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PREPARATIONS AND REACTIONS OF INORGANIC MAIN-GROUP OXIDE FLUORIDES

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I. Introduction

The aim of this article is to summarize the preparations and chemical properties of the presently known oxide fluorides of the main-group elements. We have not included physical properties except to mention those which are novel or of special interest, particularly structural properties.

In general, the replacement of fluorine atoms with oxygen atoms tends to stabilize higher oxidation states. For example, ClO_3F, ClO_2F_3, XeO_3F_2, and XeO_2F_4 exhibit the oxidation states Cl(VII) and Xe(VIII), whereas the highest oxidation state binary fluorides yield only Cl(V) in ClF_5 and Xe(VI) in XeF_6. Although the trend is, therefore, toward increased stabilization, some of the compounds covered in this article

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are exceedingly dangerous. Many are powerful oxidative fluorinating agents and *all* of the xenon compounds should be treated as potential sources of the extremely explosive XeO_3 (*1*). *Anyone planning to work with any of these materials should survey the literature carefully, should consult the chapter "Safety Precautions in Handling Noble-Gas Compounds"* (*2*), *and, preferably, should also talk with researchers who are already experienced in the field.*

II. The Oxide Fluorides of the Main-Group Elements

A. THE OXIDE FLUORIDES OF BORON, ALUMINIUM, GALLIUM, INDIUM, AND THALLIUM

The preparations, structures, and chemical reactions of the oxide fluoride Group IIIB elements were reviewed by Siegel in 1968 (*3*).

Oxide fluorides of the general formula MOF have been reported for all the Group IIIB elements. The boron compound, BOF [together with its trimer $(BOF)_3$], was observed in 1962 (*4*) among the equilibrium products of the reaction between $BF_3(g)$ and $B_2O_3(s, l)$ at high temperatures and low pressures, but no further reports of this compound seem to have appeared since. The aluminium analog, AlOF, can be prepared by treating AlOBr with BrF_3 (*5*), by heating hydrated $Al(OH)F_2$ to 475–630°C (*6*), and by the reaction of Al_2O_3 with gaseous AlF_3 (*7*). The thermal decompositions of $[AlO]^+[BF_4]^-$ (at >85°C) and $[AlO]^+[SbF_6]^-$ (at >270°C) also yield AlOF (*8*), and it has been synthesized recently in an argon matrix by cocondensation of AlF with oxygen atoms (*9*). Cryometric studies on the dissolution of Al_2O_3 in cryolite have been interpreted as indicating the presence of the dimer $Al_2O_2F_2$ (*10*). The gallium compound can be prepared as a white solid when GaOI reacts with fluorine at 20°C (*11*), by reaction of MnF_2 and Ga_2O_3 at 800°C (*12*), and by the argon matrix isolation reaction of GaF with oxygen atoms (*13*). Indium oxide fluoride can be prepared by several methods (*3, 14, 15*), the best being the sealed-tube reaction of In_2O_3 with IF_3 at 900°C (*15*). Reaction of thallium hydroxide with 40% HF gives a green solid which was first observed and identified as TlOF by Gewecke in 1909 (*16a*). This characterization was only quite recently confirmed by Grannec *et al.* (*16b*), who prepared the compound from Tl_2O_3 and 40% HF at room temperature or gaseous HF at 100°C, and by Sleight and co-workers (*16c*), thus dismissing the suggestion that Gewecke's compound might be $Tl(OH)_2F$ (*3*).

The single crystal structures of InOF and TlOF have been studied during the last 10 years. The indium compound possesses an orthorhombic unit cell in which the indium is six coordinated in a distorted octahedral manner by an ordered arrangement of oxygen and fluorine atoms. The $In(OF)_6$ octahedra are joined via edges and corners, giving a loose, three-dimensional network (*17*). TlOF crystallizes in a cubic space group and the structure is related to that of fluorite, but with the thallium atoms in a distorted eightfold coordination (*18*).

These oxide fluorides are unreactive and have virtually no chemistry.

Other oxyfluorides of the Group III metals include Al_2OF_4, prepared by reaction of AlOBr with BrF_3 (*4*), $Al_4O_5F_2$ prepared from AlOCl and AgF, and Tl_2OF_2 which is prepared by the high-pressure reaction of oxygen with TlF at 500°C (*19*). Tl_2OF_2 is formed as a white crystalline solid and has been shown to contain both univalent and trivalent thallium (*19*). Mass spectroscopic studies on the AlF_3–Al–Al_2O_3 system at 1453–1675 K and on the reaction of BF_3 with B_2O_3 at 930–1300 K have revealed the existence of $AlOF_2$ and B_2OF_4, respectively (*20, 21*).

Among the complexes detected by ^{19}F NMR in aqueous mixtures of boric acid and ammonium bifluoride are the ions $[B_2OF_6]^{2}$ and $[BOF_3]^{2}$ (*22*). Cryoscopic measurements on the NaF-rich side of the system NaF–AlF_3–Na_2O–Al_2O_3 suggest that the chief aluminium–oxygen-containing species is an $[Al_2OF_n]^{4\ n}$ complex which contains an Al–O–Al unit (*23*)

B. THE OXIDE FLUORIDES OF SILICON, GERMANIUM, TIN, AND LEAD

Although well characterized, the oxide fluorides of the Group IVB elements, like those of Group III, possess very little chemistry. The simplest known oxide fluoride of silicon is $SiOF_2$ which was revealed, by mass spectroscopy (*24*), to be present on the surface of silicon which had been etched by an HNO_3–HF mixture. It was prepared in 1969 by Langer (*25*) by the high-temperature reaction of silica with CaF_2 in an argon atmosphere and has more recently been produced in an argon matrix by reaction of SiO with fluorine and characterized as a planar molecule on the basis of its infrared spectrum (*26*). The remaining silicon oxide fluorides form a series of fluorosiloxanes, the best known of which is hexafluorodisiloxane, Si_2OF_6, a gas which was first synthesized in 1945 (*27*). It has since been prepared by reaction of SiF_4 with various compounds, such as metal oxides at 400–600°C (*28*), water (*29*), and $MgSO_4 \cdot 7H_2O$ (*30*), and was also found to be present during the preparation of $SiOF_2$ (*25*). More recent work (*31*) has shown that, with HgO, $(SiF_3)_2O$ and oligomeric fluorosiloxanes and, with H_2O,

$(SiF_3)_2O$ and fluorosiloxane polymers are obtained. Reaction of Si_2F_6 with both NO and N_2O_4 also gives $(SiF_3)_2O$ together with a variety of disproportionation products (*32*), while the reaction of SiF_2 with thionyl fluoride gives $(SiF_3)_2O$ together with a selection of other fluorosiloxanes, $SiF_3(SiF_2)_nOSiF_3$(n = 1, 2), $SiF_3OSiF_2OSiF_3$, and $(SiOF_2)_n$ (n = 2, 3) (*33*). The gas phase reaction of OF_3COF with difluorosilylene yields $(F_3SiOSiF_2)O$ (*34*).

Germanium and lead form the compounds Ge_2OF_2 and Pb_2OF_2. The existence of Ge_2OF_2 was demonstrated by mass spectroscopic studies of the vapors above a mixture of GeO_2, Ge, and NaF (*35*). Similarly, Pb_2OF_2 was reported during the solvolysis of Al_2O_3 in a PbF_2–LiF melt at 900°C, and its structure is suggested as $PbO \cdot PbF_2$ (*36*).

The only known tin oxide fluoride, $SnOF_2$, was prepared by Dehnicke in 1965 (*37*) from $SnCl_4$, ClF, and $ClONO_2$, and is believed to be polymeric in nature, containing six-coordinate tin.

C. THE OXIDE FLUORIDES OF NITROGEN

The simplest oxide fluorides of nitrogen, nitrosyl fluoride (NOF) and nitryl fluoride (NO_2F), were first prepared in 1905 and 1932, respectively, yet their chemistry was not studied in detail until the early 1960s when they were recognized as potential rocket propellants. The oxide fluorides of nitrogen were reviewed in 1965 and 1968 by Woolf (*38*) and Schmutzler (*39*), respectively, and their physical and chemical properties were also summarized by Kuznetsova (*40*).

1. *Nitrosyl Fluoride*

Nitrosyl fluoride, NOF, is a colorless gas and is usually prepared by direct fluorination of nitric oxide (*41*). It was first prepared by fluorination of NOCl by AgF (*42*) and has since been prepared by many methods (*39*). These include the reaction of readily available nitrosyl salts, such as $[NO]^+[BF_4]^-$ and $[NO]^+[SbF_6]^-$, with alkali metal fluorides at temperatures of 200–300°C, and the fluorination of NO by XeF_2 and XeF_4 (*43*). Until 1968, the time of the last review, the reactions of NOF could be placed into three categories. First, NOF is a strong oxidizing agent, reacting with a large number of elements, both metallic and nonmetallic, to give the respective fluoride and nitric oxide. It is also a useful gas-phase fluorinating agent, not only for carbon tetrachloride and dichloromethane in the production of chlorofluoromethanes, but similarly with compounds such as SO_2 which reacts at high temperature to give SO_2F_2 (*39*). Nitrosyl fluoride also reacts with a wide range of Lewis acid fluorides (*39, 44–51, 53–58*) to produce salts, e.g., with SbF_5 it produces $[NO]^+[SbF_6]^-$ (*48*) and with WF_6 it gives $[NO]^+[WF_7]^-$ and $[NO]_2^+[WF_8]^{2-}$ (*50, 51*). These reactions with acceptor fluorides are summarized in Table I. The reactions of NOF with transition metal hexafluorides were reviewed by Canterford, Colton, and O'Donnell in 1967 (*52*).

Over the last 15 years many new reactions of nitrosyl fluoride with a variety of fluorides and oxide fluorides have been studied but no new types of reaction have been observed. The recent work is discussed below.

On reaction with xenon hexafluoride (*53*) NOF forms the adduct $2NOF \cdot XeF_6$. Infrared and Raman measurements suggested the ionic formulation $[NO]_2^+[XeF_8]^{2-}$ for the solid, and later structural work (*54*) provided definitive evidence for this. Reaction with xenon oxide tetrafluoride yields a 1 : 1 adduct as a white solid (*53*). Nitrosyl fluoride reacts with technetium hexafluoride to give the salt $[NO]_2^+[TcF_8]^{2-}$ with no evidence for $[TcF_7]^-$ (*49*), and with uranium hexafluoride NOF gives $[NO]^+[UF_7]^-$ and $[NO]^+[UF_8]^{2-}$ (*45*). With ReF_7, $[NO]^+[ReF_8]^-$ is produced for which the Raman spectrum of the solid and the NMR spectrum of solutions of the salt in anhydrous HF suggest that the $[ReF_8]^-$ ion has D_{4d} symmetry (*55*). The unstable adduct $NOF \cdot IF_7$ is formed on reaction with IF_7 (*56*) and vibrational spectra of the solid suggest the presence of $[IF_8]^-$ (*57*). Reaction with AuF_5 (*58*), produced by pyrolysis of $[KrF]^+[AuF_6]^-$, yields $[NO]^+[AuF_6]^-$.

The oxide fluoride $ReOF_5$ reacts with NOF to give $[NO]^+[ReOF_6]^-$ (*55*) and with MOF_4 (M = Mo and W) it forms the salts $[NO]^+[M_2O_2F_9]^-$, $[NO]_2^+[MOF_6]^{2-}$, and $[NO]^+[MOF_5]^-$ (*46*), whereas POF_3 reacts in a 1 : 1 stoichiometry to give a white powder which contains $[PF_6]^-$ as the only fluorine species, no $[POF_4]^-$ being formed (*59*). With an excess of nitrosyl fluoride CrO_2F_2 reacts to give $[NO][CrO_2F_3]$, a complex containing polymeric fluorine-bridged anions (*47*).

In 1975 Sunder and Griffiths *et al.* studied a variety of nitrosyl salts with the anions $[MF_6]^-$, $[MF_6]^{2-}$, $[MF_6]^{3-}$, $[MF_7]^-$, and $[MF_8]^{2-}$ (M = Cr, Mo, W, Re, Rh, Ru, Os, Ir, Pd, Pt, and Au) resulting from the reaction of the appropriate metal (M) or metal fluoride with NOF and gaseous fluorine, or the metal fluoride, nitrosyl, or nitryl hexafluorometallate with NOF or NO_2F (*60a, 60b*).

Further reports on the fluorinating ability of nitrosyl fluoride include the conversion of FN_3 to NF_3 (*61*) and the fluorination of SCl_2 to give SF_4, SF_5Cl, and SF_6 (*62*).

Finally, in 1977 Christe reported the preparation of ClO_2F_3 by reaction of $[ClO_2F_2]^+[PtF_6]^-$ with NOF (*63*).

TABLE I

THE REACTIONS OF NOF AND $\mathrm{NO_2F}$ WITH FLUORIDE ION ACCEPTORS (*39*)

Fluoride ion acceptor	NOF product	$\mathrm{NO_2F}$ product
$\mathrm{BF_3}$	$\mathrm{NO[BF_4]}$	$\mathrm{NO_2[BF_4]}$
$\mathrm{C_6H_5PF_4}$	$\mathrm{NO[C_6H_5PF_5]}$	
$\mathrm{PF_5}$		$\mathrm{NO_2[PF_6]}$
$\mathrm{S_2O_5F_2}$	$\mathrm{[NO]_2[S_2O_5F_4]}$	
ClF	$\mathrm{NO[ClF_2]}$	
$\mathrm{ClF_3}$	$\mathrm{NO[ClF_4]}$	No reaction
$\mathrm{VF_5}$	$\mathrm{NO[VF_6]}$	$\mathrm{NO_2[VF_6]}$
$\mathrm{CrF_5}$		$\mathrm{NO_2[CrF_6]}^{p}$
$\mathrm{CrO_2F_2}$	$\mathrm{NO[CrO_2F_3]}^{d}$	$\mathrm{NO_2[CrO_2F_3]}^{d}$
$\mathrm{GeF_4}$	$\mathrm{[NO]_2[GeF_6]}$	$\mathrm{[NO_2]_2[GeF_6]}$
$\mathrm{AsF_3}$	$\mathrm{NO[AsF_6]}$	
$\mathrm{AsF_5}$		$\mathrm{NO_2[AsF_6]}^{q}$
$\mathrm{BrF_3}$	$\mathrm{NO[BrF_4]}$	$\mathrm{NO_2[BrF_4]}$
$\mathrm{BrF_5}$	No reaction^{a}	No reaction
$\mathrm{MoF_5}$	$\mathrm{NO[MoF_6]}$	
$\mathrm{MoF_6}$	$\mathrm{NO[MoF_7] + NOF \cdot MoF_6}^{h}$	$\mathrm{NO_2[MoF_7] + NO_2F \cdot MoF_6}^{h}$
$\mathrm{MoOF_4}$	$\mathrm{NO[MoOF_5]}$, $\mathrm{NO[Mo_2O_2F_9]}$, $\mathrm{[NO]_2[MoOF_6]}^{c}$	
$\mathrm{TcF_6}$	$\mathrm{[NO]_2[TcF_8]}^{f}$	$\mathrm{NO_2[TcF_7]}^{f}$
$\mathrm{SbF_5}$	$\mathrm{NO[SbF_6]}^{e}$	$\mathrm{NO_2[SbF_6]}$
$\mathrm{IF_5}$	$\mathrm{NO[IF_6]}^{a}$	$\mathrm{NO_2[IF_6]}$
$\mathrm{IF_7}$	$\mathrm{NO[IF_8]}^{l,m}$	$\mathrm{NO_2[IF_8]}^{m}$
$\mathrm{XeF_6}$	$\mathrm{[NO]_2[XeF_8]}^{i,j}$	$\mathrm{NO_2F \cdot XeF_6}^{g}$
$\mathrm{XeOF_4}$	$\mathrm{NOF \cdot XeOF_4}^{i}$	
$\mathrm{WF_6}$	$\mathrm{NO[WF_7]}$, $\mathrm{[NO]_2[WF_8]}^{g,h}$	$\mathrm{NO_2[WF_7]}$, $\mathrm{NO_2F \cdot WF_6}^{g,h}$
$\mathrm{WOF_4}$	$\mathrm{NO[WOF_5]}$, $\mathrm{NO[W_2O_2F_9]}$, $\mathrm{[NO]_2[WOF_6]}^{c}$	
$\mathrm{ReF_6}$	$\mathrm{[NO]_2[ReF_8]}^{g}$	
$\mathrm{ReF_7}$	$\mathrm{NO[ReF_8]}^{k}$	$\mathrm{NO_2[ReF_8]}^{k}$
$\mathrm{ReOF_5}$	$\mathrm{NO[ReF_6]}^{k}$	$\mathrm{NO_2[ReOF_6]}^{k}$
$\mathrm{OsF_6}$	$\mathrm{NO[OsF_6]}$, $\mathrm{[NO]_2[OsF_8]}$, $\mathrm{NO[OsF_7]}$	
$\mathrm{PtF_6}$	$\mathrm{NO[PtF_6]}$, $\mathrm{[NO]_2[PtF_6]}$	
$\mathrm{AuF_5}$	$\mathrm{NO[AuF_6]}^{n}$, $\mathrm{[NO]_2[AuF_6]}^{o}$	
$\mathrm{UF_5}$	$\mathrm{NO[UF_6]}$	$\mathrm{NO_2[UF_6]}$
$\mathrm{UF_6}$	$\mathrm{NO[UF_7]}$, $\mathrm{[NO]_2[UF_8]}^{b,h}$	$\mathrm{NO_2[UF_7]}$, $\mathrm{NO_2F \cdot UF_6}^{h}$

[a] Ref. (*44*); [b] Ref. (*45*); [c] Ref. (*46*); [d] Ref. (*47*); [e] Ref. (*48*); [f] Ref. (*49*); [g] Ref. (*50*); [h] Ref. (*51*); [i] Ref. (*53*); [j] Ref. (*54*); [k] Ref. (*55*); [l] Ref. (*56*); [m] Ref. (*57*); [n] Ref. (*58*); [o] Ref. (*60a*); [p] Ref. (*70*); [q] Ref. (*71*).

2. *Nitryl Fluoride*

Nitryl fluoride, $\mathrm{NO_2F}$, although reported by Moissan in 1905 (*64–66*), was first characterized by Ruff *et al.* in 1929 (*41, 67*) who prepared the compound by direct fluorination of $\mathrm{NO_2}$. Many preparations of

NO_2F have been reported (*39*) and not all will be dealt with here. However, most methods are closely related to the preparations of NOF; for example, the heating of nitryl salts such as $[NO_2]^+[PF_6]^-$ with an alkali fluoride. Like NOF, NO_2F is a colorless reactive gas which may act both as a fluorinating and an oxidizing agent, and in some cases as a complexing agent also. As with NOF, NO_2F reacts with metals giving either a mixture of oxide and fluoride or an oxide fluoride. For example, zinc reacts to give ZnO and ZnF_2, whereas reaction with chromium gives CrO_2F_2 (*39*). Nitryl fluoride also frequently acts as a fluoride ion donor and, for example, combines with SO_3 to give $NO_2(SO_3F)$ (*39*). Table I shows the reactions of NO_2F with Lewis acid fluorides in which many $[NO_2]^+$ salts are formed. Not surprisingly, both ^{14}N and ^{15}N-NMR measurements on solutions of NO_2F in HF have confirmed that $[NO_2]^+$ ions are produced and that NO_2F is completely dissociated. Further evidence for the ionization of NO_2F has been obtained from conductivity measurements (*68*). The NO_2F–HF phase diagram has also been reported with the melting point ranging between -28 and -96°C for four solvates, $NO_2F \cdot n HF$ (n = 3.50–6.66) (*69*).

Recent work has produced a number of new compounds. Like NOF, NO_2F reacts with IF_7 and $[NO_2]^+[IF_8]^-$ is given (*57*). With chromium pentafluoride $[NO_2]^+[CrF_6]^-$ is formed (*70*), with CrO_2F_2 it gives $[NO_2]^+[CrO_2F_3]^-$ (*47*), and with $ReOF_5$ it yields $[NO_2]^+[ReOF_6]^-$ in which the anion has been shown to have C_{5v} symmetry (*55*). With TcF_6 the salt, $[NO_2]^+[TcF_7]^-$, is formed (*49*) and with ReF_7, $[NO_2]^+[ReF_8]^-$ is the product (*55*). Finally, reaction of XeF_6 with a sixfold excess of NO_2F produces $NO_2F \cdot XeF_6$ which, from its vibrational spectrum (*71*), appears to be fluorine bridged and, thus, perhaps, should not be formulated as a salt, $[NO_2]^+[XeF_7]^-$.

Analysis of the Raman spectra of a variety of hexafluorometallate salts derived from reaction of NO_2F with metal fluorides, nitrosyl, and nitryl hexafluorometallates, indicates that the $[NO_2]^+$ cation in the solids formed is linear (*60b*).

3. *Other Nitrogen Oxide Fluorides*

The third nitrogen oxide fluoride to be reported was the colorless gas trifluoroamine oxide, F_3NO. It was prepared by a number of independent research groups, and by several different methods in 1966–1967 (*39*). Most preparations involve oxidative fluorination of NO or NOF, but F_3NO can also be prepared by passing an electrical discharge through a mixture of nitrogen trifluoride and oxygen, at -196°C (*72, 73*), or by the reaction of F_2 and N_2O in a glow discharge (*74*). Small amounts can be made by passing a microwave discharge through a low-pressure mixture of O_2, N_2, and F_2 at −196°C and yields are higher with a capacitor-pulsed discharge between electrodes in a low-pressure cell (*75*). It can also be prepared in about 15% yield by an alternative discharge method using an equimolar mixture of NF_3 and O_2 in a liquid nitrogen-cooled discharge tube (*76*). The most useful preparation is by the fluorination of nitrosyl fluoride using iridium hexafluoride as reported by Bartlett *et al.* in 1966 (*77*). Compared with NOF and NO_2F, F_3NO is chemically inert and is stable toward metals at room temperature. Its photolytic decomposition to FNO and, eventually, to NO has been monitored by infrared spectroscopy in a matrix (*78*). The limited reported chemistry of F_3NO mainly involves reactions with Lewis acid fluorides (*39, 72*) to form stable 1 : 1 adducts such as $F_3NO \cdot BF_3$, $F_3NO \cdot AsF_5$, and $F_3NO \cdot SbF_5$, and the 1:2 adduct $F_3NO \cdot 2BF_3$. As might be expected, these compounds are ionic and contain the cation $[F_2NO]^+$ (*39*).

Fluorinated hydroxylamine, which has the same empirical formula as trifluoroamine oxide, nitrosyl hypofluorite, ONOF, and fluorine nitrate are not true oxide fluorides and, therefore, are not included here.

D. THE OXIDE FLUORIDES OF PHOSPHORUS

The simplest oxide fluoride of phosphorus is phosphoryl fluoride, POF_3, which exists as a colorless gas (bp −39.7°C). It is generally prepared by fluorination of phosphoryl chloride with metallic fluorides (*79*) such as lead, zinc, silver, or sodium fluoride, but can also be prepared directly by reaction of MgF_2 and $Mg_2P_2O_7$ above 750°C (*80*) and, together with $P_2O_3F_4$, from the reaction of PF_5, O_2, and Mg at 300°C (*81*). It is also reported to be the initial volatile product of the reaction of PF_3 with ZnO (*82*).

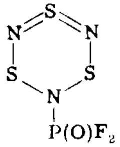
The effect of very high pressure on reaction rates is rarely studied but reactions of PF_3 with SO_2 have been shown to be strongly influenced by application of pressure. Thus, whereas reaction with SO_2 at 150°C produces elemental sulfur and POF_3 in only 5% yield at 670 atm, an 84% yield is obtained when the pressure is increased to 4000 atm (*83*). Under similar high-pressure conditions POF_3 is also obtained when PF_3 is treated with O_2 (*84*) or CO_2 (*85*).

In 1967 POF_3 was reported to react with cesium fluoride to give $Cs^+[PO_2F_2]^-$ and $Cs^+[PF_6]^-$ (*86*). More recent work by Selig and Aminadav (*59*) has shown that reaction with alkali metal and nitrosyl fluorides in a 1 : 1 ratio yields $[PF_6]^-$ as the only fluorine-containing species. Primary and secondary negative-ion formation observed in the mass spectra of POF_3–SF_6 mixtures, however, has shown that the principal ion–molecule reaction involves $[POF_4]^-$ (*87*).

Phosphoryl fluoride reacts as a base and, with BF_3, AsF_5, and SbF_5, oxygen-bridged 1:1 adducts are produced (*88*, *89*). In liquid sulfur dioxide POF_3 is weakly basic and it was in such a medium that the first transition-metal complex of this oxide fluoride, $[Mn(OPF_3)_4]^{2+}[AsF_6]_2$, was produced in 1979 via the intermediate $[Mn(SO_2)_x]^{2+}[AsF_6]_2$ (*90*).

With tris(trimethylsilyl)amine POF_3 reacts to replace one trimethylsilyl group to give *N*-(difluorophosphoryl)silylamine, $OPF_2N(SiMe_3)_2$ (*91*). Phosphoryl fluoride also undergoes oxygen exchange with vanadium pentafluoride (*92*) to give VOF_3 and PF_5.

More complex oxide fluorides of phosphorus have been reported which involve the P—O—P linkage. Pyrophosphoryl fluoride, F_2OPO POF_2, which is a liquid of boiling point 71°C, is prepared by dehydration of $HOP(O)F_2$ using P_2O_5 (*93*, *94*) or by the treatment of $HOP(O)F_2$ with BBr_5 (*95*). It also appears with POF_3 when PF_5, O_2, and Mg are heated at 300°C (*81*). The few reported reactions of $P_2O_3F_4$ involve cleavage of the P—O—P bond. For example, it reacts with $SiCl_4$ to give the white crystalline solid $Si(PO_2F_2)_4$ (*96*) and with CrO_3 to give the unstable $CrO_2(PO_2F_2)_2$, which, with an excess of oxide fluoride, yields $Cr(PO_2F_2)_3$ (*97*). Similarly, reaction with K_2CrO_4, $NaMoO_4$, and $NaWO_4$ produces $K_2CrO_2(PO_2F_2)_4$, $NaMoO_2(PO_2F_2)_4$, and $NaWO_2(PO_2F_2)_4$, respectively (*97*). Similar P—O—P bond cleavage occurs in the reaction of $P_2O_3F_4$ with *N*,*N′*-bis(trimethylsilyl)sulfur diimide, which yields 1 (*98*), with the acyl halides, $R_fC(O)X$, which give the carboxylic anhydride, $R_fC(O)OPOF_2$ (*99*), and with CF_3OOH which gives CF_3OOPOF_2 (*100*). Reaction with xenon difluoride yields FXe $OPOF_2$ and $Xe(OPOF_2)_2$ (*101*). Its reaction with $POF_2N(SiMe_3)_2$ is more unusual; here a trimethylsilyl group is replaced by a POF_2 group to give the bis(difluorophosphoryl) derivative $(POF_2)_2N(SiMe_3)$ (*91*).



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Other oxide fluorides include the highly volatile F_2POPF_2, which was reported in 1966 as the product of the reaction between Cu_2O and PF_2I (*102*), and $F_2POP(O)F_2$, prepared in 40% yield by photolysis of $P(O)F_2Br$ in the presence of mercury at 23°C (*103*). Both compounds are of structural interest, the latter because it contains both P(III) and P(V) and the former because its structure, particularly with respect to the degree of $p\pi{-}d\pi$ bonding involved, has been a source of disagreement between electron diffraction specialists. One interpretation is that it is a rigid structure of C_1 symmetry (*104*) while another favors it existing as a number of possible staggered conformers (*105*).

The remaining compounds form three series of polymers, $P_nO_{2n-1}F_{n+2}$ ($n = 1$–13), which may be regarded as the linear polymer $[PO_2F]_n$, $P_nO_{2n}F_{n+2}$ ($n = 2$–11) and $P_nO_{2n+1}F_{n+2}$ ($n = 2$–10) (*106*).

E. THE OXIDE FLUORIDES OF ARSENIC, ANTIMONY, AND BISMUTH

There are very few reported oxide fluorides of these elements. A solid removed from the sealed tube reaction of As_2O_3 with AsF_5 at 320°C analyzed as AsOF (*107*) but this compound was never fully characterized and its existence is still in doubt. The only recognized oxide fluoride of arsenic is $AsOF_3$ (bp 26°C), prepared by fluorination of an equimolar mixture of $AsCl_3$ and As_2O_3, and by thermal decomposition of $AsF_3(NO_3)_2$ (*108*). The reaction of Sb_2O_3 with SbF_5 in a 1:1 ratio at 150–450°C produced three forms of crystalline SbOF, whose structures have been determined by X-ray crystallography (*109–111*). The oxide fluorides $SbOF_3$ and SbO_2F are white, hygroscopic, nonvolatile solids prepared by the thermal decomposition of $SbF_3(NO_3)_2$ and $SbF(NO_3)_4$, respectively (*108*).

The sealed tube reaction of Bi_2O_3 with BiF_3 at 670°C produces BiOF together with three phases having the composition Bi_xF_{3-2x} ($x = 0$–0.15, 0.41–0.62, and 0.62–0.74) and a δ-phase with $x = 1.1$–1.20 (*112*). Single crystals of BiOF have been studied by infrared spectroscopy (*113*).

Layers of the $(Bi_6O_7F)^{3+}$ cation have been observed in the structure of $Bi_6O_7FCl_3$ (*114*).

Several oxide fluoride anions of arsenic and antimony(V) are of interest because of their structural relationships to other simple oxide fluorides and to their isoelectronic analogs, $[M_2F_{11}]^-$. The anions $[As_2F_{10}O]^{2-}$, point group C_s (*115–117*), and $[Sb_2F_{10}O]^{2-}$, point group C_2 or C_1 (*115, 118*), contain single As—O—As and Sb—O—Sb bridges with bond angles of 137 and 135°, respectively. The related $[As_2F_8O_2]^{2-}$ ion is a centrosymmetric dimeric anion containing an As_2O_2 ring with approximately D_{2h} (exactly C_1) symmetry (*115, 119*), while $[Sb_3F_{12}O_3]^{3-}$ is a trimeric species containing a six-membered Sb_3O_3 ring (*115, 118*).

F. THE OXIDE FLUORIDES OF SULFUR

Thionyl fluoride, SOF_2, and sulfuryl fluoride, SO_2F_2, are well-known oxide fluorides of sulfur and have been reported in the literature for many years. The third simple oxide fluoride of sulfur, SOF_4, was reported as early as 1902 but was then forgotten until rediscovered in 1948. There also exists a large number of complex sulfur oxide fluorides generally involving —O— and —O—O— bridging between sulfur atoms, with —S—S— linkages extremely rare.

There have been several reviews of sulfur oxide fluorides, by Williamson in 1966 (*120*), Ruff in 1966 (*121*), Macalso in 1969 (*122*), and Cady in 1960 (*123*) and 1971 (*124*).

1. *Thionyl Fluoride*

SOF_2 is a colorless gas (bp −44°C). It was first prepared by the reaction of $SOCl_2$ with ZnF_2. Subsequently many other preparative methods have been used but the reaction of $SOCl_2$ with SbF_3 in SbF_5, or with NaF in CH_3CN have proved to be the best. A more recent preparation of SOF_2 is by the reaction of elemental sulfur with a Cl_2–HF mixture (*125*).

The chemistry of SOF_2 was reviewed in 1970 by Davis *et al.* (*126*). Fluorination of SOF_2 using ClF (*127*) or O_2F_2 (*128*) yields SOF_4. Thionyl fluoride is a weak Lewis base, using its lone pair on oxygen for donation. Reaction with SbF_5 has been shown, by ^{19}F-NMR spectroscopy, to yield a 1 : 1 adduct (*129*). Later Raman studies on this system and on the SOF_2–AsF_5 system have revealed that these adducts are weakly oxygen bridged (*88*). As reported earlier SiF_2 reacts with SOF_2 at low temperature (*33*) to produce a series of fluorosiloxanes. A recent ^{19}F-NMR study of the CH_3F–SbF_5–SOF_2 system has revealed the salt $[CH_3SOF_2]^+[Sb_2F_{11}]^-$, and although the corresponding AsF_5 system has produced the corresponding arsenic salt the reaction does not go to completion and $CH_3F \cdot AsF_5$ is also obtained (*130*). Thionyl fluoride has been shown to react with $[Cl_2F]^+[AsF_6]^-$ at −78°C to give $[OSClF_2]^+[AsF_6]^-$ in 85% yield. The other reaction products are SOF_4, SO_2F_2, Cl_2, and $[SOF_3]^+[AsF_6]^-$, which can be accounted for by the competing reaction of SOF_2 with liberated ClF to give sulfur oxide tetrafluoride and chlorine. Similar products are also produced when thionyl fluoride reacts with ClF and AsF_5 (*131*). The X-ray crystal structure of $[OSClF_2]^+[AsF_6]^-$ has been obtained (*132*) and a mechanism for the reactions has been suggested (*131*).

2. *Sulfuryl Fluoride*

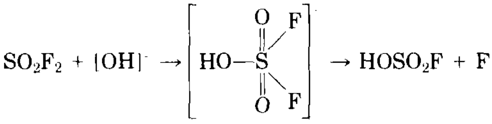
Like SOF_2, SO_2F_2 is a colorless gas (bp −58°C). It was first prepared in 1901 by direct fluorination of SO_2 (*133*) but has since been prepared by other methods too numerous for them all to be mentioned here. The most successful preparations, however, include the fluorination of SO_2Cl_2 with SbF_3 (*134*), the reaction of KSO_2F with chlorine (*135*), and the thermal decomposition of barium fluorosulfate at 500°C (*136*).

A recent electron diffraction study has shown that the structure is consistent with those predicted by the Valence Shell Electron Pair Repulsion Theory (*137*).

Sulfuryl fluoride dissolves rapidly in water but may be removed from solution in dynamic vacuum. Hydrolysis is slow in water but rapid in basic solutions, the net reaction being

$$SO_2F_2 + 2[OH]^- \rightarrow [SO_3F]^- + F^- + H_2O \qquad (1)$$

The reaction is considered to be a nucleophilic displacement of fluoride in which the controlling process is



$$SO_2F_2 + [OH]^- \rightarrow \left[HO{-}\overset{\overset{O\quad F}{\|\diagup}}{\underset{\underset{O\quad F}{\|\diagdown}}{S}} \right]^- \rightarrow HOSO_2F + F^- \qquad (2)$$

Sulfuryl fluoride has also been shown to react readily with aqueous solutions of the nucleophiles NH_3, $[PhO]^-$, and $[CN]^-$ giving $SO_2(NH_2)_2$, $PhOSO_2F$, and $[SO_4]^{2-}$, respectively. In these reactions the nucleophile is thought to attack the sulfur atom of SO_2F_2 and displace the fluoride ion (*138*).

Generally, however, sulfuryl fluoride is a chemically inert gas. For example, it shows no evidence of reaction with SbF_5 (*88*). However, despite being a weaker base than thionyl fluoride, it combines with AsF_5 to form a 1 : 1 oxygen-bridged adduct (*88*). This surprising result implies a reversal in the usual relative Lewis acidities of AsF_5 and SbF_5.

3. *Sulfur Oxide Tetrafluoride*

SOF_4 can be prepared by fluorination of SOF_2 using elemental fluorine (*139*) or the fluorides ClF [127], ClF_3, and BrF_5 (*140*) (300°C, 70–90 atm press.). Few reactions of SOF_4 have been studied but it can behave as both a fluoride ion acceptor, as, for example, in the formation of $Cs^+[SOF_5]^-$ (*86, 141*), and a fluoride ion donor, as in the formation of the ionic complexes $[SOF_3]^+[MF_6]^-$ ($M = As$ and Sb) (*131, 142–144*).

4. *Complex Oxide Fluorides of Sulfur* (*124*)

The remaining sulfur oxide fluorides fall into two categories, those which contain the SO_3F group as the structural unit and those whose structural group is SF_5. The former consists of peroxodisulfuryl difluoride $S_2O_6F_2$, the series of polysulfuryl difluorides $S_2O_5F_2$–$S_7O_{20}F_2$, FSO_3F, $SF_4(SO_3F)_2$, and $FSO_3(OF)$. The latter group consists of SF_5OF, $(SF_5)_2O$, SF_5OOSF_5, SF_5OSO_2F, SF_5OOSO_2F, $(SF_5O)_2SO_2$, $(SF_2O)_2SF_4$, $SF_5OSF_4OOSF_4OSF_5$, and $SF_5OSF_4OOSF_5$.

Peroxodisulfuryl difluoride, (FO_2SOOSO_2F) (*124*), is a colorless liquid (bp 67°C) and was first prepared in small amounts by Wannagat and Mennicken (*145*) in 1955. In 1956 Dudley and Cady obtained the compound as a by-product in the synthesis of SO_3F_2, by reaction of SO_2 with an excess of fluorine in the presence of AgF_2 below 170°C (*146*). The compound can also be prepared by the photochemical reaction of SO_3 and fluorine (*147, 148*), the reaction of SO_3 with SO_3F_2 (*146, 149*), the reaction of fluorine or SO_3F_2 with metal fluorosulfates, and by the low-temperature electrolysis of fluorosulfuric acid (*150*). This compound is extremely reactive and tends to decompose to produce SO_3F radicals. As a strong oxidizing agent it oxidizes CO to CO_2, PF_3 to POF_3, SOF_2 to SO_2F_2, and S_2O_5F and liberates iodine from aqueous KI (*124*). Reaction with mercury gives the product $Hg(SO_3F)_2$ and reaction with KCl gives KSO_3F, whereas, with KI and KBr, $K^+[I(SO_3F)_4]^-$ and $K^+[Br(SO_3F)_4]^-$ are produced. Halide ion replacement by $[SO_3F]^-$ also occurs when CrO_2Cl_2 is converted to $CrO_2(SO_3F)_2$ (*124*). It will also substitute chlorine in $SnCl_2F_2$ to give $SnF_2(SO_3F)_2$ (*151*). The reactions with the halogens are interesting (*124, 152a*). Fluorine reacts to give SO_3F_2, chlorine gives $Cl(SO_3F)$, bromine yields $Br(SO_3F)$ and $Br(SO_3F)_3$, and iodine yields $I(SO_3F)$, $I(SO_3F)_3$, $I_3(SO_3F)$, and even $I_7(SO_3F)$. Peroxodisulfuryl difluoride has also been used in organic chemistry in adding across double bonds to place an SO_3F group on each carbon atom (*124*).

This was the status of the chemistry of $S_2O_6F_2$ at the time of the last review in 1974 (*152b*); however, over the last 20 years this compound has dominated sulfur oxide fluoride chemistry. The method of preparation by the low-temperature electrolysis of dilute solutions of KSO_3F in fluorosulfuric acid has been improved by increasing the concentration of the dissolved salt (*153*), and three new preparative routes have been developed. The reaction of CrF_5 with SO_3 in a 1:5 molar ratio yields good quality $S_2O_6F_2$ (*154*), photolysis of $ClOSO_4F$ at ambient temperature for 2–4 h gives a yield of 94–97% (*155*), and, for large-scale preparation, the reaction of $Cs[AgF_4]$ with SO_3 is most suitable (*156*). The low-temperature combination of HSO_3F and $O_2^+[AsF_6]^-$ also yields $S_2O_6F_2$ (*157*).

New examples of the oxidizing ability of this oxide fluoride include the oxidation of SbF_3 to $SbF_3(SO_3F)_2$, $SbF_4(SO_3F)$, and $Sb_2F_9(SO_3F)$ (*158*) and the oxidation of AsF_3 to give the colorless viscous liquid $AsF_3(SO_3F)_2$ (*159*). A study of the iodine–peroxydisulfuryl difluoride system has also confirmed the existence of the previously unkown solids $I(SO_3F)_3$, $I(SO_3F)$, and $I_3(SO_3F)$, and a new compound, $I_7(SO_3F)$, was also characterized (*160*). Transition metal carbonyls are all oxidized by $S_2O_6F_2$ (*161*); for example, $Cr(CO)_6$ reacts to give $Cr(SO_3F)_3$ and $V(CO)_6$ gives $VO(SO_3F)_2$. A number of other oxofluorosulfates, $MnO(SO_3F)$, $CoO(SO_3F)$, $NiO(SO_3F)$, $Ag_2O(SO_3F)_2$, and $TlO(SO_3F)$, have also been prepared by the reaction of $S_2O_6F_2$ with metal carbonates or oxides (*162*). The compound also oxidizes both graphite and boron nitride to yield the salts $C_{12}^+[SO_3F]^-$ and $[BN]_4^+[SO_3F]^-$, the latter being the first example of a first-stage boron–nitride salt (*163*). Intercalation of $BrSO_3F$ gives $C_{12}BrSO_3F$ which, with $S_2O_6F_2$, yields $C_{16}Br(SO_3F)_3$ (*164*). The claim that $S_2O_6F_2$ oxidizes arsenic to the unusual polyatomic cations $[As_4]^{2+}$ and $[As_2]^{2+}$ (*165*), however, has to be subject to doubt until it has been demonstrated that the colors observed are not due to sulfur cations. The oxidation of germanium in $HSO_3F–S_2O_6F_2$ mixtures has given rise only to $GeF_2(SO_3F)_2$; $Ge(SO_3F)_4$ is stable only when complexed as $M_2[Ge(SO_3F)_6]$ ($M = Cs$ or ClO_2). In the tin system simple alternative routes to the previously known $Sn(SO_3F)_4$ and $M_2[Sn(SO_3F)_6]$ are found and, in addition, a new compound, $Cs[Sn(SO_3F)_5]$, has been produced and identified by Mössbauer spectroscopy as a novel structural type with an oligomeric anion (*166*).

In the organic area a number of fluorosulfate-containing molecules have been synthesized under stringent moderating conditions via hydrogen radical abstraction with $S_2O_6F_2$ [Eq. (3)].

$$RH + 2\cdot OSO_2F \rightarrow ROSO_2F + HOSO_2F \qquad (3)$$

Reactions have been described for RH = amines, alcohols, aromatics, aliphatics, perfluoroalkyls, hydrogen halides, and thiols (*167*). Another recent use of $S_2O_6F_2$ in organic chemistry has been in the synthesis of lactones by the remote oxidation of carboxylic acids using a solution of peroxodisulfuryl fluoride in HSO_3F (*168*). Further reactions involving halide-ion replacement include the formation of the green solid $UF_3(SO_3F)_2$ from UF_5 (*169*), $U(SO_3F)_4$ from UCl_4 (*170*), and $M_2Sn(SO_3F)_6$ from $M_2(SnCl)_6$ (M = K, Cs, and NO) (*171*). Reichert and Cady prepared a new compound pentafluoroselenium fluorosulfate, F_5SeOSO_2F, by the reaction of $(SeF_5O)_2$ with peroxodisulfuryl fluoride (*172*).

The simplest member of the polysulfuryl difluorides is $S_2O_5F_2$. This colorless liquid (bp 51°C) was first prepared in 1951 by the addition of SbF_5 to refluxing SO_3 (*173*), and was subsequently prepared by the reaction of As_2O_5 with HSO_3F (*174*) and by the reaction of cyanuric acid with HSO_3F (*175*). Recently, Raman and ^{19}F-NMR data have shown that reaction of SO_3 with PF_5 produces $S_nO_{3n-1}F_2$ ($n = 3$–7) (*176*).

The molecular structures of $S_2O_5F_2$ and $S_3O_8F_2$ in the vapor phase have been determined by electron diffraction (*177*). However, there has been little chemistry reported for any of these compounds, the exception being the formation of a range of fluorosulfates by reaction of $S_2O_5F_2$ with the oxides and oxide halides of nitrogen in anhydrous CH_3CN (*178*).

In 1956 SO_3F_2 (*124*) was prepared by Dudley *et al.* by the catalytic reaction of SO_3 with fluorine (*179*). It can now also be prepared by the photochemical (*139, 148*) or thermal (*146*) reaction of fluorine with $S_2O_6F_2$. The gas can be explosive and, consequently, few reactions have been studied. However, it has been reported to react with iodine (*180*) to give $IF_3(SO_3F)_2$.

Of those complex oxide fluorides involving the $—SF_5$ structural unit, although there has been recent interest in the vapor-phase structures [e.g., F_5SOSF_5 (*181*)] and the kinetics of the thermal decomposition of SF_5OOSF_5 in the presence of CO has been reported (*182*), very little chemistry has been studied. Only the chemistry of SOF_6, prepared by fluorination of thionyl fluoride as described by Ruff in 1968 (*183*), has been cursorily examined. It decomposes slowly to give SF_6 and O_2 (*184*) and is reduced by bromine, iodine, nitric oxide, nitrogen dioxide, and phosphorus trifluoride (*185, 186*) to give SOF_4.

In 1978 two new sulfur oxide fluorides were discovered, both of which contained the SF_5 moiety. DesMarteau reported SF_5OOF and evidence for SF_5OOOSF_5 (*187*), and the existence of the unstable SF_5OOOSF_5 was confirmed by Czarnowski and Schumacher, who obtained it by the reaction of SF_5OF with Cl_2 in the gas phase at or above 180°C (*188*). Its thermal decomposition at temperatures between 213 and 243°C has been shown to result in the production of only SOF_5 and

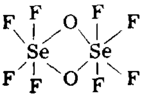
F_5SOF (*188*), the latter, of course, decomposing to give SF_6 and O_2 (*184*).

G. THE OXIDE FLUORIDES OF SELENIUM, TELLURIUM, AND POLONIUM

Selenium forms the simple oxide fluorides $SeOF_2$, SeO_2F_2, and $SeOF_4$ (cf. SOF_2, SO_2F_2, SOF_4). $SeOF_2$ is a colorless, fuming, volatile liquid (bp 125°C). It can be prepared by fluorination of SeO_2 with SeF_4 (*189*), ClF (*190*), HF (*191*), or a mixture of fluorine and nitrogen (*192*). It can also be produced by the reaction of a fluorine–oxygen mixture with selenium at 200°C (*192*) and by treating SeF_4 with TeO_2 (*193*).

SeO_2F_2 is a colorless gas (bp −10°C) and can be prepared by the reaction of SeO_3 with potassium fluoroborate at 65–70°C (*194*). SeO_3 also reacts with SeF_4 to produce SeO_2F_2 (*195*), with PF_5 to give SeO_2F_2 and POF_3 (*176*), and with SbF_3 in liquid SO_2 to give SeO_2F_2 and a polymeric crystalline substance that contains $[SeO_3F]^-$ and $[Se_nO_{3n+1}]^{2-}$ anions (*196*). Small quantities of the oxide fluoride are also produced by the reaction of SeO_3 with an excess of AsF_5 (*197*), and by the treatment of SeO_2 with gaseous fluorine (*198*). Its vapor phase structure, solved recently by electron diffraction, is consistent with the geometry predicted by the Valence Shell Electron Pair Repulsion Theory (*137*). Like $SeOF_2$, SeO_2F_2 is generally unreactive, but does form 1:1 adducts with 2,2′-bipyridine, pyridine, R_3N, and dioxane (*199*), and reacts with $KSeO_4$ to give colorless crystals of $K[SeO_3F]$ (*194*). With anhydrous HNO_3 it gives nitronium fluoroselenate and the vibrational spectrum of the $[SeO_3F]^-$ anion has been assigned (*200*). The potassium and cesium salts of $[SeO_2F]^-$ have been prepared by the reaction of SeO_2 with the appropriate fluoride in the melt and in solution in dimethyl sulfoxide and in 48% HF. The related salt, $K_2SeO_2F_2$, has also been prepared by heating $K[SeO_2F]$ with KF at ~300°C and the geometry of the $[SeO_2F_2]^{2-}$ anion has been studied by Raman spectroscopy (*201*). The reaction of SeO_2F_2 with KHF_2 in the presence of a large excess of HSO_3F has provided one of the least dangerous and most efficient ways of producing $HOSeF_5$ (*202*). The tellurium analogs of the above oxide fluorides are unknown.

Pyrolysis of $Na^+[SeOF_5]^-$ gives the dimer, SeO_2F_8 (*203, 204*) and TeO_2F_8 is similarly produced by pyrolysis of $Li^+[TeOF_5]^-$ (*203, 204*). No evidence for $TeOF_4$ as an intermediate has been found, which contrasts with the selenium case in which a $SeOF_4$ intermediate was identified (*205*). However, this is stable only at temperatures below −100°C. Thermal decomposition of $Se_2O_2F_8$ and $Te_2O_2F_8$ has been studied by mass spectrometry, electric deflection, and flight-time analysis on a molecular beam generated directly from the decomposition products. In both cases the principal products are the tetrafluoride, molecular oxygen, and oxide difluoride (*206*). Although $(SeOF_4)_2$ is stable to hydrolysis, the tellurium analog reacts. It also reacts rapidly with fluoride ion donors to form high polymers (*205*). The high viscosity of the liquid phase of $SeOF_4$ has been explained on the basis of a polymerization process. From the liquid a homogeneous fraction may be separated which, because of its high volatility, is thought to be the oligomer $(SeOF_4)_2$ or $(SeF_4)_2$. Vapor density measurements and mass spectra favor the dimeric formulation (**2**) containing the four-membered ring.



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Such a structure is supported by the ^{19}F-NMR spectrum (*205*) and has been confirmed more recently by electron diffraction for $Se_2O_2F_8$ and for the tellurium analog (*207*).

Two other well-established oxygen–fluorine derivatives of selenium are pentafluoroselenium hypofluorite, F_5SeOF (*208–210*), and bis-pentafluoroselenium peroxide, $F_5SeOOSeF_5$ (*207, 211*). Both are white solids obtained by the reaction of SeO_2 with a fluorine–nitrogen mixture. The product obtained is dependent upon the reaction conditions. At 80°C SeF_5OF is produced and at 110–120°C the peroxide is formed. The former is the much more reactive compound and rapidly oxidizes KI to iodine. It decomposes in the presence of many reagents (e.g., CF_3OOCF_3, NO_2, N_2F_4, SO_2, Cl_2, and Br_2) or if heated to temperatures greater than 85°C or exposed to UV light. It reacts with $S_2O_6F_2$ to give SeF_5OSO_2F (*210*). The instability of the analogous tellurium compound TeF_5OF may be a consequence of atomic size and attempts to synthesize it have resulted in decomposition to TeF_6 and oxygen (*211*). Recently, however, it has been used, presumably in solution, to derive pentafluorooxytellurium-substituted fluorocarbons (TeF_5OR_f) from fluoroolefins (*212*).

Work by Smith and Cady in 1970 (*209*) showed strong evidence for the existence of Se_2OF_{10} and this was finally isolated by Reichert and Cady (*213*) and Seppelt (*210*) in 1972. Seppelt later prepared the tellurium analog (*214*). The selenium compound is prepared by fluorination of SeO_2 (*213*) or by thermal decomposition of $Xe(OSeF_5)_2$ at 130°C (*210*). Recent electron diffraction studies on the selenium and tellurium compounds (*214*) have given rise to speculation that the chalcogen–oxygen bonds are $d\pi$–$p\pi$ double bonds (*181*).

Other reported selenium oxide fluoride species include $SeF_4(OF)_2$ (*215*) and $Se_3O_3F_{10}$. The latter can be formulated as $(F_5SeO)_2SeO$ and is prepared in 49% yield by reaction of $Hg(OSeF_5)_2$ with $SeOCl_2$ (*216*). Reaction of PF_5 with SeO_3 yields a series of compounds of general formula $Se_nO_{3n-1}F_2$, ranging from SeO_2F_2 to $Se_4O_{11}F_2$ (*176*).

In 1956 Campbell and Robinson (*217*) described tellurium fluorides of formulas $Te_3O_2F_{14}$ and $Te_6O_5F_{26}$ along with a species Te_2F_{10} which was later recognized as Te_2OF_{10} (*218, 219*). Only this last compound, however, has been structurally investigated (*219–221*). The discovery of *trans*-$F_2Te(OTeF_5)_4$, as a minor product in the reaction of As $(OTeF_5)_3$ with fluorine (*222*) and as a product of the fluorination of $Te(OTeF_5)_4$, and its structural investigations (*223, 224*), has led to the syntheses of $Te(OTeF_5)_4$, by the reaction of TeF_4 with $B(OTeF_5)_3$ at 80°C, *cis*- and *trans*-$F_4Te(OTeF_5)_2$, by vacuum distillation and low-temperature fractional crystallization of the product of the reaction of TeF_4 with $Xe(OTeF_5)_2$ at 110°C, *cis*- and *trans*-$F_2Te(OTeF_5)_4$, by the reaction of $Te(OTeF_5)_4$ with fluorine in 1,1,2-trichlorotrifluoroethane and separation by low-temperature fractional crystallization of the products in *n*-C_6F_{14}, $FTe(OTeF_5)_5$, by the reaction of $Te(OTeF_5)_4$ and SeF_2 and recrystallization of the product from *n*-C_6F_{14}, and $Te(OTeF_5)_6$, by the reaction of $Te(OTeF_5)_4$ with $Xe(OTeF_5)_2$ (*225*). The tellurium hexakis[pentafluorotellurate](VI) crystalizes in two forms, one trigonal and one triclinic, both of which are composed of discrete $Te(OTeF_5)_6$ molecules in which the central tellurium is, in each case, bonded octahedrally to the six oxygens of the $OTeF_5$ groups, which are themselves also almost octahedral (*225*). A number of these compounds, together with their relatives in which the $OTeF_5$ group is substituted by F, have been used in an interesting multinuclear magnetic resonance and Mössbauer study which has demonstrated that, in all cases, F is more electronegative than $OTeF_5$ (*226*).

In preparing reagents for the transfer of the F_5TeO group in reactions with fluorides (*227, 228*) the species $B(OTeF_5)_3$ was produced. This has proved to be a very useful reagent. Its decomposition at 140°C gives BF_3, TeF_6, and TeO_3 together with a colorless, highly viscous liquid of possible formula $F_3Te(OTeF_4)_{n-3}OTeF_5$ ($n = \sim 25$) (*228*). The exact nature of this polymer is still unresolved.

New ionic species such as $[Te_x(OTeF_5)_{3-x}]^+$ have been observed in the products of the reaction of $Te(OTeF_5)_4$ with AsF_5 (*229*).

The synthesis and characterization of compounds of the type M_2TeOF_4 (M = Cs or K) and $M_2TeO_2F_2$ (M = Cs or Rb) have been

TABLE II

KNOWN HALOGEN OXIDE FLUORIDE DERIVATIVES

Chlorine	Bromine	Iodine
$ClOF$		
ClO_2F	BrO_2F	IO_2F
$ClOF_3$	$BrOF_3$	IOF_3
ClO_3F	BrO_3F	IO_3F
ClO_2F_3	BrO_2F_3	IO_2F_3
$ClOF_5$		IOF_5
ClO_3OF[a]		IOF_4OF[b]

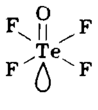
[a] This compound, fluorine perchlorate, does not possess a Cl—F bond and is not a true oxide fluoride. Details of its history, preparation, and chemical and physical properties can be found in Ref. (*234*).

[b] This compound is also not a simple oxide fluoride but the first example of an iodine hypofluorite. Details of its preparation, properties, and chemistry are given in Ref. (*235*).

reported, the M_2TeOF_4 compounds being obtained in the reaction [Eq. (4)] under nitrogen at 500–550°C. Infrared and Raman spectra are

$$TeO_2 + Cs[TeF_5] + 3CsF \rightarrow 2(Cs_2[TeOF_4]) \qquad (4)$$

consistent with the formation of a square, pyramidal $[TeOF_4]^{2-}$ ion (**3**). The $M_2TeO_2F_2$ species were prepared by the reaction of TeO_2 with the alkali metal fluoride at 800°C in a nitrogen atmosphere. Vibrational



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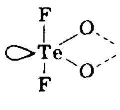

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spectra showed evidence of oxygen bridging and a $[TeO_2F_2]^{2-}$ ion with oxygens in equatorial positions giving C_{2v} symmetry (**4**) (*230*).

Polonium oxide fluorides are unknown.

H. THE OXIDE FLUORIDES OF THE HALOGENS

The known oxide fluorides of the halogens are listed in Table II. Those of chlorine were reviewed in 1969 (*231*), and more comprehensively by Christe and Schack in 1976 (*232*), while the preparations, structures, and properties of oxide fluorides of bromine were summarized by Gillespie and Spekkens in 1978 (*233*).

1. Halogenyl Fluorides: ClO_2F, BrO_2F, and IO_2F

ClO_2F and BrO_2F are pyramidal in shape and monomeric in the gas phase (*236, 237*), whereas IO_2F is polymeric.

Chloryl fluoride can be prepared by careful fluorination of the shock-sensitive chlorine oxides, ClO_2 (*238*) or Cl_2O by AgF_2 (*239*), by the reaction of ClF_3 with H_2O (*240*) or UO_2F_2 (*241, 242*), or by the reaction of ClF with oxygen (*243*). A new, improved, high-yield preparation was devised by Christe *et al.* (*244*) in 1975 and involved the low-temperature reaction of $NaClO_3$ with ClF_3.

ClO_2F is a colorless gas at room temperature and is a powerful oxidizing and fluorinating agent. Reactions of ClO_2F with ClF, ClF_3, ClF_5, OF_2, and F_2 in UV radiation (*245*) at temperatures ranging from -80 to $+10°C$ produce $ClOF_3$ which is used as an oxidizer in rocket engines. Reactions with UF_4 and UF_5 give UF_6 (*246*). Chloryl fluoride can behave as a fluoride ion acceptor and, with CsF (*247*) at $-80°C$, the salt $Cs^+[ClO_2F_2]^-$ is produced. With the Lewis acids BF_3, PF_5, AsF_5, SbF_5, and VF_5, it acts as a fluoride ion donor and forms salts which incorporate the cation $[ClO_2]^+$ and the anions $[BF_4]^-$, $[PF_6]^-$, $[AsF_6]^-$, $[SbF_6]^-$, and $[VF_6]^-$ (*238*). With PtF_6 (*248, 249*) ClO_2F forms $[ClO_2F]^+[PtF_6]^-$ and some $[ClF_6]^+[PtF_6]^-$, and with IrF_6 (*249*), $[ClO_2]^+[IrF_6]^-$ is produced. It fluorinates Al_2O_3 to give AlF_3, $SnCl_4$ to give $[ClO_2]_2{}^+[SnF_6]^{2-}$ and AsF_3, and Sb_2O_3 oxidatively to give $[ClO_2]^+[AsF_6]^-$ and $[ClO_2]^+[SbF_6]^-$ (*238*). Finally, reaction with $O_2{}^+[AsF_6]^-$ yields colored species containing oxygen fluoride radicals (*250*) and not $(ClO_2F_3)_n$ as suggested previously.

Although monomeric in the gas phase, yellow bromyl fluoride is associated in the condensed phases (*236*) and is unstable above its melting point of $-9°C$, decomposing to BrF_3, bromine, and oxygen (*238*). It is said to be most conveniently prepared by the action of BrF_5 on $KBrO_3$ at $-50°C$ (*238*), but some experimentalists obtain $BrOF_2$ and $KBrO_2F_2$ (*251*). It is also possible to obtain $KBrO_2F_2$ according to Eq. (5),

$$BrF_5 + KBrO_3 \rightarrow KBrO_2F_2 + BrF_3 + \tfrac{1}{2}O_2 \qquad (5)$$

whereas, in the presence of fluorine and a greater excess of BrF_5, another oxygen is replaced and $KBrOF_4$ is formed (*252*). BrO_2F is also prepared from $KBrO_2F_2$ and HF (*253*), and by cocondensing BrF_5 and H_2O in a 5 : 1 ratio at −196°C (*254*) and allowing the mixture to warm to −60°C. Bromyl fluoride explodes violently on hydrolysis (*254*). Although it was first believed not to react with Lewis acids, it behaves as a fluoride ion donor like ClO_2F and IO_2F, and forms the $[BrO_2]^+$ cation. The adducts $[BrO_2]^+[MF_6]^-$ (M = As and Sb) were prepared (*255*) by cocondensation of bromyl fluoride with an excess of pentafluoride at −196°C followed by slow warming to room temperature. However, if the mixtures are inadequately homogeneous then side reactions giving Br_2^+ and $[BrF_4]^-$ salts may occur (*255*). Reaction with PtF_6 (*256*) at −120°C yields a brown product containing $[BrO_2F]^+[PtF_6]^-$ and $[BrO_2]^+[PtF_6]^-$. As a fluoride ion acceptor it will produce salts such as $K^+[BrO_2F_2]^-$ (*257*), which can also be made indirectly by the reaction of BrF_5 with $KBrO_3$, and are stable up to 360°C (*252*). Finally, with KrF_2 fluorination occurs (*253*) and $BrOF_3$ is the initial product formed before complete conversion to BrF_5 takes place.

Iodyl fluoride was first prepared, as a white powder, in 1953, by thermal decomposition of IOF_3 (*258*). It can also be made by fluorination of I_2O_5 (*238*) at 20°C in anydrous HF. Like chloryl fluoride, it reacts with Lewis acids (*259–261*) to form complexes such as $[IO_2]^+[AsF_6]^-$, and with Lewis bases to form complexes involving the anion $[IO_2F_2]^-$, e.g., KIO_2F_2, prepared by reaction of KF with IO_2F in anhydrous HF (*259*). The species $[IO_2F_2]^-$ and HIO_2F_2 have been observed in solutions of IF_5 in aqueous HF (*262*) in contrast to an earlier report.

2. *Perhalogenyl Fluorides: ClO_3F, BrO_3F, and IO_3F*

ClO_3F and IO_3F were first synthesized in the early 1950s, whereas BrO_3F was not isolated until 1969 and the detailed chemical behavior of this compound still awaits investigation. The preparation and chemistry of ClO_3F itself was comprehensively reviewed in 1967 (*263*).

Perchloryl fluoride can be prepared by direct fluorination of potassium chlorate (*264*), or by fluorination of $KClO_4$ with HSO_3F (*265*), SbF_5 (*266*), or a HSO_3F–SbF_5 mixture (*267*). This acid solvolysis of perchlorates was studied in detail by Wamser *et al.* (*268*) who prepared ClO_3F by the reaction of $KClO_4$ or $CsClO_4$ with AsF_5, SbF_5, or BF_3, in HF, AsF_3, IF_5, or BrF_5, at temperatures varying from −40 to 35°C. It can also be formed by the action of ClF_3 on NO_2ClO_4 (*269*).

ClO_3F is a stable, colorless gas (bp −47°C). Its solubility in water has been measured and it has been shown that there is a slow reaction to give $[ClO_4]^-$, F^-, and H^+. Rate laws and rate constants for the reactions of ClO_3F with I^-, OH^-, and NH_3 have been obtained (*270*). It is used extensively either alone or mixed with halogen fluorides, as an oxidant for rocket fuels (*271*), and the UV photolysis of ClO_3F with ClF_3, ClF_5, ClF, OF_2, and F_2 produces $ClOF_3$ (*272*). It is a mild fluorinating agent and with NH_2OH at temperature between −70 and −20°C in ethyl alcohol it gives $(NH_3OH)F$ and unstable $(NH_3OH)ClO_3$, which decomposes to give $(NH_3OH)NO_3$ and ClO_3 (*273*). With UF_4 at 240–310°C, UF_6 is formed via a uranium oxide fluoride of unknown composition (*274*). There is no reaction between UF_5 and ClO_3F at temperatures up to 130°C (*274*). As a mild fluorinating agent ClO_3F has proved to be useful in organic chemistry. Unlike chloryl fluoride it does not react with Lewis acids such as SbF_5 and is insoluble in HF.

Perbromyl fluoride was first prepared as a colorless, reactive gas by the reaction of $KBrO_4$ with SbF_5 in HF (*275*) and its vibrational spectra (*276*) have confirmed that, like its chlorine analog, it has a tetrahedral structure.

Periodyl fluoride can be prepared by passing fluorine through a solution of HIO_4 in HF (*274*) and by the reaction of $KIOF_4$ with HSO_3F (*260*). It is a white crystalline solid, stable to 100°C. It possesses some fluoride ion-donating properties and a solution of the oxide fluoride in HF reacts with BF_3 and AsF_5 (*238*) to yield compounds that contain the $[IO_3]^+$ cation.

3. *Halogen Oxide Trifluorides: $ClOF_3$, $BrOF_3$, and IOF_3*

Chlorine oxide trifluoride was first synthesized in 1965 by the fluorination of the hazardous compound Cl_2O, an alkali metal chlorite, or $ClONO_2$ (*271*). However, these results were not reported in the open literature until 1972 and, prior to this, in 1970, Bougon *et al.* had prepared $ClOF_3$ by the reaction of ClF_3 with OF_2 in UV radiation (*277*). It can also be made by UV irradiation of an oxygen–chlorine–fluorine mixture (*272*), by reaction of ClO_2F or ClO_3F with ClF, ClF_3, ClF_5, OF_2, or F_2 (*272*), and by fluorination of $ClNO_3$ or the complex $CsF \cdot ClNO_3$ (*278*).

The predicted gas-phase structure has recently been confirmed by an electron diffraction study and the previous structural work has been summarized (*279*).

$ClOF_3$ is a powerful oxidizing fluorinating agent. As a powerful oxidant it proves a useful supporter of combustion of rocket fuels such as N_2H_4. It is a Lewis base, like NOF, and forms ionic 1 : 1 adducts (*271, 280, 281*) with BF_3, PF_5, AsF_5, VF_5, SbF_5, TaF_5, NbF_5, and BiF_5. The vibrational spectra of these adducts indicates the formation of

$[ClOF_2]^+$ (*271, 280, 281*). Similarly, with UF_5, the salt $[ClOF_2]^+[UF_6]^-$ is produced (*281*), and, with SiF_4, $[ClOF_2]_2^+[SiF_6]^{2-}$ is the product (*238*). Reaction with $MoOF_4$ yields the $[ClOF_2]^+$ salts of the anions $[MoOF_5]^-$ and $[Mo_2O_2F_9]^-$ (*46*). With strong Lewis bases (*282, 283*) such as CsF, RbF, and KF, $ClOF_3$ acts as a fluoride ion acceptor and forms stable 1 : 1 adducts as white crystalline solids. With the weaker base NOF there is no reaction. Attempts to prepare $[ClOF_4]^+$ salts by reaction of $ClOF_3$ with a SbF_5–F_2 mixture, or with PtF_6, failed (*249*). However, the latter does react to give $[ClOF_2]^+[PtF_6]^-$ (*284*). The preparation of $[NF_4]^+[ClOF_4]^-$ by the reaction of $[NF_4]^+[SbF_6]^-$ with $CsClOF_4$ was also attempted, but this also failed (*285*). $ClOF_3$ reacts with Cl_2 and Cl_2O to produce ClF, with $ClOSO_2F$ to give $S_2O_5F_2$, SO_2F_2, ClO_2F, and ClF, and with N_2F_4, HNF_2, and NF_2CFO to give NF_3O and N_2Cl (*284*). Finally, as with ClO_2F, reaction with $O_2^+[SbF_6]^-$ yields colored species which probably contain the O_2F radical (*250*).

$BrOF_3$ was first prepared in 1976 by the reaction of $KBrOF_4$ with $O_2^+[AsF_6]^-$ in BrF_5 solution (*286*) but can also be made by reaction of the same potassium salt with HF (*253*). It is a moderately stable, colorless liquid and, like $ClOF_3$, is amphoteric. For example, salts containing the $[BrOF_4]^-$ ion [e.g., see Ref. (*287*)] and ionic 1 : 1 adducts containing the cation $[BrOF_2]^+$ [e.g., with BF_3, AsF_5, and SbF_5 (*288*)] have been prepared. The adduct $[BrOF_2]^+[SbF_6]^-$ has also been prepared by the reaction of $IO_2F_3 \cdot SbF_5$ with BrF_5 (*288*).

IOF_3 was prepared as white crystals from I_2O_5 and IF_5 (*258*) in 1953 following claims of the existence of the compound made by Ruff and Braida in 1934. It is stable at temperatures up to 110°C at which it dismutates to give IF_5 and IO_2F (*238*). It reacts with BrF_5 (*253*) to give BrO_2F, and with the fluoride ion acceptor IO_2F_3 to give the oxygen-bridged polymer, $[IO_2F_4 \cdot IOF_2]_n$ (*289*). Pure $KIOF_4$ has been prepared (*287*) and it has been shown that the $[IOF_4]^-$ ion is present in equilibrium with IF_5 and H_2O (1 : 1 ratio) in MeCN (*287*).

4. *Halogen Dioxide Trifluorides: ClO_2F_3, BrO_2F_3, and IO_2F_3*

The first and last members of the series, ClO_2F_3 and IO_2F_3, are well characterized while BrO_2F_3, on the other hand, has been observed only from the mass spectra of the products of partial hydrolysis of BrF_5 and BrF_3 (*290*).

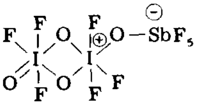
ClO_2F_3 is a stable volatile gas formed by reaction of $[ClO_2F_2]^+[PtF_6]^-$ with the Lewis bases NO_2F or NOF at −78°C (*63, 291*) and is easily separated from the by-product, ClO_2F, by fractional condensation. The existence of $[ClO_2F_2]^+$ salts suggests that ClO_2F_3 may act as a fluoride ion donor, but this has never been proved experimentally.

A purple solid, formed from the low-temperature reactions of ClF with O_2F_2 and ClF_3 with oxygen (*238*), is an isomer of the oxide fluoride reported above. This purple solid is a vigorous oxidizing agent and has been formulated, from its vibrational spectra, as $FClOOClF_2$. The reaction of O_2F_2 with an excess of ClF gives a blue compound believed to be $F_2ClOOClF_2$ (*238*).

Iodine dioxide trifluoride was first obtained by Engelbrecht and Peterfy in 1969 (*292*) by sublimation from the solution resulting from the reaction of $HOIOF_4$ with oleum (*292, 293*). It is a yellow, volatile, crystalline solid (vapor pressure ~2.0 mm Hg at 20°C). On exposure to direct sunlight, or on heating to about 97°C, it decomposes yielding IOF_3 and oxygen (*292, 293*). The standard enthalpy of formation of the crystalline compound has been determined as -984.0 ± 18.0 kJ mol^{-1} based on enthalpies of reaction with aqueous acidic iodide solution (*294*). The ^{19}F-NMR spectrum has been reported by several authors (*292, 293, 295–297*), the final conclusion being that molten IO_2F_3 and its solutions in BrF_5 and perfluoro(methyl)cyclohexane contain the compound as a cyclic trimer with *cis*-oxygen bridges in the boat conformation, the I=O bonds being perpendicular to the plane containing the bridging bonds. However, a single-crystal X-ray study has shown that IO_2F_3 exists as a dimer in the crystalline state and that it is centrosymmetric with oxygen bridge and trans-equatorial oxygens (*298*). It is clear, from mass spectrometric (*296*) and combined electron deflection and mass spectrometric measurements (*299*), that the vapor also contains dimeric and trimeric species. Flight-time distributions in the electron deflection and mass spectrometry of a modulated molecular beam show that the molecule is essentially dimeric at room temperature and that decomposition to monomer is significant at 100°C and almost complete at 185°C (*299*). The vibrational spectra of IO_2F_3 are well documented (*296, 297*) but definitive assignments have not been possible. Although it has been concluded, on the basis of the vibrational data, that the solid, melt, and solution spectra are indicative of the presence of cyclic oxygen-bridged trimers in each case (*297*), this was in advance of the X-ray work. Since the spectra of the three phases are so similar it seems likely that IO_2F_3 may, in fact, be dimeric in all three.

The fluoride ion acceptor properties of IO_2F_3 were demonstrated at the very beginning by Engelbrecht and co-workers who showed that, with HF, the acid $HOIOF_4$ is obtained (*293, 296*). A ready, exothermic reaction also occurs with typical fluoride ion donors such as CsF and NO_2F (*300*). So, chemically, IO_2F_3 may be regarded as a Lewis acid.

In order to ascertain the fluoride ion donor properties, its reaction with SbF_5 has been studied by several independent groups (*289, 296, 300*). On standing, an IO_2F_3–SbF_5 mixture slowly crystallizes to form a white solid (mp 94°C) of 1 : 1 composition. The Raman spectrum is inconsistent with an ionic formulation, $[IO_2F_2]^+[SbF_6]^-$, since the value of $\nu(I{=}O)$ is lowered rather than raised. From ^{19}F NMR and Raman spectroscopic studies (*289, 296, 300*) it was proposed that the adduct is an oxygen-bridged polymer. The crystal structure has recently been determined (*301*) and has confirmed the overall correctness of the spectroscopic work. *cis*-Bridging oxygen atoms link octahedrally coordinated iodine and antimony atoms to form dimers, $(F_4IO_2SbF_4)_2$. The bridging atoms are more closely associated with the iodine and, although the covalent bridging interaction is dominant, there is a contribution to the structure from the ionic formulation $[SbF_4]^+[IO_2F_4]^-$. Antimony pentafluoride is a strong Lewis acid but fails to extract a fluoride ion from IO_2F_3. Indeed it seems that the reverse is true and, at first sight, it is tempting to speculate that IO_2F_3 is the stronger Lewis acid. However, to permit such a comparison of acidities it is necessary to consider the mechanism of the reaction. As proposed by Gillespie and Krasznai (*289*), the initial step probably involves the formation of an oxygen-bridged adduct (5) in which the antimony holds a negative and the iodine a positive charge.



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A number of other adducts of IO_2F_3 with Lewis acid pentafluorides have also been reported. These are also oxygen-bridged polymers, $(IO_2F_4 \cdot MF_4)_n$ (M = As, Nb, Ta, and I) (*289*). A similar reaction also occurs with IOF_3 (*289*) and the nature of the product in this case has been clearly defined as $[IO_2F_3 \cdot SbF_5]_2$ by an X-ray single crystal structure determination (*302*). Like $[IO_2F_3 \cdot SbF_5]_2$, the adduct is cyclic and dimeric, consisting of two IOF_2 and two IO_2F_4 units linked by asymmetric oxygen bridges.

The uncontrolled reaction of XeF_2 with IO_2F_3 is violent and produces $XeF_2 \cdot IF_5$, IO_2F, and O_2. However, low-temperature reaction has been shown to yield novel adducts (*303*). New adducts have also been prepared by the reaction of IO_2F_3 with $XeOF_4$ (*304*). Detailed investigations of the Raman and NMR spectra of these species are in progress.

The complexes KIO_2F_4 and $KIO_2F_4 \cdot 2IF_5$ have also been isolated, but these are prepared from KIO_4 and IF_5 (*289*), and *cis*- and *trans*-$CsIO_2F_4$ have been made by the interaction of $CsIO_4$ with either anhydrous HF, BrF_5, ClF_3, ClF_5, or F_2 (*305*). The vibrational spectra of the latter mixtures have been recorded and partial assigments for both *cis*- and *trans*-$[IO_2F_4]^-$ have been made. The $CsIO_2F_4$ salt dissolves in CH_3CN with the formation of $[IO_2F_4]^-$ anions but undergoes solvolysis in anhydrous HF to give $HOIF_4O$. Reaction of $CsIO_2F_4$ with BiF_5 in anhydrous HF has been shown to be an excellent route to $HOIOF_4$ and reaction with NF_4SbF_6 gives solutions containing $HOIOF_4$, $[NF_4]^+$, and $[HF_2]^-$. The decomposition of these mixtures has yielded the first iodine hypofluorite, $FOIOF_4$, in good yield. The reaction of $CsIO_2F_4$ with $ClOSO_2F$ has yielded another novel compound, $ClOIOF_4$ (*305*).

5. *Halogen Oxide Pentafluorides: IOF_5 and $ClOF_5$*

$ClOF_5$ has been produced, in small amounts only, by the photochemical reaction of ClF_5 with OF_2, in a nickel vessel (*306*) and no reactions have been reported.

IOF_5 (*307–310*) is formed by the reaction of IF_7 with water, silica, or I_2O_5. The considerable amount of spectroscopic data on the vapor, which have established a C_{4v} point group symmetry and suggested a nearly octahedral geometry [e.g., see (*310*)], have recently been embellished with a combined electron diffraction–microwave study which shows that the axial I–F distance is slightly greater than the corresponding equatorial distance and that the $IOF_{(equatorial)}$ angle is appreciably greater than 90° (*311*). The compound is a colorless liquid at room temperature and forms $ClOF_3$ on reaction with ClF (*272*) and an intercalation compound with graphite (*312*) with partial oxidation of the host. It forms 1:1 and 1:2 adducts with SbF_5 and a 1:1 adduct with AsF_5 (*313*). Raman and ^{19}F NMR of these adducts suggests that the IOF_5 is bonded to the pentafluoride via the oxygen atom (*313*).

6. *Chlorine Oxide Fluoride: ClOF*

This oxide fluoride was first reported, in 1930 by Ruff and King, as a solid which melted to a red liquid at −70°C, but was unstable in the gaseous state (*314*). In 1967 Bougon (*240*) suggested that ClOF should occur during the hydrolysis of ClF_3 and this was shown to be the case when ClOF was identified as the primary hydrolysis product by infrared spectroscopy (*315*). It is also formed during photolysis of an argon matrix of ClF and ozone (*316*).

I. THE OXIDE FLUORIDES OF XENON

Of all the noble gases only xenon has, so far, been shown to yield oxide fluorides. The best known of these, xenon oxide tetrafluoride, was first prepared in 1963. XeO_2F_2 and $XeOF_2$ are also well characterized and the compounds, XeO_3F_2 and XeO_2F_4 have also been synthesized. The chemistry of these up to 1972–1973 has been authoritatively reviewed (*317*).

1. Xenon Oxide Tetrafluoride

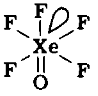
$XeOF_4$ is prepared by the controlled, partial hydrolysis of xenon hexafluoride (*318*, *319*). It can also be prepared by interaction of XeF_6 with silica (*320*). However, whether H_2O or SiO_2 is used, static reactions require careful monitoring because of the possibility of producing the explosive compound XeO_3. The flow preparation devised by Smith (*318*) has some advantages for the less experienced. Other reasonably safe methods of preparation involve the reaction of XeF_6 with $(SiF_3)_2O$ (*321*) and the heating of a $Xe–F_2–O_2$ mixture to 235°C (*317*), where the $Xe : F_2$ ratio used is approximately 1 : 4 and the $Xe : O_2$ ratio approximately 1 : 10. In this latter preparation XeF_4 is produced as the major impurity but the much more volatile $XeOF_4$ is easily removed by vacuum distillation at 0°C. Although the hazards involved in preparing this colorless liquid (mp 46°C) restricted its early study, it has been well characterized by vibrational, NMR and microwave spectroscopy, and mass spectrometry (*317*). Molecular $XeOF_4$ has been shown to be square pyramidal in shape with the oxygen atom in the apical position. In the liquid state ^{19}F-NMR relaxation-time measurements suggest associative interactions (*322*). This is further supported by the asymmetry of the ν_1, Xe=O stretching motion, Raman band of liquid $XeOF_4$. In solution of $XeOF_4$ in liquid HF, moreover, the band consists of two components whose intensities vary with $XeOF_4$ concentration, which has also been attributed to weak associative interactions between $XeOF_4$ molecules (*323*).

Controlled hydrolysis of $XeOF_4$ is difficult. The expected intermediate, XeO_2F_2, is not obtained and XeO_3 is the eventual product (*310*).

Intercalation of $XeOF_4$ into graphite has been shown to lead to the production of $C_{8.7}XeOF_4$ (cf. $C_{8.5}IF_5$), which is stable at 0°C but decomposes slowly above room temperature liberating mainly $XeOF_4$ and minor amounts of xenon (*324*).

In several ways $XeOF_4$ is similar to XeF_6. It forms complexes with both fluoride ion acceptors and fluoride ion donors. In the case of the former, reaction with SbF_5 produces the adducts $XeOF_4 \cdot SbF_5$ and $XeOF_4 \cdot 2SbF_5$ which, on the basis of Raman and ^{19}F-NMR studies, can be formulated as $[XeOF_3]^+[SbF_6]^-$ and $[XeOF_3]^+[Sb_2F_{11}]^-$ (*323, 325–328*). The $[XeOF_3]^+$ cation is isoelectronic with IOF_3 (*328*). The adduct, $2XeOF_4 \cdot AsF_5$, has also been detected but dissociates above −25°C (*323*). The first transition metal complex of $XeOF_4$ was formed on reaction with vanadium pentafluoride as reported by Moody and Selig in 1966 (*329*). A fourfold excess of oxide fluoride reacts with VF_5 to produce the adduct $2XeOF_4 \cdot VF_5$. The adduct formed with AsF_5 at −78°C decomposes before reaching room temperature (*325*). A study of the $XeOF_4$–PtF_6 system, by Christe and Wilson (*330*), resulted in the formation of a yellow-brown mixed solid which contained $[XeOF_3]^+$, $[PtF_6]^-$, and $[XeF_5]^+$.

Reaction of $XeOF_4$ with the fluoride ion donors, CsF, RbF, KF, and NOF, have also been reported. The alkali metal fluorides form the addition complexes $CsF \cdot XeOF_4$, $3RbF \cdot 2XeOF_4$, and $3KF \cdot XeOF_4$ at room temperature but thermogravimetric analysis has shown the existence of other stoichiometries at higher temperatures (*325*). NOF reacts with $XeOF_4$ in a 1:1 ratio to form a white solid (mp 40°C) (*53*). These adducts may contain the $[XeOF_5]^-$ ion although a fluorine-bridged polymeric species involving $XeOF_4$ molecules is more likely (*53*). Perhaps the most interesting advance in xenon oxide fluoride chemistry recently is the characterization of the $[XeOF_5]^-$ and $[(XeOF_4)_3F]^-$ anions which comprise a new class of xenon(VI) oxyfluoro anions. Vibrational spectroscopy and X-ray powder diffraction have shown that $[XeOF_5]^-$ displays a stereochemically active lone pair (**6**)



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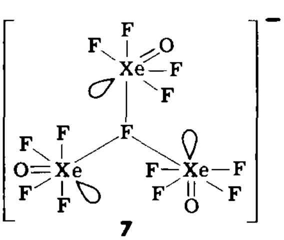

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and that the $[(XeOF_4)_3F]^-$ polyanion consists of three equivalent $XeOF_4$ groups bonded to an F^- ion (*331*) (**7**). Single crystal X-ray studies have confirmed the presence of the latter in the cesium salt $Cs[(XeOF_4)_3F]^-$ (*332*).

In 1971, Bartlett *et al.* reported the molecular adduct $XeF_2 \cdot XeOF_4$ which is isostructural with $XeF_2 \cdot IF_5$ (*333*). In 1975, Holloway and Schrobilgen (*58*) studied the reaction of $XeOF_4$ with the powerful oxidative fluorinating agents $[KrF]^+[SbF_6]^-$ and $[KrF]^+[Sb_2F_{11}]^-$. The species, $[XeOF_4 \cdot XeF_5]^+$ and O_2^+ were formed and not $[XeOF_5]^+$ as reported earlier by Bartlett *et al.* (*334*).

Reaction of $XeOF_4$ with $B(OTeF_5)_3$ in n-C_5F_{12} gave $OXe(OTeF_5)_4$ which reacts further with the oxide tetrafluoride to produce $OXeF_3(OTeF_5)$, $OXeF_2(OTeF_5)_2$, and $OXeF(OTeF_5)_3$ (*335*).

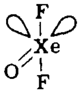
2. *Xenon Dioxide Difluoride*

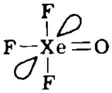
This compound was first prepared as a colorless crystalline solid (mp 38.0°C) by Huston in 1967 (*336*) by the reaction of XeO_3 with $XeOF_4$. The by-product, XeF_2, and unreacted $XeOF_4$ are more volatile than XeO_2F_2, the latter considerably so, and are easily removed. The structure of the solid from single-crystal neutron diffraction data has been shown to consist of layers of XeO_2F_2 molecules based on trigonal bipyramids with the fluorines occupying the axial positions. There are weak $Xe{=}O \cdots Xe$ bridges in the structure (*337*).

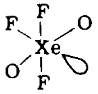
XeO_2F_2 is much less stable than $XeOF_4$ but can be stored for several days at room temperature in suitable pretreated containers. It hydrolyzes to give XeO_3 and reacts with XeF_6 to give $XeOF_4$ (*336*). The only complexes of XeO_2F_2 reported were made by Gillespie and Schrobilgen in 1974 (*327*). Raman (*327*) and later ^{19}F-NMR studies (*328a*) showed that reaction with SbF_5 yields a 1 : 2 adduct which can be formulated as $[XeO_2F]^+[Sb_2F_{11}]^-$, in which the $[XeO_2F]^+$ ion has the expected trigonal-pyramidal geometry. This ion appears to be unstable in SbF_5, decomposing to give $[XeF]^+$ and O_2 (*328a*). The new XeO_2F_2 derivatives, $XeO_2(OTeF_5)_2$ and $XeO_2F(OTeF_5)$, have also recently been synthesized and characterized (*328b*).

3. *Xenon Oxide Difluoride*

Although there were several early reports of the existence of $XeOF_2$, only that by Ogden *et al.* (*338*) was supported by experimental evidence. It was prepared as a yellow solid by the low-temperature hydrolysis of XeF_4. It has since been prepared when condensed intimate mixtures of XeF_4 and H_2O (1 : 1.1 molar ratio) are allowed to warm to −80 to −50°C (*254*). The bright-yellow, nonvolatile solid is stable up to −25°C but the compound is best handled below −40°C in a moisture-free atmosphere. More recently the preparations of $XeOF_2$, $Cs[XeOF_3]$, and $Cs[XeO_2F_3]$ have been reported and information about their structures has been deduced from their Raman spectra (*339*). $XeOF_2$ was obtained from the interaction of XeF_4 and water in HF solvent and the structure proposed (**8**) is consistent with the Raman spectrum. On addition of CsF at low temperature and slow warming to 0°C while pumping, $Cs[XeOF_3]$ was obtained. By altering the conditions, $Cs[XeO_2F_3]$ was also isolated. The Raman spectra of these two compounds are consistent with the geometries shown (**9, 10**) (*339*). Few reactions of $XeOF_2$ have been studied; however, in contact with SbF_5, AsF_5, or Hg it has been found that it decomposes explosively [Eq. (6)] (*254*):


8


9


10

$$2XeOF_2 \rightarrow XeO_2F_2 + XeF_2 \qquad (6)$$

4. *Xenon Trioxide Difluoride and Xenon Dioxide Tetrafluoride*

XeO_3F_2 was prepared by Huston in 1968 (*340*) from the room temperature reaction of XeF_2 with sodium perxenate and can also be obtained from the reaction of XeF_2 with XeO_4 (*341*). Its vibrational spectra have been recorded (*341*). XeO_3F_2 has a greater volatility than XeO_2F_2. Its reactions with ClF_3 and ClF_5 result in their oxidation to ClO_3F, but SbF_5 and IF_7 apparently form solid adducts. Xenon hexafluoride, however, abstracts oxygen to give $XeOF_4$ together with XeO_2F_4. The latter is decomposed to $XeOF_4$ and oxygen by more than brief contact with XeF_6 but this reaction is moderated in $XeOF_4$. The xenon(VIII) compound is even more volatile than XeO_3F_2 and was characterized only from its mass spectrum (*342*).

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