of preparation which is identical to that of other peroxyacyl acids involves the use of 90% H_2O_2 and excess trifluoroacetic acid or anhydride (*81*).



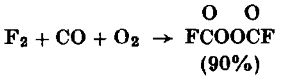
$$CF_3CO_2H + H_2O_2 \rightarrow CF_3\overset{O}{C}O_2H + H_2O$$

The peroxy acid is prepared *in situ* and its synthesis has paved the way for greatly facilitated organic syntheses which traditionally utilize hydrogen peroxide or other unfluorinated peroxy acids. The chemistry of $CF_3C(O)O_2H$ can be divided into two phases: the initial work utilizing only the acid and syntheses involving the use of the $CF_3C(O)O_2H \cdot BF_3$ adduct. The utilization of the BF_3 adduct was pioneered by Hart who has reviewed this work (*116*, *117*).

The reaction of $CF_3C(O)O_2H$ with some nitrogen derivatives was shown to be a facile method of preparing nitro compounds. Thus, aniline (*82*, *83*), nitroso (*30*, *81*, *83*), and oxime (*86*) derivatives were conveniently oxidized under mild conditions and in high yield to the nitro function. The formation of nitrobenzene derivatives was somewhat hampered by electron-withdrawing substituents on the ring which facilitated the formation of phenols and subsequent oxidation products. The hydroxylation of aromatic ethers (*153*) and other benzene derivatives (*53*, *152*) was studied and may lead to the formation of quinones owing to additional oxidation. Peroxytrifluoroacetic acid has also been used in the Baeyer–Villiger oxidation of ketones to lactones (*201*) and esters (*84*), and has been suggested as a method of determining aliphatic ketones and aldehydes (*120*). Last, the epoxidation of alkenes (*85*) in a buffered solution occurs readily and in good yield.

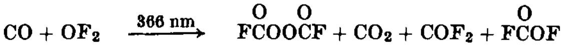
B. BIS(PERFLUOROACYL) PEROXIDES, $R_fC(O)OOC(O)R_f$

The simplest member is bis(fluoroformyl) peroxide which has been prepared by Schumacher *et al.* (*13*, *14*) by the direct fluorination of carbon monoxide in the presence of oxygen. This preparation affords the



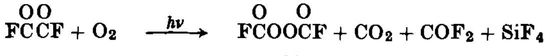
$$F_2 + CO + O_2 \rightarrow \underset{(90\%)}{F\overset{O}{C}OO\overset{O}{C}F}$$

highest reported yield and also enables a facile isolation of the product. Schumacher and co-workers (*129*) found that the low-energy photolytic reaction between carbon monoxide and oxygen difluoride resulted in the formation of the peroxide. Although these preparations are direct, they



$$CO + OF_2 \xrightarrow{366\ nm} F\overset{O}{C}OO\overset{O}{C}F + CO_2 + COF_2 + F\overset{O}{C}OF$$

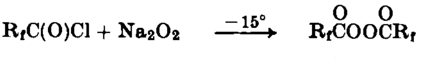
are hampered by the use of mixtures of fluorine and carbon monoxide which has resulted in explosions (*229*) and by the lack of availability of oxygen difluoride. Bis(fluoroformyl) peroxide has also been prepared in lower yields by Czerepinski and Cady (*56*) from the photolysis of oxalyl fluoride and oxygen.



$$F\overset{O}{C}\overset{O}{C}F + O_2 \xrightarrow{h\nu} \underset{(46\%)}{F\overset{O}{C}OO\overset{O}{C}F} + CO_2 + COF_2 + SiF_4$$

This method utilizes readily available starting materials and does not involve the potential hazards of the previous methods. The authors also suggest that because of the photolytic decomposition of the peroxide, higher yields may be accomplished by reducing the photolysis time and recycling the starting materials.

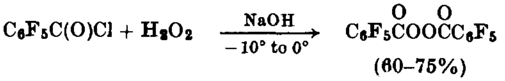
The higher members of the bis(perfluoroacyl) peroxide family appear primarily in the patent literature (*33, 69, 159, 187, 257, 258*). Their preparation is analogous to that of the nonfluorinated compounds and involves the reaction of the corresponding perfluoroacyl chloride or bromide with an aliali metal or alkaline earth peroxide. The reactions



$$R_fC(O)Cl + Na_2O_2 \xrightarrow{-15^\circ} \underset{(80\%)}{R_f\overset{O}{C}OO\overset{O}{C}R_f}$$

are carried out in a heterogeneous solvent system with an aqueous metal peroxide solution and water-insoluble (e.g., ether, Freon) solution of the perfluoroacyl halide. As in the case of peroxytrifluoroacetic acid, the peroxides are normally prepared prior to their use and reacted in dilute solution or stored below room temperature owing to their shock sensitivity.

Bis(pentafluorobenzoyl) peroxide was reported by Kobrina and Yakobson (*140*) and Tatlow and co-workers (*34*). Both methods of preparation were essentially the same and do not differ significantly from the method of preparing other bis(perfluoroacyl) peroxides. Unlike the



$$C_6F_5C(O)Cl + H_2O_2 \xrightarrow[-10^\circ\ to\ 0^\circ]{NaOH} \underset{(60\text{–}75\%)}{C_6F_5\overset{O}{C}OO\overset{O}{C}C_6F_5}$$

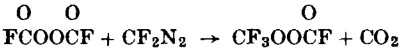
aliphatic members of this series, bis(pentafluorobenzoyl) peroxide was not reported as being shock-sensitive and melting points were recorded as 76°–78° (40–60 petroleum ether) and 72° ($CHCl_3/MeOH$).

Synthetic reactions utilizing bis(perfluoroacyl) peroxides have been limited to $F(O)COOC(O)F$ and $C_6F_5(O)COOC(O)C_6F_5$. Cauble and Cady (*50*), in addition to forming CF_3OOCF_3, $F\overset{O}{C}OOCF_3$, and CF_3OOOCF_3 from the photolytic reaction of fluorine and the former peroxide, also isolated $FC(O)OF$. Fox and co-workers (*91*) prepared $FC(O)ONF_2$ from $FC(O)OOC(O)F$ and N_2F_4 in a rapid reaction at 25° which indicates a reasonably weak O–O bond. Fox and Franz (*90*) obtained $FC(O)OSO_2F$ via photolysis with SO_2 and estimated the electronegativity of the $FC(O)$ group to be between that of CF_3O and OF. Schumacher and co-workers (*12*) found that $F(O)COOC(O)F$ formed NO_2, CO_2, and COF_2 with NO, whereas with NO_2, FNO_2 and CO_2 result. The kinetics of the polymerization of C_2F_4 by $F(O)COOC(O)F$ have been studied by Schumacher *et al.* (*11*), who concluded that a maximum activation energy of 31 ± 3 kcal/mole was required to decompose the peroxide. A reversible reaction of $F(O)COOC(O)F$ with KF led to the formation of a new cyclic peroxide, $\overline{OCF_2OOC}{=}O$ (*172a*).

The reactions of bis(pentafluorobenzoyl) peroxide have been limited to fluorinated and unfluorinated benzene derivatives and naphthalene (*34*, *140*). The products, which are in low yield because of tar formation, consist primarily of the corresponding biphenyls and pentafluorobenzoate esters. Other fluoroacyl peroxides have been used as polymerization initiators (*31*, *32*, *38*, *68*, *69*, *132*, *258*, *259*).

C. TRIFLUOROMETHYL PEROXY ESTERS, $R_fC(O)OOCF_3$

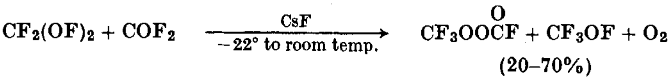
The fluorinated peroxy esters characterized to date are limited to derivatives of the trifluoromethylperoxo group. Cauble and Cady (*50*, *51*) reported trifluoromethyl peroxyfluoroformate, the first member of this class of compounds, as a low yield by-product in the photolysis of bis(fluoroformyl) peroxide and fluorine. Talbott (*229*) prepared $CF_3OO\overset{O}{C}F$ in higher yields by the photolysis of bis(fluoroformyl) peroxide and difluorodiazirine. When a low-energy photolysis was carried out by



$$F\overset{O}{C}OO\overset{O}{C}F + CF_2N_2 \rightarrow \underset{\text{(major products)}}{\underset{(18\%)}{CF_3OO\overset{O}{C}F}} + CO_2$$

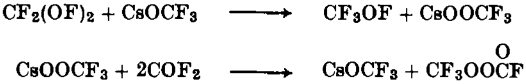
using borosilicate glass rather than quartz, the $\mathrm{CF_2N_2}$ was consumed but nearly quantitative recovery of $\mathrm{F\overset{O}{C}OO\overset{O}{C}F}$ resulted.

More recent preparative methods (*2, 61*) have substantially facilitated the preparation of $\mathrm{CF_3OO\overset{O}{C}F}$. The methods are essentially the same and involve the reaction of $\mathrm{CF_2(OF)_2}$ with $\mathrm{COF_2}$ in the presence of CsF.



$$\mathrm{CF_2(OF)_2 + COF_2 \xrightarrow[-22^\circ\ \text{to room temp.}]{CsF} \underset{(20\text{–}70\%)}{CF_3OO\overset{O}{C}F} + CF_3OF + O_2}$$

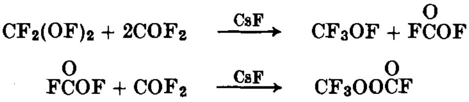
Although the reaction can be carried out by the direct combination of the reactants, significantly higher yields were reported when the $\mathrm{CsOCF_3}$ salt was present in addition to uncomplexed $\mathrm{COF_2}$ and when a lower reaction temperature was used. In reactions run at 25°, a marked time dependence was found with maximum yields of $\mathrm{CF_3OO\overset{O}{C}F}$ occurring within 3 hr. By isolating the product after a 1.5-hr reaction time and recycling the starting materials, the yield was increased to ~40% as compared to a 20% yield after a 3-hr reaction period. The major product reported by both groups was $\mathrm{CF_3OF}$ which suggested that the first step in the reaction is the fluorination of $\mathrm{CsOCF_3}$ by $\mathrm{CF_2(OF)_2}$. The formation of $\mathrm{CF_3OO\overset{O}{C}F}$ in the reaction was rationalized via the formation of $\mathrm{CsOOCF_3}$ (*61, 62*) or $\mathrm{F\overset{O}{C}F}$ (*2*).



$$\mathrm{CF_2(OF)_2 + CsOCF_3 \longrightarrow CF_3OF + CsOOCF_3}$$

$$\mathrm{CsOOCF_3 + 2COF_2 \longrightarrow CsOCF_3 + CF_3OO\overset{O}{C}F}$$

or



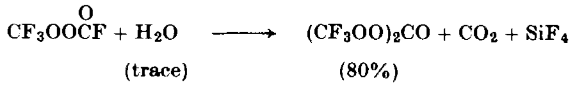
$$\mathrm{CF_2(OF)_2 + 2COF_2 \xrightarrow{CsF} CF_3OF + F\overset{O}{C}OF}$$

$$\mathrm{F\overset{O}{C}OF + COF_2 \xrightarrow{CsF} CF_3OO\overset{O}{C}F}$$

As the authors have stated, these are rather idealized reaction pathways and either can be supported based on the empirical evidence from which it is derived.

Bis(trifluoromethylperoxy) carbonate, $\mathrm{(CF_3OO)_2CO}$, was reported by Talbott (*229*) as a vapor phase hydrolysis product of $\mathrm{CF_3OO\overset{O}{C}F}$. When

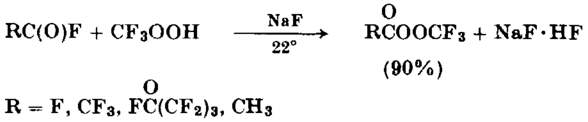
$CF_3OO\overset{O}{C}F$ was hydrolyzed using only trace amounts of water, the hydroperoxide, CF_3OOH, was not isolated; instead, $(CF_3OO)_2CO$ was formed.



$$CF_3OO\overset{O}{C}F + \underset{(trace)}{H_2O} \longrightarrow \underset{(80\%)}{(CF_3OO)_2CO} + CO_2 + SiF_4$$

This reaction as well as the hydrolysis to produce CF_3OOH involves attack on the glass vessel to provide additional water.

The improved synthesis of $CF_3OO\overset{O}{C}F$ has resulted in a practical method for preparing CF_3OOH and thereby offers a more general route to trifluoromethyl peroxy esters. DesMarteau and co-workers (*28*) have synthesized a series of these esters in high yield by the reaction of acyl fluorides and the hydroperoxide. In the case of difunctional acid fluorides, the relative amounts of reactants were adjusted to give the monoperoxy esters or the bis(peroxy) esters. Although the reaction appeared general, there were cases in which the desired peroxy esters were not isolated.



$$RC(O)F + CF_3OOH \xrightarrow[22^\circ]{NaF} \underset{(90\%)}{R\overset{O}{C}OOCF_3} + NaF\cdot HF$$

$$R = F, CF_3, F\overset{O}{C}(CF_2)_3, CH_3$$

When C(O)FCl, $F\overset{O}{C}\overset{O}{C}F$, $F\overset{O}{C}OO\overset{O}{C}F$, or $CF_3O\overset{O}{C}F$ were reacted, the only peroxy ester isolated was $CF_3OO\overset{O}{C}F$, in addition to COF_2, CO_2 and Cl_2, or O_2. The recurrence of $CF_3OO\overset{O}{C}F$ may, at first glance, indicate a common reactive intermediate in each of these reactions. But, the stability of each of these reactants in the presence of NaF should eliminate the initial decomposition of the starting material to give COF_2 which could readily form the isolated peroxide. The authors suggest the possible formation and subsequent decomposition of the peroxy ester to give $CF_3OO\overset{O}{C}F$, but from the varied peroxy esters that would result, their decomposition to solely $CF_3OO\overset{O}{C}F$ would seem fortuitous.

These peroxy esters appear to be stable at room temperature in glass vessels, but explosions occurred with $CF_3OO\overset{O}{C}(CF_2)_3\overset{O}{C}F$ when warmed to 70° and with $CH_3\overset{O}{C}OOCF_3$ when warmed rapidly from −196° to 25°. Talbott reported (*229*) $F\overset{O}{C}OOCF_3$ and $(CF_3OO)_2CO$ to be extremely hydrolytically unstable and DesMarteau and co-workers have also found that the substituted trifluoromethyl peroxy esters quantitatively hydrolyze with equimolar amounts of water to CF_3OOH and the corresponding acid within 24 hr. The most hydrolytically stable peroxy ester was found to be $CH_3\overset{O}{C}O_2CF_3$ which, after 5 weeks, was only 90% hydrolyzed. The physical constants and vapor pressure data for these peroxy esters are tabulated below in Table VII (*28*, *61*).

TABLE VII

PHYSICAL PROPERTIES OF TRIFLUOROMETHYL PEROXY ESTERS

Compound	Melting point (°C)	Boiling point (°C)	$\log P_{mm}$	ΔH_{vap} (kcal/mole)
$F\overset{O}{C}OOCF_3$	—	−14.2	$8.112 - 1353.0/T$	6.19
$(CF_3OO)_2CO$	−85.8	41	$8.2045 - 1672.4/T$	7.34
$CF_3\overset{O}{C}OOCF_3$	*a*	8.9	$8.5664 - 1603.4/T$	7.34
$CH_3\overset{O}{C}OOCF_3$	−83.0	64.2	$7.9163 - 1698.8/T$	7.77
$CF_3OO\overset{O}{C}(CF_2)_3\overset{O}{C}F$	*a*	100.2	$9.0086 - 2287.7/T$	10.5
$(CF_3OO\overset{O}{C}CF_2)_2CF_2$	−77	116.2	$9.2322 - 2472.7/T$	11.3

[a] Glasses.

The spectral properties for the peroxy esters are tabulated in Table VIII.

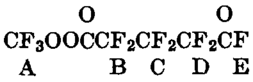
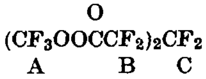
XII. Polyoxides

A. BIS (PERFLUOROALKYL) TRIOXIDES, R_fOOOR_f'

On the basis of thermodynamic calculations, Benson (*26*) predicted that nonfluorinated alkyl trioxides would have a sufficient half-life, with regard to disproportionation into radicals, to be isolable below 25°.

TABLE VIII

SPECTRAL PROPERTIES OF TRIFLUOROMETHYL PEROXY ESTERS

Peroxide	Infrared spectrum (cm^{-1})	Ref.	^{19}F NMR (ppm)[a]	Ref.	J Value (Hz)
$CF_3OOC(O)F$ A B	1917vs, 1300vs, 1247 vs,1172vs, 1007m, 932m, 753m, 691m, 615m	*51*	A 70.7(d) B 33.4(q)	*61*	$J_{AB} = 2$
$(CF_3OO)_2CO$ A	1896s, 1431w, 1296vs, 1242vs, 1222vs, 1162w, 1135w, 1115vs, 1014w, 939w, 735m, 607w	*28*	A 69.6	—	—
$CF_3OOC(O)CF_3$ A B	1859vs, 1298vs, 1244vs, 1212vs, 1110sh, 1068vs, 939m, 890w, 847w, 741s, 680w, 568w, 520w, 447w	*28*	A 74.0 B 77.2	*28*	—
$CF_3OOC(O)CH_3$ A B	1850s, 1424w, 1366w, 1288s, 1224vs, 1158s, 1114s, 1066w, 1007w, 997w, 985w, 940w, 832m, 738w, 662w, 608w, 559w, 580w, 567w	*28*	A 65.6 B ^1H δ − 2.3	*28*	—
 $CF_3OO\overset{O}{C}CF_2CF_2CF_2\overset{O}{C}F$ A B C D E	1882s, 1854s, 1295vs, 1203vs, 1132s, 1099s, 1014m, 809w, 760w, 732w, 703w, 679w, 645w, 585w	*28*	A 68.6 B 116(t, d) C 123(d) D 117.5(d, t) E −23.3	*28*	$J_{BE} = 2$ $J_{BD} = 10$ $J_{CE} = J_{DE} = 7$
 $(CF_3OO\overset{O}{C}CF_2)_2CF_2$ A B C	1896s, 1431w, 1296vs, 1242vs, 1162w, 1135w, 1115vs, 1014w, 939w, 735m, 607w	*28*	A 68.6 B 116.0 C 122.5	*28*	—

[a] Relative to $CFCl_3$.

Although two such trioxides have been identified at low temperatures by Bartlett and Günther (*25*), these compounds decompose well below room temperature. In comparison, the perfluoroalkyl trioxides have been isolated and found to be stable at and above 25°.

The first reported preparation of a perfluoroalkyl trioxide was by Ginsburg *et al.* (*109*) by the photolysis of hexafluoroazomethane and oxygen. Characterization of this compound was limited and no supporting spectral data were presented, although the elemental analysis agreed reasonably well with this formulation. More definitive syntheses of this compound by Thompson (*232, 234*) and Anderson and Fox (*1, 4, 5*) appeared simultaneously. Thompson's fluorination of various metal trifluoroacetates resulted not only in this trioxide, but also gave higher perfluoroalkyl trioxides. Although this method provides one of the few routes to $C_2F_5OOOR_f$ derivatives, the low yield precludes it as a useful method for preparing CF_3OOOCF_3.

$$\begin{array}{lcccc} CF_3CO_2M + F_2/N_2 \rightarrow & CF_3OOOCF_3 & + CF_3OOOC_2F_5 & + C_2F_5OOOC_2F_5 \\ & (1\text{–}5\%) & (<1\%) & (\text{trace}) \end{array}$$

The reaction of OF_2 and COF_2 is a superior method for preparing CF_3OOOCF_3. The yield in this reaction is dependent on the prior use of the CsF. With previously unused CsF and a reaction time of 16 hr the yields were ~10%, but after using the CsF twice and extending the reaction time to 4 days, the yield approaches 90%. 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.

$$\begin{array}{cc} OF_2 + COF_2 \xrightarrow{CsF} & CF_3OOOCF_3 \\ & (10\text{–}85\%) \end{array}$$

$$OF_2 + CsOCF_3 \rightarrow CF_3OOF + CsF$$
$$CF_3OOF + CsOCF_3 \rightarrow CF_3OOOCF_3 + CsF$$

or

$$CF_3OOF + COF_2 \rightarrow CF_3OOOCF_3$$

This mechanism was confirmed by Solomon *et al.* (*214*) by using ^{17}O-labeled COF_2 and OF_2.

$$COF_2 + {}^{17}OF_2 \xrightarrow{CsF} CF_3O^{17}OOCF_3$$
$$C^{17}OF_2 + OF_2 \xrightarrow{CsF} CF_3{}^{17}OO^{17}OCF_3$$

The location of ^{17}O was determined by ^{17}O NMR and the two environments determined by peak areas as obtained from a sample of $CF_3{}^{17}O^{17}O{}^{17}OCF_3$ prepared from $C^{17}OF_2$ and $^{17}OF_2$. In addition, the intermediate CF_3OOF was isolated by using a large excess of OF_2 to prevent the formation of the trioxide.

In extending this reaction to $CsOC_2F_5$, Solomon (*207*) was unable to isolate the fluoroperoxide, but, instead, isolated $CF_3OOOC_2F_5$ and $C_2F_5OOOC_2F_5$. The yields were not reported. The few products isolated from this reaction makes it a much more attractive method for preparing the $C_2F_5OOOR_f$ derivatives than by the fluorination of trifluoroacetate salts.

Recent work with respect to the reactions of $CF_2(OF)_2$ by Anderson and Fox (*2, 3*) and DesMarteau (*61*) has led to another method of preparing CF_3OOOCF_3. The reactions are similar in that they involve $CF_2(OF)_2$ and $CsOCF_3$ and differ only in that DesMarteau preforms the $CsOCF_3$ and utilizes a lower reaction temperature and shorter reaction time. Because of the necessity of preparing $CF_2(OF)_2$ and the lower yield (<20%), this method does not offer any advantages over the method utilizing OF_2.

Other methods which lead to CF_3OOOCF_3 include the reaction of CF_3OOSO_2F and CF_3OF (*197*)

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

and a photolytic method (*243*)

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

This preparative method provides a good alternative synthesis for CF_3OOOCF_3 when OF_2 is not available. Some reaction chemistry of CF_3OOOCF_3 has been reported (*6a*).

B. TRIFLUOROMETHYL(TRIFLUOROMETHYLPEROXODIFLUOROMETHYL) TRIOXIDE, $CF_3OOCF_2OOOCF_3$

Higher perfluoroalkyl members of this family of compounds have received little attention and have been reported only by Thompson and Solomon as described above. An interesting derivative of bis(trifluoromethyl) trioxide from the reaction of $CF_2(OF)_2$ and $CsOCF_3$ was a novel

TABLE IX

SPECTRAL PROPERTIES OF PERFLUOROAKLYL TRIOXIDES

Trioxide	Infrared spectrum (cm^{-1})	Ref.	^{19}F NMR (ppm)[a]	Ref.	J Values (Hz)
CF_3OOOCF_3 A	2600–3400w, complex, 2123vw, 1290s, 1252s, 1169s, 1067vw, 997vw, 929vw, 897m, 773w,sh, 699w	*4*, *122*, *253a*	A 72.4 (−80°) A 68.7	*4* *232*	—
$CF_3OOOCF_2CF_3$ A B C	1381w, 1292s, 1245vs, 1208s, 1178s, 1082s, 916w, 749m	*233a*	A 68.7 B 96.4(q) C 83.8(t)	*232*	$J_{BC} = 1.5$
$(CF_3CF_2O)_2O$ A B	—	—	A 83.0 B 95.0	*232*	—
$CF_3OOOCF_2OOCF_3$ A B C	1285s, 1250vs, 1215m, 1180s, 1125vs, 960w, 920w, 885m, 763s, 715w, 690w, 640w, 610m, 580m, 550w	*61*	A 69.5 B 79.2(q) C 69.8(t)	*61*	$J_{BC} = 4.0$

[a] Relative to $CFCl_3$.

peroxide trioxide, $CF_3OOOCF_2OOCF_3$ (*61*). The isolation of this compound may be explained by the reaction of $CF_2(OF)_2$ with $CsOCF_3$,

$$CF_3OCs + CF_2(OF)_2 \rightarrow CF_3OOCF_2OF + CsF$$

followed by reaction with the postulated intermediate, $CsOOCF_3$.

$$CF_3OOCF_2OF + CsOOCF_3 \rightarrow CF_3OOOCF_2OOCF_3 + CsF$$

The perfluoroalkyl trioxides, unlike the unfluorinated derivatives, are stable at 25° when stored in glass or metal containers. CF_3OOOCF_3 undergoes a slow decomposition to CF_3OOCF_3 and O_2 at 70° (*1*). The decomposition of this trioxide was followed via ^{19}F NMR at room temperature and the half-life determined to be 65 weeks (*233*). The bond dissociation energy, $D(CF_3O{-}OOCF_3)$, was calculated from these data to be 29–30 kcal/mole, which is in reasonable agreement with the predicted value of 20 ± 6 kcal/mole (*26*) for alkyl trioxides. Although there are no thermal stability data for $CF_3OOOC_2F_5$ and $C_2F_5OOOC_2F_5$, they would be expected to be similar to CF_3OOOCF_3. The thermal stability of $CF_3OOCF_2OOOCF_3$ is considerably less than that of the perfluoroalkyl trioxides and the compound undergoes explosive decomposition at 40° to CF_3OOCF_3, COF_2, and O_2.

Physical constants determined for CF_3OOOCF_3 include a melting point of −138° and a boiling point of −16° with a vapor pressure curve of $\log P_{mm} = 7.705 - 1241/T$ and Trouton constant of 22.1 eu. In comparison, the vapor pressure curve for $CF_3OOOCF_2OOCF_3$ of $\log P_{mm} = 7.141 - 1440/T$ gave an extrapolated boiling point of 65° and a Trouton constant of 21.5 eu. The physical constants for the other perfluoroalkyl trioxides have not been determined. The infrared and ^{19}F NMR data for these trioxides are found in Table IX.

The synthesis of bis(trifluoromethyl) tetraoxide was suggested [*233b*], but definitive proof is lacking. It may have resulted in very low yield from the fluorination of trifluoroacetate salts. However, the only evidence offered for the presence of the tetraoxide is a single NMR resonance at $\phi 69$ in an impure sample. Therefore, the existence of perfluoroalkyl tetraoxides remains to be confirmed.

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