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# Advances in the Chemistry of Organofluorine Hypohalites and Related Compounds

F.M.Mukhametshin

Organofluorine compounds containing the groups O-Hal and O-O-Hal are surveyed. Methods of preparation, physical and chemical properties, structure, and possibilities of practical application are examined. A list of 247 references is included.

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## I. INTRODUCTION

A major achievement of organofluorine chemistry, based on the use of elementary fluorine, has been the discovery and study of new classes of compounds. Several of them contain functional groups that are essentially strong oxidants, which makes preparation of their hydrocarbon analogues almost impossible. Examples of such compounds are, in particular, many known organofluorine hypohalites and related *O*-halogenoperoxides.

These two groups of compounds owe their existence and relative stability to the alkyl fluorine atoms. This stabilising effect comprises (i) shielding of the carbon skeleton by the fluorine atoms and (ii) the inductive effect of fluoroalkyl groups, which strengthens the oxygen–halogen bond. Among the hypohalites the hypofluorites are more common than the corresponding hypochlorites. The less common peroxides are roughly equally represented by both halogens.

The first results on the synthesis and isolation of organofluorine hypohalites appeared in 1948, when trifluoromethyl hypofluorite $CF_3OF$ was identified[1]; the hypochlorite $CF_3OCl$ was first described in 1968;[2] and the *O*-halogenoperoxides have been characterised quite recently. Methods of preparation and individual properties of hypofluorites have been surveyed in several general[3–5] and specialised[6–8] reviews.

The present Review summarises the vast amount of published information on the preparation and properties of organofluorine hypofluorites and on the related hypochlorites and *O*-halogenoperoxides. It covers publications that had appeared by the end of 1977 inclusive. Perfluoroacyl hypofluorites[8] are not considered.

## II. METHODS OF PREPARATION

Existing methods for the directed preparation of organofluorine hypohalites and *O*-halogenoperoxides can be arbitrarily divided into catalytic and non-catalytic. Each group includes various modifications, determined essentially by the type of initial organofluorine or other compound, the type of catalyst, and the experimental conditions. Carbonyl-containing compounds have been most widely used as starting materials for the preparations of organofluorine hypohalites. Reactants for production of the O–Hal group are elementary fluorine to obtain hypofluorites and chlorine monofluoride for hypochlorites. The same reactants are employed in the preparation of organofluorine *O*-halogenoperoxides.

### 1. Hypofluorites

The chief method for the preparation of organofluorine hypofluorites is the catalysed action of fluorine on perfluoroacyl fluorides[9–19]:

$$R_FC(=O)F + F_2 \xrightarrow{cat.} R_FCF_2OF .$$

Fluorides of sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, barium, lanthanum, iron, copper, nickel, and silver as well as mixed compounds of the type $CsHF_2$ or $KAgF_4$ can be used as fluorination catalysts[9]. Caesium fluoride possesses extremely high catalytic activity: in its presence hypofluorites can be obtained not only from carbonyl difluoride or fluorides of mono- and per-fluorinated dicarboxylic acids[10–16] but also from the unstable peroxy-compounds $(FCOO)_2$,[15] $CF_3OOCOF$,[17] and $(SF_5OO)_2COF$.[18]

The preparation of hypofluorites in the presence of caesium fluoride is distinguished by simplicity and nearly quantitative yields of the end-products. Fluorine and the acyl fluoride are mixed in a vessel containing the catalyst, evaucated and cooled to −196 °C, which is then warmed to room temperature[11]. A disadvantage is the low ouput due to the need to use static conditions and small quantities of reactants.

Fluorides of alkaline-earth and transition metals are weaker catalysts than caesium fluoride, and require higher reaction temperatures (25–100 °C). Their catalytic activity has been examined in detail only in the conversion of carbonyl difluoride into trifluoromethyl hypofluorite. The reaction can be conducted in a flow system[1].

In general the formation of hypofluorites from acyl fluorides consists essentially in the addition of fluorine at the carbonyl multiple bond. The reaction mechanism has not been finally established: two possible alternatives, determined by the nature of the catalyst, are postulated. In the case of alkali-metal fluorides, especially caesium fluoride, it is assumed[20,21] that an alkoxide (I) is formed, which then reacts with fluorine:

$$R_FC(=O)F + CsF \rightarrow \underset{(I)}{R_FCF_2\bar{O}\overset{+}{C}s}$$

$$(I) + F_2 \rightarrow R_FCF_2OF + CsF .$$

The second stage is classified[22] as nucleophilic substitution $S_N2$ at the fluorine atom. However, it is more correct to regard it as a one-electron transfer process, as e.g. in the fluorination of the trinitromethyl anion by perchloryl fluoride[23].

In the case of fluorides of metals of variable valency (silver, copper, nickel) the role of the catalyst is essentially[21] to generate fluorine atoms, which initiate a radical process. A mechanism suggested[21] for the fluorination of carbonyl difluoride is

$$F_2 \xrightarrow{cat.} 2\dot{F}$$
$$\dot{F} + COF_2 \rightarrow CF_3\dot{O}$$
$$CF_3\dot{O} + \dot{F} \rightarrow CF_3OF$$
$$2CF_3\dot{O} \rightarrow CF_3OOCF_3 .$$

The chief arguments in favour of such a mechanism are the formation of trifluoromethyl peroxide and the inability of catalysts of this type to form alkoxides with perfluoroacyl fluorides. A heterogeneous mechanism has also been suggested[24], with formation of trifluoromethyl peroxide involving chemisorption processes:

$$AgF_2 + CoF_2 \rightarrow Ag(OCF_3)_2$$
$$Ag(OCF_3)_2 + F_2 \rightarrow [F_2 \cdot Ag(OCF_3)_2] \rightarrow AgF_2 + CF_3OOCF_3 .$$

None of the schemes is entirely satisfactory. The true mechanism of formation of trifluoromethyl hypofluorite and peroxide is probably catalytic, as indicated in particular by results for the activated adsorption of fluorine[25] and the dipole moment of carbonyl difluoride (0.95 D).[4]

Acyl fluorides can be converted catalytically into hypofluorites not only heterogeneously but also homogeneously. Thus at −20 °C carbonyl difluoride and fluorine do not interact, but in the presence of even small quantities of nitrosyl fluoride under the same conditions nearly quantitative yields of trifluoromethyl hypofluorite are formed[10]. The catalytic action of nitrosyl fluoride is attributed to the ease of its addition to the carbonyl bond:

$$COF_2 + NOF \rightleftarrows CF_3ONO$$
$$CF_3ONO + F_2 \rightarrow CF_3OF + NOF .$$

Because the addition of fluorine at the carbonyl bond is so strongly exothermic, catalysis by fluorides of metals of variable valency is in effect limited to the preparation of trifluoromethyl hypofluorite. Since this product has high thermal stability, it can be prepared not only from carbonyl difluoride but also from such compounds as carbon monoxide [24,26], carbon dioxide[26,27], carbonyl dichloride, and methanol† [11,26]. In all the above cases silver fluoride deposited on copper catalyses the formation of both intermediate and final products:

$$CO + F_2 \xrightarrow{cat.} COF_2$$
$$COF_2 + F_2 \xrightarrow{cat.} CF_3OF .$$

Caesium fluoride, which is incapable of sorbing fluorine and carbon monoxide, plays no part at the stage of formation of carbonyl difluoride[24]. Copper fluoride has a weak catalytic effect on both stages. The fluorination of carbon dioxide to trifluoromethyl hypofluorite in the presence of silver fluoride (or difluoride) is a complicated degradative process accompanied by the evolution of oxygen and other products. In the presence of the more active caesium fluoride, however, carbon dioxide is smoothly converted into difluoromethylene bishypofluorite[11,28–30]:

$$CO_2 + 2F_2 \xrightarrow{CsF} CF_2(OF)_2 .$$

† The fluorination of methanol probably involves intermediate formation of carbonyl difluoride.

The high yield of this product and the possibility of obtaining it from fluoroformyl hypofluorite[13]

$$FC(=O)OF + F_2 \xrightarrow{CsF} CF_2(OF)_2$$

suggest that the activation of carbon dioxide by the catalyst is analogous to that of an acyl fluoride or hexafluoroacetone[12]:

$$O{=}C{=}O + CsF \rightleftarrows [O{=}CF\bar{O}\overset{+}{C}s] \xrightarrow{F_2} FC(=O)OF + CsF$$
$$(CF_3)_2C{=}O + CsF \rightleftarrows (CF_3)_2CF\bar{O}\overset{+}{C}s \xrightarrow{F_2} (CF_3)_2CFOF + CsF .$$

Despite unsuccessful attempts to isolate the intermediate fluoroformyl hypofluorite, it is difficult to imagine a different reaction path for carbon dioxide and fluorine in the presence of caesium fluoride.

Non-catalytic methods for the preparation of hypofluorites can be divided into gas-phase, liquid-phase, and solid-phase according to the state of aggregation of the substances to be fluorinated. The first group has been used primarily to obtain trifluoromethyl hypofluorite by the fluorination of carbon monoxide, carbon dioxide, or carbonyl difluoride. The other two groups are suitable with certain limitations for obtaining higher perfluoroalkyl hypofluorites.

In the absence of a catalyst carbon monoxide and fluorine react smoothly at 300–400 °C.[31] A good yield of trifluoromethyl hypofluorite is achieved by the use of two reaction vessels connected in series, the first of which serves for the formation of carbonyl difluoride.

Carbon dioxide reacts with fluorine at 200–300 °C:[32]

$$CO_2 + F_2 \rightarrow CF_3OF + {}^1/_2O_2$$

The reaction is autocatalytic, presumably with regeneration of the fluorooxy-radical OF. Above 350 °C oxygen is accompanied by other products, which have not been identified. In the photochemically initiated reaction detailed investigation[33–35] has revealed the formation of the primary active radicals O : C(OḞ) and O : CF.Ȯ. The same radicals probably occur as intermediates in the thermal process.

Ultraviolet irradiation of a mixture of carbonyl difluoride and fluorine gives an approximately 80% yield of trifluoromethyl hypofluorite[36]:

$$F_2 + h\nu \rightarrow 2\dot{F}$$
$$\dot{F} + COF_2 \rightarrow CF_3\dot{O}$$
$$CF_3\dot{O} + F_2 \rightarrow CF_3O\dot{F} + F$$
$$2CF_3\dot{O} \rightarrow CF_3OOCF_3 .$$

The mechanism of this reaction has recently been reinterpreted[37]

$$F_2 + h\nu \rightarrow 2\dot{F}$$
$$\dot{F} + COF_2 \rightarrow \dot{C}F_2OF$$
$$2\dot{C}F_2OF \rightarrow (CF_2OF)_2^*$$

$$(CF_2OF)_2^* \xrightarrow[\text{conversion}]{\text{internal}} (CF_2OF)_2$$
$$(CF_2OF)_2^* \xrightarrow{\text{walls}} CF_3OF + COF_2$$
$$(CF_2OF)_2^* + COF_2 \rightarrow (CF_3O)_2 + COF_2$$
$$(CF_2OF)_2 + F_2 \rightarrow 2CF_3OF$$
$$F \xrightarrow{\text{walls}} {}^1/_2F_2$$

but this is not convincing. In contrast to the photoprocess the thermally initiated reaction is reversible, with equilibrium displaced towards formation of trifluoromethyl hypofluorite below 250 °C.[38]

Among the above methods the fluorination of carbon monoxide has the greatest preparative value. Its advantages consist in comparatively simple apparatus, high purity of the final product (especially in the presence of caesium fluoride),

and the ready availability of carbon monoxide. Among other gas-phase reactions, in which trifluoromethyl hypofluorite has been isolated as a by-product, we may note the ultraviolet-initiated fluorination of hexafluoroacetone[39] and the interaction of chlorotrifluoroethylene with nitrogen fluoride oxide[40], tetrafluoroethylene with dioxygen difluoride[41], and tetrafluoromethane with oxygen under the influence of $\gamma$-rays[42]. The formation of trifluoromethyl hypofluorite from methane or fluoroform and oxygen difluoride[43] is of some interest.

In the liquid-phase and solid-phase fluorination of organic compounds hypofluorites have been obtained by treating the starting material with fluorine in a static or flow-type reaction vessel at temperatures between 20° and −78 °C. The fluorine should be diluted with an inert gas; its concentration must be raised from 5–10% at the start of the experiment to 20–50% at the end. The interest taken by research workers in these methods is indicated by examples in which hypofluorites have been obtained from trichloro- and trifluoroethanol, hexafluoroacetone hydrate, trichloronitropropan-2-ol, perfluoro-t-butyl alcohol[44–48], trichloroacetic esters[49], higher polyfluorinated alcohols, salts of trifluoroacetic, oxalic, and higher perfluorinated acids[46,48,50–52], trifluoroacetyl nitrate[45,46], and other compounds[53,54]. Nevertheless, they are ineffective as methods of preparation.

The chief defects of these methods are lack of selectivity and low yields. For example, the sodium salt of hexafluoroacetone hydrate gives four different hypofluorites[45]:

$$(CF_3)_2C\begin{matrix}OH\\ONa\end{matrix} \xrightarrow{F_2,N_2} (CF_3)_2CFOF + (CF_3)_2C(OF)_2 + CF_3CF(OF)_2 + C_2F_5OF\ .$$

Three hypofluorites are formed from sodium trifluoroacetate[50]:

$$CF_3C\begin{matrix}O\\ONa\end{matrix} \xrightarrow{F_2,N_2} CF_2(OF)_2 + C_2F_5OF + CF_3CF(OF)_2\ .$$

Hexafluoroacetone hydrate, in contrast to the sodium salt, gives heptafluoroisopropyl hypofluorite and a large number of by-products[44]:

$$(CF_3)_2C(OH)_2 \xrightarrow{F_2,N_2} (CF_3)_2CFOF + CF_3COF + CF_4 + C_2F_6 + COF_2 + CO_2\ .$$

Trifluoroethanol and trifluoroacetyl nitrite are converted into pentafluoroethyl hypofluorite in at most 20% yield. Under mild conditions sodium oxalate gives difluoromethylene bishypofluorite[55], but with rise in temperature trifluoromethyl hypofluorite and peroxide are obtained[51]:

$$(COONa)_2 \begin{matrix}\xrightarrow{21°C} CF_2(OF)_2\\ \xrightarrow{84°C} CF_3OF + CF_3OOCF_3\end{matrix}\ .$$

Highly selective fluorination occurs only with perfluoro-t-butyl alcohol, which it is advisable to use in the form of an alkoxide[47]:

$$(CF_3)_3CONa \xrightarrow{F_2,N_2} (CF_3)_3COF\ .$$

Attempts have been made to use oxygen difluoride to introduce a fluorooxy-group into an organofluorine molecule. On ultraviolet irradiation, a mixture of dichlorotetrafluoroacetone and the difluoride gives mainly chlorodifluoromethyl hypofluorite[56]. When perfluoroalkenes are treated with the difluoride to obtain the oxides[57], trifluoromethyl and other hypofluorites are formed as by-products.

It has recently been shown that it is fundamentally possible to prepare trifluoromethyl hypofluorite by the electrochemical fluorination of carbon monoxide, carbonyl dichloride and difluoride[58–60], and more complicated compounds[61], but the yields are appreciably inferior to those of chemical fluorination.

## 2. Hypochlorites

Initial compounds investigated for the catalytic preparation of organofluorine hypofluorites have been carbonyl difluoride[2,62–69], perfluoroacyl fluorides[65,69–73], and perfluoroketones[69–73], with as catalysts potassium, rubidium, and caesium fluorides[2,67,69,70,72], hydrofluoric acid and Lewis acids [boron(III), arsenic(III), arsenic (V), and antimony(V) fluorides][65,66,71,73], nitrosyl fluoride[10,66,71], magnesium fluoride, and fluorinated aluminium oxide[62,68,74]. The first three types of catalysts possess a wide spectrum of action; magnesium fluoride and alumina have been tested only in the chlorofluorination of carbonyl difluoride.

The reaction of carbonyl difluoride with chlorine monofluoride yields trifluoromethyl hypochlorite:

$$COF_2 + ClF \xrightarrow{cat.} CF_3OCl\ .$$

Perfluorinated acyl fluorides and ketones give higher perfluoroalkyl hypochlorites:

$$R_FCOF \xrightarrow{cat.} R_FCF_2OCl$$
$$(R_F)_2CO \xrightarrow{cat.} (R_F)_2CFOCl\ .$$

Catalysis by alkali-metal fluorides is essentially the same as in the preparation of hypofluorites[73]. Owing to the polarity of chlorine monofluoride[75], however, the second stage—attack on the anionoid centre of the alkoxide—is considerably facilitated in comparison with fluorine:

$$R_F-\bar{O}\ \ Cl^{\delta+}\ \ +\ \ |\ \ |\ \ \rightarrow R_FOCl + CsF\ .$$
$$Cs^+\ \ F^{\delta-}$$

This is confirmed by the great selectivity, the mild conditions, and the nearly theoretical yields of hypochlorites.

The effect of polarisation of chlorine monofluoride in the ground state is clearly illustrated by the absence of reaction with carbon dioxide[70]:

$$CO_2 + 2ClF \xrightarrow{CsF} CF_2(OCl)_2\ .$$

A possible reason for the negative result is that the monofluoride (dipole moment 0.88 *D*) is removed from the reaction zone, by forming with the catalyst a complex—caesium difluorochlorate $Cs^+Cl^-F_2$—that is inert towards carbon dioxide[76].

On passing from alkali-metal fluorides to acids the action of the catalyst is directed at chlorine monofluoride. With catalysis by hydrogen fluoride as example it is assumed[73] that activation increases the positive charge on the chlorine atom by protonation:

$$\overset{\delta+\ \ \delta-}{Cl-F} + H-F \rightarrow \overset{+}{Cl}-\overset{\sim}{\overbrace{F\cdots H\cdots F}}\ .$$

This is followed by electrophilic attack on the carbonyl oxygen and stabilisation of the carbocation:

$$\rangle C{=}O + \overset{+}{Cl}-\overset{\sim}{\overbrace{F\cdots H\cdots F}} \longrightarrow \left[\rangle \overset{+}{C}-OCl\right]\cdot HF_2 \longrightarrow \rangle CFOCl + HF\ .$$

In the case of catalysis by boron, arsenic, and especially antimony fluorides the reaction velocity is increased by their tendency to give onium complexes with donors of the fluoride ion, e.g. chloronium hexafluoroantimonate $Cl^+SbF_6^-$.[77]

Nitrosyl fluoride is a homogeneous catalyst in the formation of hypochlorites. As noted above it forms covalent adducts (nitrites) with carbonyl compounds. The ability of such nitrites to be converted into hypochlorite derivatives under the influence of chlorine monofluoride is shown by the

example of perfluoroisopropyl nitrite[10]:

$$(CF_3)_2CONO + ClF \rightarrow (CF_3)_2CFOCl + NOF .$$

It is significant that nitrosyl fluoride not only has a direct catalytic effect but also confers catalytic properties on the surfaces of the reaction vessels: trifluoromethyl hypochlorite is formed no less smoothly in stainless-steel and polychlorotrifluoroethylene reaction vessels that have been treated with nitrosyl fluoride and then evacuated than in the presence of nitrosyl fluoride as catalyst[10,71]. The nature of the activation is unknown, although it is undoubtedly connected with the high sorbability of nitrosyl fluoride.

"Fluorinated aluminium oxide" is a catalyst distinguished by a highly developed specific surface. It is prepared by treating γ-alumina with chlorine trifluoride[62,68,74]. In its presence trifluoromethyl hypochlorite can be obtained from carbonyl difluoride and chlorine trifluoride, although the product is contaminated with tetrafluoromethane and chloryl fluoride[74,78]:

$$COF_2 + ClF_3 \xrightarrow{cat.} [CF_3OClF_2] \xrightarrow{COF_2} CF_3OCl + CF_4 + FClO_2 .$$

Non-catalytic methods for obtaining hypochlorites use hydroxy-compounds—alcohols and ketone hydrates—as starting materials[72,79-82]. *O*-Chlorination is characterised by great selectivity, which enables hydrogen, alkyl, and aryl derivatives to be employed:

$$X(CF_3)_2C{-}OH \xrightarrow[-HF]{ClF} X(CF_3)_2C{-}OCl$$
$$X = H,\ CH_3,\ Ar,\ CF_3 .$$

A bishypochlorite can be obtained from hexafluoroacetone hydrate[72]:

$$(CF_3)_2C(OH)_2 \xrightarrow{2ClF} (CF_3)_2C(OCl)_2 .$$

However, an attempt to apply the reaction to perfluoropinacol was unsuccessful[79]:

$$(CF_3)_2C(OH){-}C(OH)(CF_3)_2 \xrightarrow{2ClF} (CF_3)_2C(OCl){-}C(OCl)(CF_3)_2 .$$

### 3. Organofluorine Halogenoperoxides

As with the hypohalites, catalytic methods are of the greatest interest for obtaining organofluorine halogenoperoxides. In the presence of caesium fluoride carbonyl and oxygen difluorides readily interact to give a good yield of trifluoromethyl fluoroperoxide[83,84]:

$$COF_2 + OF_2 \xrightarrow{CsF} CF_3OOF .$$

The mechanism is similar to that discussed above for the hypohalites[85].

The mechanism of the formation of trifluoromethyl fluoroperoxide from the hydroperoxide

$$CF_3OOH \xrightarrow{CsF,F_2} CF_3OOF$$

is not entirely clear[86]. Possibly caesium fluoride activates the hydroperoxide by forming the hydrogen bond $CF_3OOH...F^-Cs^+$, which facilitates subsequent attack by the halogen. This view is suggested by the ease with which the same hydroperoxide is converted into the ClO-derivative by chlorine monofluoride in the presence of sodium fluoride[87]:

$$CF_3OO{-}H{\cdots}F{-}Na \ (Cl{-}F) \xrightarrow[-110^\circ C]{} CF_3OOCl + NaF \cdot HF .$$

According to patent claims[88,89] this is a general method for the production of organofluorine chloroperoxides.

Other methods are the reaction of fluoroalkenes with dioxygen difluoride, demonstrated with hexafluoropropene as example[90,91], and the fluorination of salts of perfluoro-acids, in particular sodium trifluoroacetate[52]:

$$CF_3CF{=}CF_2 + O_2F_2 \xrightarrow[-183^\circ C]{} \underset{(75\%)}{CF_3CF(OOF)CF_3} + \underset{(25\%)}{CF_3CF_2CF_2OOF}$$
$$CF_3C(=O)ONa + F_2 \rightarrow CF_3OOF + C_2F_5OOF .$$

Because of possible ambiguity in the results very little preparative value attaches to these reaction.

## III. PHYSICAL PROPERTIES AND STRUCTURE

Under ordinary conditions the great majority of hypofluorites obtained hitherto are gases having the characteristic odour of fluorine. In relation to physical properties, spectra, and structure the most fully studied of this group is trifluoromethyl hypofluorite. At −95 °C it condenses into a colourless liquid of density 1.9 g $cm^{-3}$. The heat of evaporation, the standard heat of formation from the elements, and the Trouton constant are respectively 3710 cal $mole^{-1}$, −181.5 kcal $mole^{-1}$, and 20.8.[4] The energy of the oxygen–fluorine bond has been estimated as 43.5 ± 0.5 kcal $mole^{-1}$,[92] and its refraction is 3.89.[93] Components of the dipole moment have been found from data on the rotational spectrum[94]. This compound does not solidify at −215 °C.

The boiling point rises as fluorine atoms in the trifluoromethyl group are replaced by other atoms or groups. For example, chlorodifluoromethyl[56] and dichlorofluoromethyl hypofluorites boil at −25 and 0 °C respectively.

Difluoromethylene bishypofluorite boils at −64 °C. When placed in liquid nitrogen, it is converted into a transparent vitreous material[28]#. The heat of evaporation is 4445 cal $mole^{-1}$, and the standard heat of formation −130.5 kcal $mole^{-1}$. The vapour pressure curve can be calculated by means of the equation[55]§

$$\lg p = 7.530 - 971.6/T .$$

The energy of the oxygen–fluorine bond has not been accurately determined, but is most probably less than in trifluoromethyl hypofluorite.

Among perfluoroalkyl hypochlorites only the first two—trifluoromethyl and pentafluoroethyl—are gaseous under ordinary conditions. The higher hypochlorites are colourless or slightly yellowish liquids. Trifluoromethyl hypochlorite boils at −45.8 [69] or −47 °C,[70] and solidifies at −164 °C.[70] The heat of vaporisation is 4684 [70] or 5090 [69] cal $mole^{-1}$, and the Trouton constant 20.7 [70] or 22.4.[69] The temperature dependence of the vapour pressure between −131 and −54 °C is given by the equation[70]

$$\lg p = 7.413 - 1025/T .$$

The corresponding physical constants for pentafluoroethyl and heptafluoroisopropyl hypochlorites will be found in Refs. 69 and 70.

Some idea of the physical properties of the halogenoperoxides is given by published data on trifluoromethyl fluoroperoxide[86] and chloroperoxide[87]. The former condenses at

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# Another worker[30] obtained a viscous liquid.

§ Here and subsequently *p* represents pressure in mmHg, and *T* K is the temperature.

−69.4 °C to a colourless transparent liquid of density 1.65 g $cm^{-3}$. The heat of vaporisation is 4360 cal $mol^{-1}$, and the vapour density equation between −117 and −70 °C is

$$\lg p = 6.8764 - 673.9/T - 28442/T^2 .$$

This peroxide does not solidify in liquid nitrogen. Trifluoromethyl chloroperoxide boils at −22 °C , and its melting point is −132 °C. Other constants for this compound can be found in Ref. 87.

The infrared spectrum of trifluoromethyl hypofluorite contains 12 fundamental absorption bands, among which that in the region of 945 $cm^{-1}$ corresponds to oxygen–fluorine stretching vibrations[95–97]. The molecule has $C_S$ symmetry and is a somewhat distorted tetrahedron. Bond lengths and angles are

C—F 1.319±0.003 Å; C—O 1.395±0.006 Å; O—F 1.421±0.006 Å;

∠FCF 109.4±1°; ∠COF 104.8±0.6°[98, 99].

For analysis of the infrared spectra in terms of absorption by carbon–fluorine bonds see Ref. 100. The infrared spectrum of difluoromethylene bishypofluorite contains 15 main bands, 2 of which in the region of 916 and 933 $cm^{-1}$ have been assigned to absorption by the hypofluorite group (stretching vibrations)[101]. This molecule has $C_{2v}$ symmetry.

Detailed analysis of the infrared spectra of hypofluorites has established that electron-accepting substituents (difluoroamino, nitro, trifluoromethyl)[8] shift the band due absorption by FO-groups to lower wavenumbers, in the limit to 882 $cm^{-1}$. It is interesting that in the Raman spectrum of trifluoromethyl hypofluorite the ν(O–F) band is more intense than the ν(C–O) band, whereas the opposite relation applies in the infrared spectrum[102]. This was attributed[102] to the more covalent character of the oxygen–fluorine than of the carbon–oxygen bond.

The many papers on the fluorine-19 magnetic resonance spectra of hypofluorites[10,11,28,29,44,45,55,103–105] have established the most important fact of a considerable down-field shift in the fluorine lines due to FO-groups (140–160 ppm relative to the standard fluorochloroform), which indicates a decrease in electron density on the fluorine atom. This should tend to increase the energy of the carbon–oxygen bond in hypofluorites. Indeed, mass-spectrometric measurements of the ionisation of trifluoromethyl hypofluorite[106] and calorimetric determinations on difluoromethylene bishypofluorite[107] show that the energy of this bond exceeds on the average by 10–15 kcal $mole^{-1}$ those in hydrocarbon derivatives of similar structure (alcohol, ethers). Further support is provided by PPDP/2 quantum-chemical calculations on the trifluoromethyl hypofluorite molecule[108].

Investigations have been published[69,70,86,87] on the infrared and nuclear magnetic resonance spectra of organofluorine hypochlorites and halogenoperoxides.

## IV. CHEMICAL PROPERTIES

The reactivity of organofluorine hypohalites and halogenoperoxides is determined by the tendency to rupture of the oxygen–halogen bond, the weakest in the molecule. Because of the relatively low energy of rupture of this bond, radical processes are most typical of these two groups of compounds. However, in conformity with the diminished electron density on the halogen atom, the hypofluorites also undergo heterolytic reactions, in which they act as electrophiles.

The highly exothermic character of processes involving these two groups of compounds often leads to the formation of a relatively large number of by-products from direct decomposition of these compounds, interaction of the substrate with the decomposition products, rearrangements, etc. The following discussion of thermolysis and photolysis reveals several views on such reactions.

### 1. Thermolysis

Trifluoromethyl hypofluorite and difluoromethylene bishypofluorite are thermally the most stable among organofluorine hypofluorites. In an enclosed space the former begins to decompose at ~200 °C, and the rate becomes appreciable above 250 °C. In an already passivated nickel reaction vessel reversible decomposition takes place[109]:

$$CF_3OF \rightleftarrows COF_2 + F_2 .$$

Furthermore, small quantities of trifluoromethyl peroxide are formed. Above 400 °C decomposition becomes irreversible owing to interaction of fluorine with the material of the vessel. Degradation of trifluoromethyl hypofluorite in a cold-glow electrical discharge (quartz vessel) yields tetrafluoromethane, carbon dioxide, oxygen, and silicon tetrafluoride, whereas in a metal vessel the first two products are accompanied by carbonyl difluoride and fluorine[109]. Degradation is retarded by additions of carbonyl difluoride to the hypofluorite.

Difluoromethylene bishypofluorite does not decompose at 150 °C for several hours; at 250 °C after 3 h it is possible to recover 40% of the initial compound. Such slow thermal decomposition is described by the equation[55]

$$CF_2(OF)_2 \xrightarrow{\Delta} COF_2 + {}^1/_2O_2 + F_2 .$$

Under explosive conditions[107] a more complicated mixture is formed:

$$CF_2(OF)_2 \xrightarrow{\text{explosion}} COF_2 + CF_3OF + CF_3OOCF_3 + CF_3OOF + CF_4 .$$

Another stable member of this group is tetrafluoroethylidene bishypofluorite, which at 150 °C is only 5% decomposed after 6.5 h:[45]

$$CF_3CF(OF)_2 \begin{cases} \xrightarrow{\Delta} CF_4 + COF_2 + {}^1/_2O_2 \\ \xrightarrow{\Delta SiO_2} CO_2 + {}^1/_2O_2 + {}^3/_2SiF_4 . \end{cases}$$

Higher perfluoroalkyl hypofluorites are less stable. The decomposition products depend on the structure of the alkyl group: primary derivatives give alkanes and carbonyl difluoride, secondary yield alkanes and acyl fluorides, and tertiary form alkanes and ketones[44]—e.g.

$$CF_3CF_2OF \xrightarrow{\Delta} CF_4 + COF_2$$

$$(CF_3)_2CFOF \xrightarrow{\Delta} CF_4 + CF_3C(=O)F$$

$$(CF_3)_3COF \xrightarrow{\Delta} CF_4 + (CF_3)_2CO .$$

The tendency to form alkanes is due to stabilisation of intermediate alkoxy-radicals by homolytic fission of a carbon–carbon bond:

$$CF_3CF_2OF \xrightarrow{\Delta} CF_3CF_2\dot{O} + F$$

$$CF_3CF_2\dot{O} \rightarrow \dot{C}F_3 + COF_2$$

$$CF_3CF_2OF + \dot{C}F_3 \rightarrow CF_4 + CF_3CF_2\dot{O} \quad \text{etc.}$$

Thermal breakdown of higher perfluoroalkyl hypofluorites is evidently a chain process, in which the presence of traces of hydrocarbons, e.g. methane, may have a similar effect to heating[44]:

$$CF_3CF_2OF + CH_4 \rightarrow HF + \dot{C}H_3 + CF_3CF_2\dot{O}$$

$$CF_3CF_2\dot{O} \rightarrow \dot{C}F_3 + COF_2 \quad \text{etc.}$$

This indicates that hypofluorites are potentially explosive, and requires that appropriate precautions should be observed when working with them.

Perfluoroalkyl hypochlorites are considerably inferior to the corresponding hypofluorites in thermal stability. For example, trifluoromethyl hypochlorite decomposes completely when heated to 165 °C:[69]

$$CF_3OCl \xrightarrow{\Delta} CF_3\dot{O} + \dot{Cl}$$
$$CF_3OCl + \dot{Cl} \rightarrow Cl_2 + CF_3\dot{O}$$
$$2CF_3\dot{O} \rightarrow CF_3OOCF_3$$
$$CF_3\dot{O} \rightarrow COF_2 + F \cdot$$

Products of the thermal breakdown of pentafluoroethyl hypochlorite under still milder conditions are carbonyl difluoride, trifluoroacetyl fluoride, chlorotrifluoromethane, chlorine, and chlorine monofluoride. The thermal stability of the hypochlorites diminishes in the sequence

$$CF_3OCl > C_2F_5OCl > (CF_3)_3COCl \geqslant (CF_3)_2CFOCl.$$

Hydrogen- and alkyl-containing hypochlorites are stable only at room or slightly higher temperatures. Their thermal decomposition yields polyfluorinated derivatives: e.g.

$$CH_3C(CF_3)_2OCl \begin{cases} \rightarrow CF_3COCH_3 + CF_3Cl \\ \not\rightarrow CF_3COCF_3 + CH_3Cl \cdot \end{cases}$$

The relatively high stability of organofluorine halogenoperoxides is somewhat unexpected: trifluoromethyl fluoroperoxide and chloroperoxide can be kept at room temperature for a long time[86,87]. Heating the halogenoperoxide vapours to 100 °C is accompanied by decomposition:

$$CF_3OOF \xrightarrow{\Delta} CF_4 + O_2$$
$$CF_3OOCl \xrightarrow{\Delta, SiO_2} COF_2 + CO_2 + SiF_4 + FClO_2 \cdot$$

## 2. Photolysis

The character of the breakdown products resulting from the ultraviolet irradiation of organofluorine hypohalites and halogenoperoxides depends on the conditions. Gaseous trifluoromethyl hypofluorite gives a low yield of trifluoromethyl peroxide[36]. Photolysis in an argon matrix[110] (with $\lambda < 400$ nm at 8 K, followed by infrared analysis of the products) yields only carbonyl difluoride. Monitoring photolysis of the hypofluorite by electron spin resonance (e.s.r.) (at −196 °C, mixed with nitrogen trifluoride or carbon tetrafluoride) revealed the peroxy-radical $CF_3OO^{\cdot}$, whose formation was attributed to the presence of traces of oxygen[111]. Intermediate formation of the radical $CF_3OOO^{\cdot}$ has been explained[112] by photosensitised oxidation of carbon monoxide to the dioxide on ultraviolet exposure of a mixture of the hypofluorite with the monoxide and oxygen. The quantum yield of carbon dioxide is ~$10^4$ molecules.

Photodecomposition of trifluoromethyl hypochlorite at room temperature gives a high yield (91%) of trifluoromethyl peroxide, and has been proposed as a method of preparation of the latter[69]:

$$2CF_3OCl \xrightarrow{h\nu} CF_3OOCF_3 + Cl_2 \cdot$$

In an argon matrix ($\lambda < 280$ nm), however, breakdown of the hypochlorite is more complicated[110]:

$$CF_3OCl \xrightarrow{8K, h\nu} CF_3OOCF_3 + CF_3OF + COF_2 + COFCl \cdot$$

In relation to the photodecomposition of organofluorine halogenoperoxides it is known that they serve as sources of perfluoroalkylperoxy-radicals, the products of whose further breakdown depend on the nature of the initial compound[87,113]:

$$CF_3OOF \xrightarrow{h\nu} CF_3O\dot{O} + \dot{F} \rightarrow CF_4 + O_2$$
$$CF_3OOCl \xrightarrow{h\nu} CF_3O\dot{O} + ClO_2 + O_2 \cdot$$

## 3. Reactions with Inorganic Compounds

Perfluoroalkyl hypofluorites display both fluorinating and oxidising properties towards inorganic compounds. Their fluorinating power is somewhat weaker than that of elementary fluorine; nevertheless, they can replace the latter in many reactions.

Water hydrolyses hypofluorites considerably more slowly than perfluoroacyl fluorides[6]. They react with aqueous alkalis to form perfluorocarboxylates and oxygen[11,44,45]; a *gem*-bishypofluorite yields the carbonate[55]:

$$R_FCF_2OF + 4NaOH \rightarrow R_FCOONa + 3NaF + 2H_2O + {}^1/_2O_2$$
$$CF_2(OF)_2 + 6NaOH \rightarrow Na_2CO_3 + 4NaF + 3H_2O + O_2 \cdot$$

Very dilute aqueous alkalis resemble water in their hydrolytic action. Recommendations[92] for the purification of trifluoromethylhypofluorite from traces of carbonyl difluoride are based on this property.

Like elementary fluorine, hypofluorites readily react with dry alkali-metal halides on being heated, with evolution of the corresponding halogens[6]:

$$CF_3OF + 2NaCl \rightarrow COF_2 + 2NaF + Cl_2 \cdot$$

The redox reaction with aqueous potassium iodide

$$CF_3CF_2OF + 2KI + H_2O \rightarrow CF_3COOK + I_2 + KHF_2$$

has been proposed[6,44,45] for the detection and determination of fluorooxy-groups.

Hypofluorites withstand the action of strong inorganic acids. For example, perfluoro-t-butyl hypofluorite is only 5% decomposed after contact with 98% sulphuric acid for 2 h.[44]

Dry quartz and Pyrex glass do not react with trifluoromethyl hypofluorite at room temperature[6]. Copper, nickel, and stainless steel begin to react only when strongly heated[6]. Alkali metals and mercury interact with hypofluorites on simple contact[114]. In the presence of mercury decomposition is a radical process[44]:

$$(CF_3)_3COF + Hg \rightarrow (CF_3)_3C\dot{O} + {}^1/_2HgF_2$$
$$(CF_3)_3C\dot{O} \rightarrow (CF_3)_2CO + \dot{C}F_3$$
$$(CF_3)_3COF + \dot{C}F_3 \rightarrow (CF_3)_3C\dot{O} + CF_4 \quad \text{etc.}$$

Interaction with ferrocene occurs similarly. Because of the change in colour this reaction can be used to detect fluorooxy-groups[44]:

$$CF_3CF_2OF + 2Fe(C_5H_5)_2 \rightarrow CF_3COF + 2\overset{+}{F}e(C_5H_5)_2 \cdot$$
(orange) (dark blue)

In the absence of impurities trifluoromethyl hypofluorite does not react with hydrogen at room temperature, but a reaction giving carbonyl difluoride and hydrogen fluoride can be initiated by copper powder[6]. The most significant example of the great fluorinating power of this hypofluorite is its reaction with xenon to form the difluoride[115]:

$$2CF_3OF + Xe \xrightarrow{250°C} XeF_2 + CF_3OOCF_3 \cdot$$

The reactions of trifluoromethyl hypofluorite with sulphur and nitrogen derivatives are important. At 0 °C elementary sulphur forms mainly the tetrafluoride, disulphur difluoride, and carbonyl difluoride, presumably contaminated with the unstable trifluoromethyl fluorothiosulphite and bistrifluoromethyl thiosulphite[116]. Addition at the carbon–sulphur multiple bond is observed with thiocarbonyl dichloride[116], when one of the addition products could not be isolated in the free state:

$$Cl_2C{=}S \xrightarrow[-78°C]{CF_3OF} \begin{cases} \rightarrow Cl_2CF{-}S{-}OCF_3 \\ \rightarrow [Cl_2C(OCF_3){-}SF] \xrightarrow{2CF_3OF} SF_4 + COF_2 + CF_3OCFCl_2 \cdot \end{cases}$$

The less reactive carbonyl sulphide reacts with trifluoromethyl hypofluorite to form bistrifluoromethyl sulphite and carbonate together with trifluoromethyl fluoroformate[116]. Electron spin resonance has established[117] that the radicals $(CF_3O)_2S^{\cdot}COOCF_3$ and $(CF_3O)_2S^{\cdot}COF$ are formed as active intermediate species.

Radical reactions include also those of trifluoromethyl hypofluorite with sulphur dioxide and tridoxide and with sulphur tetrafluoride. When heated to 175–185 °C sulphur dioxide is converted into a complicated mixture in which trifluoromethyl fluorosulphate and fluoropyrosulphate have been identified together with bistrifluoromethyl sulphate and pyrosulphate[118].

The reaction with sulphur trioxide is more unambiguous:

$$CF_3OF + SO_3 \rightarrow CF_3OOSO_2F \ .$$

Even in this case, however, trifluoromethyl and fluorosulphonyl peroxides have been isolated among the by-products. Detailed investigations indicate[92] that the reaction mechanism involves the primary stages

$$CF_3OF \rightleftarrows CF_3\dot{O} + \dot{F}$$
$$SO_3 + \dot{F} \rightarrow \dot{S}O_3F$$
$$2\dot{S}O_3F \rightleftarrows FSO_2OOSO_2F$$
$$CF_3\dot{O} + \dot{S}O_3F \rightarrow CF_3OOSO_2F$$
$$2CF_3\dot{O} \rightarrow CF_3OOCF_3 \ .$$

Reaction with sulphur tetrafluoride involves intermediate formation[119,120] of the radical $CF_3OS^{\cdot}F_4$, which under thermal conditions[121] abstracts a fluorine atom from the hypofluorite:

$$CF_3OSF_4 + CF_3OF \rightarrow CF_3OSF_5 + C\dot{F}_2O \ .$$

Ultraviolet exposure produces also bistrifluoromethyl tetrafluorodioxosulphate, in 10% yield[122]. It is significant that the reaction with sulphur tetrafluoride depends appreciably on the presence of particular impurities. For example, dissolved oxygen may be responsible for the formation of peroxy-compounds, and tetrafluorohydrazine for *NN*-difluoroamidosulphates[123]:

$$CF_3O\dot{S}F_4 + O_2 \rightarrow CF_3OSF_4O\dot{O} \xrightarrow{CF_3O\dot{S}F_4} CF_3OSF_4OOSF_4OCF_3$$
$$CF_3O\dot{S}F_4 + N_2F_4 \rightarrow CF_3OSF_4NF_2 + \dot{N}F_2 \ .$$

As a consequence of the ease of fission of the nitrogen–nitrogen bond tetrafluorohydrazine causes decomposition of trifluoromethyl hypofluorite even in the dark at room temperature[124]:

$$CF_3OF + NF_2 \rightleftarrows N_2F_4 \begin{cases} \rightarrow COF_2 + NF_3 \\ \rightarrow NOF + NF_3 + CF_4 \end{cases} .$$

For a similar reason the hypofluorite breaks down in the presence of nitrogen dioxide[125]:

$$CF_3OF + NO_2 \rightleftarrows FONO + CF_3\dot{O} \quad (N_2O_4)$$
$$CF_3\dot{O} + NO_2 \rightarrow FONO + COF_2; \quad FONO \rightarrow FNO_2 \ .$$

However, ultraviolet initiation yields *NN*-difluoro-*O*-trifluoromethylhydroxylamine[124,126–128]:

$$CF_3OF + N_2F_4 \xrightarrow{h\nu} CF_3ONF_2 + NF_3 \ .$$

Formation of similar derivatives from difluoroamine and difluoromethylene bishypofluorite[129] is a heterogeneous process involving an alkali-metal fluoride:

$$CF_2(OF)_2 + HNF_2 \xrightarrow{KF} CF_2(ONF_2)OF + CF_2(ONF_2)_2 \ .$$

Perfluoro-t-butyl hypofluorite reacts with tetrafluorohydrazine in perfluoropentane on ultraviolet irradiation to form a peroxide and nitrogen trifluoride by homolysis of the oxygen–fluorine bond[130]:

$$2(CF_3)_3COF + N_2F_4 \xrightarrow[-60°C]{h\nu} (CF_3)_3COOC(CF_3)_3 + NF_3 \ .$$

It has been stated[131] that the bond undergoes heterolytic fission in the absence of a solvent and radiation, to give a hydrazinium salt as a crystalline adduct:

$$(CF_3)_3COF + N_2F_4 \rightarrow (CF_3)_3C\overset{+}{O}\overset{+}{N}_2F_5 \ .$$

However, this has proved incorrect[247].

Perfluoroalkyl hypochlorites also exhibit strong polarisation of the oxygen–halogen bond and a tendency to undergo electrophilic processes. For example, they are very readily hydrolysed by water, with the rate of hydrolysis decreasing in the sequence[79]

$$(CF_3)_3COCl > CH_3C(CF_3)_2OCl > (CF_3)_2CHOCl > CF_3CH_2OCl \gg (CH_3)_3COCl \ .$$

Hypochlorites react smoothly with sulphur dioxide to form the corresponding alkyl chlorosulphates in theoretical yield[132,133]:

$$R_FOCl + SO_2 \xrightarrow{-20°C} R_FOSO_2Cl \ .$$

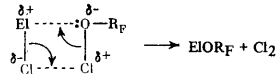
The reactions of hypochlorites with compounds containing negatively polarised halogen (boron trichloride, phosphorus chlorotetrafluoride, and hydrogen chloride) are probably of ionic type[134–136]:

$$R_FOCl \begin{cases} \xrightarrow{BCl_3} (R_FO)_3B + 2Cl_2 \\ \xrightarrow{PClF_4} R_FOPF_4 + Cl_2 \end{cases} .$$

Among these the reaction of trifluoromethyl hypochlorite with hydrogen chloride is especially interesting, yielding trifluoromethanol (m.p. −82 °C), which was stable up to −20 °C:[136]

$$CF_3OCl + HCl \xrightarrow{-120°C} \begin{cases} CF_3OH + Cl_2 \\ COF_2 + HF \end{cases} .$$

From general considerations it may be suggested that in all three cases positive polarisation of the halogen in the hypochlorite and a deficit of electrons in the other reactant result in a cyclic transition state:




El = H, > B, ≫ P

The reactions of hypochlorites with fluorine on heating and with tetrafluorohydrazine on ultraviolet irradiation are of radical type[69]:

$$CF_3OCl \begin{cases} \xrightarrow[65°C]{F_2} CF_3OF + Cl_2 \\ \xrightarrow[h\nu]{N_2F_4} CF_3ONF_2 + Cl_2 \end{cases} .$$

In contrast to certain organofluorine hypohalites, the halogenoperoxides react only by a radical mechanism. With trifluoromethyl fluoroperoxide products resulting from cleavage at oxygen–fluorine and oxygen–oxygen bonds could be isolated depending on the nature of the substrate. The former bond is broken when the fluoroperoxide is treated with nitrogen dioxide[137]:

$$CF_3OOF + N_2O_4 \rightarrow CF_3OONO_2 + FNO_2 \ .$$

The reactions with sulphur dioxide and tetrafluoride involve fission of the peroxy-bond[138]:

$$CF_3OOF + SO_2 \rightarrow CF_3OSO_2F + CF_3OSO_2OSO_2F$$
$$CF_3OOF + SF_4 \rightarrow CF_3OSF_4OCF_3 + CF_3OSF_5 \ .$$

Attempts to bring trifluoromethyl chloroperoxide into reaction with sulphur dioxide[87] and the hypochlorite into reaction with ozone[139] have been unsuccessful.

### 4. Reactions with Organic Compounds

The considerable literature on the reactions of organofluorine hypohalites and halogenoperoxides with organic derivatives covers addition at the multiple bonds C:O, C:N, and C:C, as well as the fluorination of various saturated compounds.

Among carbonyl derivatives the fullest information has been obtained for the action of the difluoride on trifluoromethyl hypofluorite, leading to formation of trifluoromethyl peroxide[140–146]:

$$CF_3OF + COF_2 \rightleftarrows CF_3OOCF_3 \ .$$

The reactants are heated in a static reaction vessel[142,143] or in the presence of a catalyst in a flow[24,143]. The optimum temperature of the uncatalysed preparation lies in the range 220–275 °C: up to 250 °C the equilibrium is displaced towards formation of the peroxide, and at higher temperatures slow decomposition of the latter begins. As could be expected, the yield is increased by raising the pressure in the system: thus with 100 atm at 275 °C the yield of the peroxide reaches 91%.[142]

Detailed kinetic investigations have been made[140,145–148] on these processes. The rate-determining stage is breakdown of the hypofluorite with cleavage of the oxygen–fluorine bond:

$$\left.\begin{array}{l} CF_3OF \rightarrow CF_3\dot{O} + \dot{F} \quad \text{slow} \\ \dot{F} + COF_2 \rightarrow CF_3\dot{O} \\ 2CF_3\dot{O} \rightarrow CF_3OOCF_3 \end{array}\right\} \text{rapid}$$

The possibility of the catalytic preparation of trifluoromethyl peroxide was discovered when the hypofluorite conterminated with carbonyl difluoride was stored in a steel vessel for a year[143]. Further investigations showed that the reaction is accelerated by the presence of fluorides of silver, copper, nickel, mercury, cobalt, iron[143,144], and caesium[24]. The fact that the peroxide is formed under mild conditions (at room temperature) casts doubt on the suggested[21] radical initiation of the process. In the presence of the most active catalyst (caesium fluoride) the reaction is probably analogous to the formation of trifluoromethyl hypofluorite from carbonyl difluoride and fluorine:

$$COF_2 + CsF \rightarrow CF_3\bar{O}\overset{+}{C}s$$
$$CF_3\bar{O}\overset{+}{C}s + CF_3OF \rightarrow CF_3OOCF_3 + CsF \ .$$

Activation of carbonyl difluoride by the remaining catalysts is probably not a chemisorption process. According to a patent[149] the peroxide can be obtained by the action of chlorine trifluoride on carbonyl difluoride in the presence of a fluoride of an alkali-earth metal, which is a modification of the method based on the action of fluorine on carbonyl difluoride[143].

Difluoromethylene bishypofluorite, unlike trifluoromethyl hypofluorite, does not give normal addition products at the carbonyl bond[150–153]. As a consequence of degradation the main products are bistrifluoromethyl trioxide and trifluoromethyl fluoroperformate:

$$CF_2(OF)_2 + COF_2 \xrightarrow{CsF} CF_3OOOCF_3 + CF_3OOC(O)F \ .$$

The latter compound on cautious hydrolysis gives the hydroperoxide[154]:

$$CF_3OOC(O)F \xrightarrow{H_2O} CF_3OOH \ .$$

The reaction of trifluoromethyl hypofluorite with difluorocarbamoyl fluoride is also anomalous, with formation of *NN*-difluoro-*O*-trifluoromethylhydroxylamine instead of the expected peroxide[155]:

$$NF_2COF + CF_3OF \rightarrow \begin{cases} NF_2OCF_3 \\ NF_2CF_2OOCF_3 \end{cases}$$

The fluorination of perfluoroglutaryl difluoride yields perfluorofuran, whose precursor is assumed to be an unstable fluorocarbonylperfluoroalkyl hypofluorite[16]:

$$FC(O)(CF_2)_3C(O)F + F_2 \xrightarrow{CsF} \left[FO(CF_2)_4C(O)F\right] \xrightarrow{-COF_2} \begin{array}{c} O \\ CF_2 \quad CF_2 \\ CF_2{-}CF_2 \end{array} \ .$$

The action of fluorine in cyclising copper and nickel hexafluoroacetylacetonates into cyclic peroxides is probably of the same type[53].

Under conditions of thermal and photochemical initiation trifluoromethyl hypofluorite reacts with carbon monoxide to form the fluoroformic and oxalic esters[156–159]. The mechanisms of photolysis and thermolysis differ in the first stage, which serves as source of trifluoromethoxy-radicals:

$$CF_3OF \xrightarrow{h\nu} CF_3\dot{O} + \dot{F}$$
$$CF_3OF + CO \xrightarrow{\Delta} CF_3\dot{O} + \dot{C}OF$$
$$CF_3\dot{O} + CO \rightarrow CF_3O\dot{C}O$$
$$CF_3O\dot{C}O + CF_3OF \rightarrow CF_3OC(O)F + CF_3\dot{O}$$
$$2CF_3O\dot{C}O \rightarrow CF_3OC(O)C(O)OCF_3 \ .$$

At room temperature in the dark no reaction takes place[159]. As a consequence of degradation, photolysis of a mixture of the hypofluorite with hexafluoroacetone forms small quantities of bistrifluoromethyl carbonate[160]:

$$(CF_3)_2CO + CF_3OF \xrightarrow{h\nu} (CF_3O)_2CO \ .$$

The reaction with carbon monoxide, like that discussed above with sulphur dioxide, provides additional evidence of the differing reactivities of fluorooxy- and chlorooxy-derivatives. Carbon monoxide reacts with the more active hypochlorites under mild conditions to give nearly quantitative yields of perfluoroalkyl chloroformates[61,69,79–81,159,161–163]:

$$R_FOCl + CO \rightarrow R_FOCOCl \ .$$

A kinetic scheme has been suggested[164] for the photochemical process, analogous to the formation of trifluoromethyl fluoroformate; with a pressure of 100 mmHg at 30 °C the quantum yield is $10^4$ molecules of the hypochlorite. In the dark, reaction between carbon monoxide and trifluoromethyl hypochlorite probably begins with bimolecular initiation, which is secured by the relatively low energy of the oxygen–chlorine bond (~38 kcal mole$^{-1}$):[165]

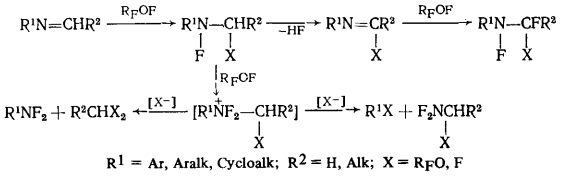
$$CF_3OCl + CO \rightarrow CF_3\dot{O} + \dot{C}OCl \ .$$

The capacity for addition at the carbonyl bond in organofluorine hypochlorites parallels their stability. For example, the very unstable *O*-chlorinated perfluoropinacol obtained *in situ* has only a weak chlorinating and oxidising action on benzaldehyde[166]:

$$(CF_3)_2C(ONa)-C(ONa)(CF_3)_2 \xrightarrow[CFCl_3]{Cl_2} \left[(CF_3)_2C(OCl)-C(OCl)(CF_3)_2\right] \xrightarrow[CCl_4]{h\nu,\ PhCHO} \rightarrow PhCOOH + PhCOCl + (CF_3)_2CClCCl(CF_3)_2 \ .$$

The direction of addition of organofluorine hypohalites to compounds containing multiple carbon–nitrogen bonds is consistent with the electrophilic character of the former and

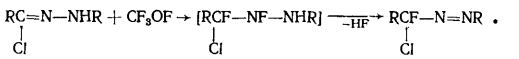
the donor power of the nitrogen atom. Because of the instability of the initial adducts the reaction is usually accompanied by degradation with formation of the corresponding *N*-fluoroamines or fluorination of the carbon–nitrogen bond. It has been shown for Schiff bases as example[167–170] that fluorination occurs mostly when the methine group is unsubstituted, but degradation occurs when alkyl or alkoxyl is attached to the carbon atom:



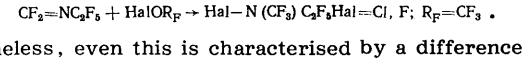
$R^1$ = Ar, Aralk, Cycloalk; $R^2$ = H, Alk; X = $R_FO$, F

Compounds in which the substituent X = $CF_3O$ are rarely met among the products. If the reaction is conducted in an inert solvent (e.g. fluorochloroform), derivatives with X = F are obtained. If alcohols are added to the reaction mixture, ethers and acetals (X = AlkO) are formed.

Because of the good yields of difluoroamines it has been proposed to use the reaction between hypofluorites and Schiff bases as a method of preparation[169]. Hypofluorites prove quite useful also for obtaining azoalkanes[171]:

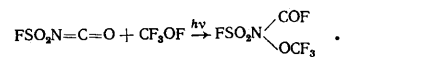


Perfluoroaza-alkenes react with organofluorine hypohalites under more severe conditions:

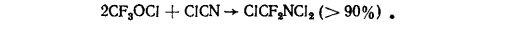


Nevertheless, even this is characterised by a difference in reactivity: hypochlorites do not require heating, whereas fluorooxy-derivatives have a fluorinating effect at high temperatures. This has been regarded[172] as indicating a transition from an ionic to a radical mechanism.

A radical mechanism obviously operates in the reaction between perfluoroguanidine and difluoromethylene bishypofluorite[173,174], from which a large number of products have been isolated. The only case in which a stable *N*-trifluoromethoxy-derivative has been obtained (in 30% yield) is the photochemical reaction between fluorosulphonyl isocyanate and trifluoromethyl hypofluorite[175]:



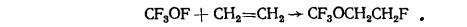
The reaction between trifluoromethyl hypochlorite and cyanogen chloride reveals the strong chlorofluorinating effect of the former on nitriles[72,176]:



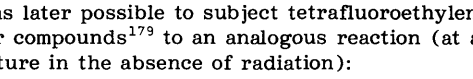
Discussion of the reactivity of organofluorine hypohalites and halogenoperoxides towards compounds containing an ethylenic bond have some bearing on the problem of anomalous electrophilic substitution, which has recently been widely discussed[177]. Since detailed examined in relation to the present compounds would be a major task outside the scope of the present Review, we shall consider only the most important points.

It must first be noted that the main criterion in assessing the nature of processes involving the ethylenic bond is the state of aggregation of the reactants. Reactions between gases usually take place by a free-radical mechanism. In the liquid phase organofluorine hypohalites and halogenoperoxides often exhibit electrophilic properties at the initiation stage, attacking the substrate at the site of maximum electron density.

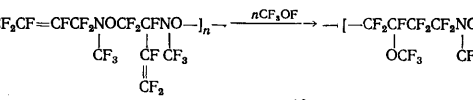
One of the earliest studies of the chemistry of hypofluorites had shown[178] that ethylene and tetrafluoroethylene react explosively with trifluoromethyl hypofluorite. Only great dilution with nitrogen and ultraviolet irradiation enabled the ethylene addition product to be isolated:



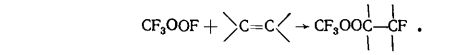
It was later possible to subject tetrafluoroethylene[41] and other compounds[179] to an analogous reaction (at a low temperature in the absence of radiation):



The stabilisation of polymeric materials by trifluoromethyl hypofluorite is a radical process[180,181]:

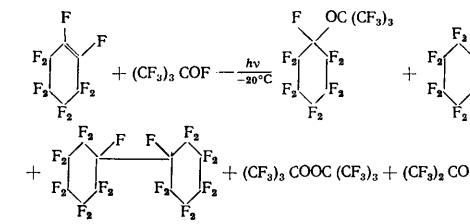


Fluoroperoxides add to alkenes[182]:



Reaction of the hypofluorite with symmetrical dichlorodifluoroethylene occurs similarly[183].

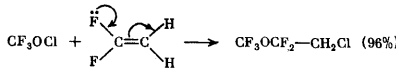
Under poorly controlled temperature conditions hypofluorites and unsaturated compounds form a large number of products, as in radical reactions of elementary fluorine. A similar result can be obtained in the case of intermediate radicals showing little tendency to attack a multiple bond. For example, the photochemical reaction of perfluoro-t-butyl hypofluorite with a perfluorocycloalkene gives a complicated mixture of peroxides, ethers, cycloalkanes, their dimers, hexafluoroacetone, and tetrafluoromethane[184]:



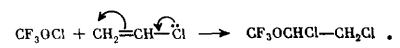
In the absence of ultraviolet radiation at 0 °C only decomposition of the hypofluorite is observed. On the other hand, with trifluoromethyl hypofluorite (ultraviolet exposure at −60 °C) the reaction is highly selective, as is indicated by the theoretical yield of perfluoromethoxycyclohexane.

The change in character of the reactions of organofluorine hypohalites and halogenoperoxides with alkenes from radical to electrophilic largely depends on the nature of the oxygen–halogen and ethylenic bonds. As in certain reactions with inorganic substances, such a change occurs primarily with hypochlorites. It is apparent in intermediate addition of the positively polarised halogen atom to the carbon atom possessing the greatest electron density.

Trifluoromethyl hypochlorite reacts with vinylidene difluoride to form in effect a single isomer[185]:



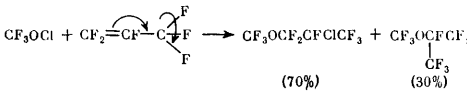
Similar orientation occurs with vinyl chloride[185]¶



Trifluoromethyl chloroperoxide reacts similarly[186]:

$$CF_2{=}CCl_2 + CF_3OOCl \rightarrow CF_3OOCF_2CCl_3\ (>50\%)$$
$$CH_2{=}CF_2 + CF_3OOCl \rightarrow CF_3OOCF_2CH_2Cl\ (>50\%)$$

with formation of 2,2,2-trichloro-1,1-difluoroethyl trifluoromethyl ether and 2-chloro-1,1-difluoroethyl trifluoromethyl ether (<10%) as by-products. Sometimes both isomers are formed, but with the "normal" addition product predominating[185,187,188]:



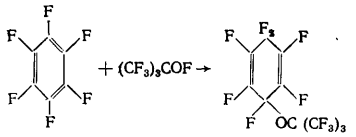

This is consistent with views on a radical-ion reaction mechanism, in which polar effects play a leading part.

The occurrence of electrophilic attack at the site of greatest electron density in the double bond is confirmed no less convincingly by many reactions involving perfluoroalkyl hypofluorites[47,189-223]. This property has not only theoretical applications but also wide synthetic use for introducing fluorine into biologically active compounds—uracil and cytosine derivatives[194-200], steroids[201-211], sugars[212-220], and aromatic compounds[189-193].

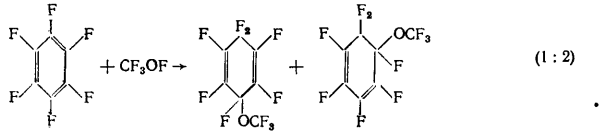
Because of the strong negative inductive effect of the perfluoro-t-butyl group electrophilic properties are most characteristically developed in the corresponding hypofluorite. The latter reacts with hexafluoropropene and with perfluoroalkoxyethylenes[47] to give predominantly the straight-chain isomers:

$$CF_3CF{=}CF_2 + (CF_3)_3COF \rightarrow CF_3CF_2CF_2OC(CF_3)_3$$
$$R_FOCF{=}CF_2 + (CF_3)_3COF \rightarrow R_FOCF_2CF_2OC(CF_3)_3$$

the yield of "anomalous" addition products not exceeding 5%. Hexafluorobenzene gives a substituted cyclohexa-1,4-diene[189]:



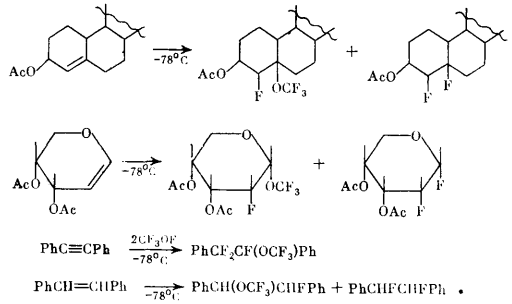
The 1,2-isomer is not formed, although in the case of trifluoromethyl hypofluorite both isomers have been isolated:



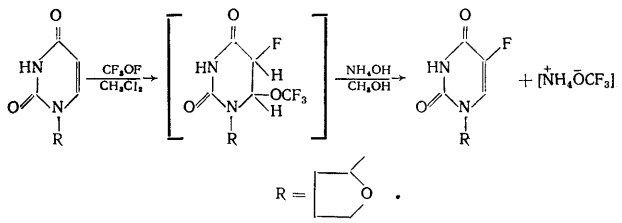

Addition of the latter hypofluorite to octafluorotoluene requires more severe conditions.

These results and the reaction with hexafluoropropene have suggested[189] that the action of hypofluorites on unsaturated compounds can be regarded as "electrophilic addition involving a fluoronium ion". It must be emphasised that this hypothesis applies only to the primary step—attack on the substrate by a polarised halogen atom—whereas the overall process obviously involves electron transfer. This is indicated in particular by the appearance of dimeric products in the reaction of hexafluorobenzene with perfluoro-t-butyl hypofluorite. It is also possible that the formation of isomeric cyclohexadienes from hexafluorobenzene and trifluoromethyl hypofluorite is a result of a cage process[177].

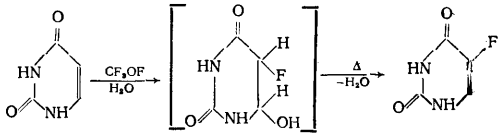
Trifluoromethyl hypofluorite adds at a double bond on reaction with steroids[190,202,204,210,211], anhydro-sugars[214,216,217,219-221], diphenylacetylene[190,204,206], stilbene[223], and uracil derivatives if an inert solvent (fluorochloroform, dichloromethane) is used. In several cases the corresponding difluorides are formed also, as a consequence of the fluorinating power of the hypofluorite:



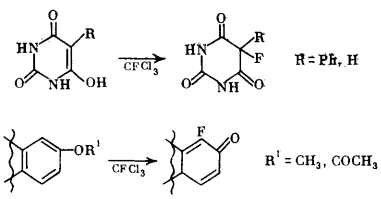
Trifluoromethoxy-derivatives are usually unstable, and pass into hydroxy-derivatives on subsequent treatment (heating) of the reaction mixtures. Treatment of such derivatives with basic reagents leads to elimination of the trifluoromethoxy-group. It is assumed[200] that an unstable alkoxide is formed, e.g. $^+NH_4O^-CF_3$ in the production of Fluorafur, an effective antitumour preparation:



Unstable intermediate products are formed also when unsubstituted uracil is treated with trifluoromethyl hypofluorite in trifluoroacetic acid containing water[195]:

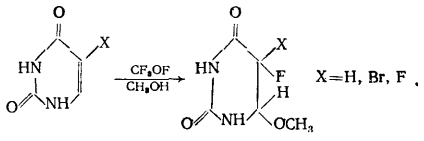


If hydroxyl, alkoxyl, or acetoxyl is present as substituent adjacent to the multiple bond, decomposition terminates in ketonisation[201-204,210,211]:

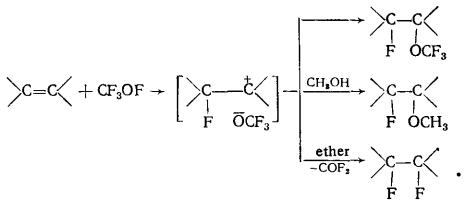


¶ Trifluoromethyl hypochlorite has been subjected to reaction also with ethylene and with tetrafluoroethylene.

If the fluorinating effect of trifluoromethyl hypofluorite is applied in the presence of methanol, the multiple bond undergoes fluoromethoxylation[199,201]:



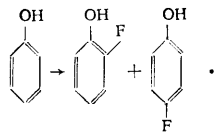
This extremely important experimental fact, together with other observations, led several authors to consider reactions between hypofluorites and activated unsaturated compounds to be ionic[199,201,203,210,216,217]. The first stage is regarded[199, 210,217] as involving formation of a carbocation, whose subsequent reactions depend on the experimental conditions and the nature of the substituents. In inert solvents the carbocation is stabilised by capture of a trifluoromethoxide anion. Electron-donor solvents (e.g. ether), which tend to stabilise the carbocation, displace the reaction towards formation of the difluoride:



Electron-donor substituents in the unsaturated compound have a similar effect. As the stronger base, methanol when present adds to the carbocation.

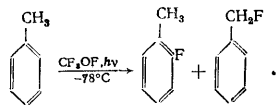
A detailed investigation of the stereochemistry of the processes, made on stilbene[223], showed *cis* addition independently of the nature of the products.

In the fluorination of aromatic compounds the electrophilic properties of hypofluorites are evident as *ortho* and (more rarely) *para* orientation when substituents such as hydroxy, alkoxy, and acylamino are present in the ring[190–193,224]:

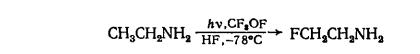


This case of "anomalous electrophilic substitution" has been reviewed[177] in terms of cage and free-radical processes.

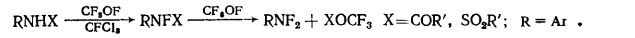
Under special conditions (ultraviolet irradiation) hypofluorites react with aromatic compounds probably by a radical mechanism. Thus toluene is fluorinated in the ring and in the side-chain[225]:



Photofluorination has enabled fluorine to be introduced into the ring and the side-chain of other aromatic hydrocarbons [226–229], and many aliphatic compounds to be fluorinated, including such polymeric materials as polycaprolactam and polyethylene[230,231]. The most suitable solvent for photofluorination is liquid hydrogen fluoride, in which the process occurs highly selectively, e.g. without affecting the amino-group[231]. This property has been utilised in the preparation of the antibacterial β-fluoro-α-alanine[232–235]:

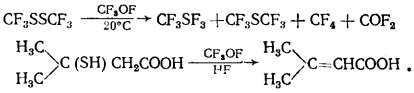


The high fluorinating power of hypofluorites is illustrated by their reactions with amines and amides to give *N*-fluorinated products[236–238]:

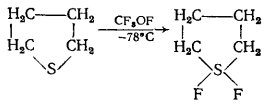


Amides in which the basicity of the nitrogen atom has been diminished constitute an exception. Thus the relatively inactive *N*-trifluoroacetyladamantylamine is fluorinated by trifluoromethyl hypofluorite at position 3 of the ring system[239].

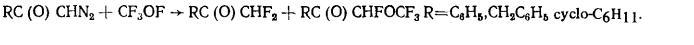
Organic compounds containing sulphur react variously with hypofluorites. Disulphides and thiols undergo degradation[240, 241]:



Aliphatic and cyclic sulphides form fluorothio-derivatives[242,243]:



Hypofluorites react very readily with compounds containing labile functional groups, e.g. with diazo-ketones[244]:



## V. POSSIBILITIES OF PRACTICAL APPLICATION

A survey of published information on the chemistry of organofluorine hypohalites enables us to recommend certain reactions for practical use.

Thus various trifluoromethyl ethers possessing an anaesthetic action can be obtained by addition to halogenated alkenes. Dehalogenation or dehydrohalogenation of such ethers is of interest for the preparation of fluorinated alkyl vinyl ethers. Perfluoromethoxyethylene was first obtained in this way[183].

Hypofluorites, being less active fluorinating agents than elementary fluorine, can be used to obtain biologically active preparations—5-fluorouracil[195], fluorobarbituric acid[201], fluorinated cytosine bases[199], Fluorafur[200], etc.

Organofluorine hypohalites themselves are effective insecticides, fungicides, and brightening agents for paper and textiles[62–64]. Hypofluorites have been recommended for the surface sterilisation of materials that cannot readily be subjected to heat[245]. An important field of application of the hypohalites is the initiation of polymerisation[62–64,246].

However, the high toxicity of organofluorine hypohalites and their reactivity towards non-fluorinated organic compounds make their use potentially dangerous. The precautionary measures usual in work with elementary fluorine must be taken when these compounds are used.

## REFERENCES

1. K.B.Kellog and G.H.Cady, J.Amer.Chem.Soc., 70, 3986 (1948).
2. D.E.Gould, L.R.Anderson, D.E.Young, and W.B.Fox, Chem.Comm., 1564 (1968).
3. A.Sennig, Chem.Rev., **65**, 385 (1965).

4. R.D.W.Kemmit and D.W.A.Sharp, Adv.Fluorine Chem., **4**, 142 (1965).
5. R.E.Banks, "Fluorocarbons and their Derivatives", Oldbourne Press, London, 1964.
6. C.J.Hoffman, Chem.Rev., **64**, 91 (1964).
7. C.J.Hoffman, Chem.Rev., **64**, 91 (1964). [sic].
8. M.Lustig and J.M.Shreeve, Adv.Fluorine Chem., **7**, 175 (1973).
9. R.C.Kennedy and G.H.Cady, J.Fluorine Chem., **3**, 41 (1973).
10. D.E.Young, L.R.Anderson, and W.B.Fox, Inorg. Nuclear Chem.Letters, **6**, 341 (1970).
11. M.Lustig, A.R.Pitochelli, and J.K.Ruff, J.Amer.Chem. Soc., **89**, 2841 (1967).
12. J.K.Ruff, A.R.Pitochelli, and M.Lustig, J.Amer.Chem. Soc., **88**, 4531 (1966).
13. R.L.Cauble and G.H.Cady, J.Amer.Chem.Soc., **89**, 5161 (1967).
14. P.G.Thompson, J.Amer.Chem.Soc., **89**, 4316 (1967).
15. M.Lustig and J.K.Ruff, Chem.Comm., 870 (1967).
16. US P.3 679 709 (1970).
17. R.Talbott, J.Org.Chem., **33**, 2095 (1968).
18. M.J.Hopkinson and D.D.Desmarteau, J.Fluorine Chem., **7**, 501 (1976).
19. D.T.Meshri and J.M.Shreeve, J.Amer.Chem.Soc., **90**, 1711 (1968).
20. R.C.Kennedy et al., Symp.on Fluorine Chemistry, Durham, 1971, A-8.
21. G.H.Cady, Anales soc.quím.argentina, **59**, No.3–4, 125 (1971).
22. J.F.Leibman and B.B.Jarvis, J.Fluorine Chem., **5**, 41 (1975).
23. V.A.Tyurikov, L.V.Okhlobystina, B.I.Shapiro, V.M.Khutoretskii, A.A.Fainzil'berg, and Ya.K.Syrkin, Izv.Akad.Nauk SSSR, Ser.Khim., 2373 (1972).
24. M.Wechsberg and G.H.Cady, J.Amer.Chem.Soc., **91**, 4432 (1969).
25. N.Watanabe and M.Takashima, J.Chem.Soc.Japan, Ind. Chem.Sect., **74**, 321 (1971).
26. US P.2 689 254 (1954); Chem.Abs., **43**, 11 681 (1955).
27. US P.3 179 702 (1965).
28. R.L.Cauble and G.H.Cady, J.Amer.Chem.Soc., **89**, 1962 (1967).
29. F.A.Hohorst and J.M.Shreeve, J.Amer.Chem.Soc., **89**, 1809 (1967).
30. F.A.Hohorst, Inorg.Synth., **11**, 143 (1968).
31. G.H.Cady, Inorg.Synth., **8**, 165 (1966).
32. J.C.Chagny et al., Note CEA, No.856, 287 (1966–1967).
33. J.Czarnowski and H.J.Schumacher, Z.phys.Chem. (Frankfurt), **58**, 149 (1968).
34. A.H.Jubert, J.E.Siecre, and H.J.Schumacher, Z.phys. Chem.(Frankfurt), **67**, 138 (1969).
35. H.J.Schumacher, Photochem.Photobiol., **7**, 755 (1968).
36. P.J.Aymonino, Proc.Chem.Soc., 341 (1964).
37. M.I.Lopez, E.Castellano, and H.J.Schumacher, J.Photochem., **3**, 97 (1974).
38. R.Veyre, Third European Symposium on Fluorine Chemistry, Aix-en-Provence, 1970, p.26.
39. P.J.Aymonino, Anales soc.quím.argentina, **55**, 47 (1967).
40. US P.3 422 159 (1966).
41. R.T.Holzmann and M.S.Cohen, Inorg.Chem., **1**, 972 (1962).
42. J.Fajer, D.R.McKenzie, and F.W.Bloch, J.Phys.Chem., **70**, 935 (1966).
43. L.B.Marantz, J.Org.Chem., **30**, 4380 (1965).
44. J.H.Prager and P.G.Thompson, J.Amer.Chem.Soc., **87**, 230 (1965).
45. P.G.Thompson and J.H.Prager, J.Amer.Chem.Soc., **89**, 2263 (1967).
46. US P.3 415 865 (1968).
47. M.S.Toy and R.S.Stringham, J.Fluorine Chem., **5**, 25 (1975).
48. US P.3 420 866 (1969).
49. J.H.Prager, J.Org.Chem., **31**, 392 (1966).
50. US P.3 442 927 (1969).
51. US P.3 344 194 (1967); Chem.Abs., **67**, 116 565 (1967).
52. US P.3 692 815 (1972).
53. R.L.Talbott, J.Org.Chem., **30**, 1429 (1965).
54. A.Ya.Yakubovich, M.A.Englin, and S.P.Makarov, Zhur.Obshch.Khim., **30**, 2374 (1960).
55. P.G.Thompson, J.Amer.Chem.Soc., **89**, 1811 (1967).
56. V.A.Ginsburg and A.A.Tumanov, Zhur.Obshch.Khim., **38**, 1410 (1968).
57. US P.3 622 601 (1971).
58. US P.3 687 825 (1972).
59. Jap.P.35 888 (1972).
60. S.Nagase, T.Abe, H.Baba, and K.Kodaira, Bull. Chem.Soc.Japan, **43**, 2980 (1970).
61. T.Abe, S.Nagase, and K.Kodaira, Bull.Chem.Soc. Japan, **43**, 957 (1970).
62. BRD P.1 953 144 (1970); Chem.Abs., **73**, 24 907 (1970).
63. BRD P.1 954 692 (1972); B.P.1 259 990 (1972).
64. BRD P.2 025 970 (1970); B.P.1 269 196 (1972); Chem. Abs., **74**, 63 905 (1971).
65. US P.3 842 156 (1974).
66. BRD P.1 958 346 (1970); Chem.Abs., **74**, 53O36 (1971).
67. BRD P.1 928 539 (1970); Chem.Abs., **72**, 54 743 (1970).
68. French P.1 589 946 (1970).
69. C.J.Schack and W.Maya, J.Amer.Chem.Soc., **91**, 2902 (1969).
70. D.E.Gould, L.R.Anderson, D.E.Young, and W.B.Fox, J.Amer.Chem.Soc., **91**, 1310 (1969).
71. B.P.1 273 408 (1972).
72. US P.3 769 312 (1973).
73. D.E.Young, L.R.Anderson, and W.B.Fox, Inorg. Chem., **9**, 2602 (1970).
74. R.Veyre, Thesis for Docteur de l'Université de Lyon en Sciences physiques, Lyon, 1969.
75. N.S.Nikolaev, V.F.Sukhoverkhov, Yu.D.Shishkov, and I.F.Alenchikova, "Khimiya Galoidnykh Soedinenii Ftora" (Chemistry of Halogen Compounds of Fluorine), Nauka, Moscow, 1968.
76. A.A.Opalovskii, Uspekhi Khim., **36**, 1673 (1967) [Russ. Chem.Rev., No.10 (1967)].
77. H.Meinert, Z.Chem., **7**, No.2, 41 (1967).
78. R.Veyre, M.Quenault, and C.Eyraud, Compt.rend., **268C**, 1480 (1969).
79. D.E.Young and L.R.Anderson, J.Amer.Chem.Soc., **92**, 2313 (1970).
80. B.P.1 259 176 (1972).
81. US P.3 755 405 (1973).
82. US P.3 716 570 (1973).
83. J.J.Solomon, A.J.Kacmarek, W.K.Sumida, and J.K.Raney, Inorg.Chem., **11**, 195 (1972).
84. L.R.Anderson and W.B.Fox, J.Amer.Chem.Soc., **89**, 4313 (1967).
85. I.N.Rozhkov, "Fifth International Symposium on Fluorine Chemistry", Zhur.Vses.Khim.Obshch.Mendeleeva, **15**, 92 (1970).
86. D.D.Desmarteau, Inorg.Chem., **11**, 193 (1972).
87. C.T.Ratcliffe, C.V.Hardin, L.R.Anderson, and W.B.Fox, J.Amer.Chem.Soc., **93**, 3886 (1971).
88. BRD P.2 103 370 (1971); French P.2 083 942 (1972); Chem.Abs., **76**, 3395 (1972).
89. US P.3 860 606 (1975).

90. J.J.Solomon, A.J.Kacmarek, et al., J.Amer.Chem.Soc., **90**, 6557 (1968).
91. US P.3 634 483 (1972).
92. J.Czarnowski et al., Z.phys.Chem.(Frankfurt), **65**, 225 (1969).
93. P.M.Christofer and L.L.Patterson, Austral.J.Chem., **21**, 2373 (1968).
94. P.Buckley and J.P.Weber, Canad.J.Chem., **52**, 942 (1974).
95. P.M.Wilt and E.A.Jones, J.Inorg.Nuclear Chem., **30**, 2933 (1968).
96. P.M.Wilt and E.A.Jones, J.Inorg.Nuclear Chem., **29**, 2108 (1967).
97. P.M.Wilt and E.A.Jones, J.Inorg.Nuclear Chem., **29**, 2112 (1967).
98. F.P.Diodati and L.C.Bartell, J.Mol.Structure, **8**, 395 (1971).
99. V.S.Mastryukov, Zhur.Strukt.Khim., **17**, 86 (1976).
100. P.J.Aymonino, J.Inorg.Nuclear Chem., **27**, 2675 (1965).
101. R.W.Mitchell and J.A.Merrit, J.Mol.Spectroscopy, **24**, 128 (1967).
102. R.R.Smardzewski and W.B.Fox, J.Fluorine Chem., **6**, 417 (1975).
103. G.H.Cady and C.J.Merril, J.Amer.Chem.Soc., **84**, 2260 (1962).
104. L.Phillips and V.Wray, J.Chem.Soc.B, 2068 (1971).
105. L.Phillips and V.Wray, J.Chem.Soc., Perkin Trans.II, 220 (1972).
106. C.J.Thynne and K.A.G.Macheil, Internat.J.Mass. Spectrom.Ion Phys., **5**, 95 (1970).
107. G.D.Foss and D.A.Pitt, J.Phys.Chem., **72**, 3512 (1968).
108. C.Sieiro, P.Gonzalez-Diaz, and Y.G.Smeyers, J.Mol. Structure, **25**, 345 (1975).
109. R.S.Porter and G.H.Cady, J.Amer.Chem.Soc., **79**, 5628 (1957).
110. R.R.Smardzewski and W.B.Fox, J.Phys.Chem., **79**, 219 (1975).
111. N.Vanderkooi and W.B.Fox, J.Chem.Phys., **47**, 3634 (1967).
112. P.J.Aymonino and M.A.Blesa, Z.phys.Chem.(Frankfurt), **80**, 129 (1972).
113. R.R.Smardzewski, R.A.DeMarco, and W.B.Fox, J. Chem.Phys., **63**, 1083 (1975).
114. R.S.Porter and G.H.Cady, J.Amer.Chem.Soc., **79**, 5625 (1957).
115. G.L.Gard, F.B.Dudley, and G.H.Cady, Noble-Gas Compounds, 109 (1963).
116. R.E.Bayley and G.H.Cady, Inorg.Chem., **9**, 1930 (1970).
117. J.R.Morton and K.F.Preston, J.Phys.Chem., **77**, 2645 (1973).
118. W.P.VanMefer and G.H.Cady, J.Amer.Chem.Soc., **82**, 6005 (1960).
119. J.R.Morton and K.F.Preston, Chem.Phys.Letters, **18**, 98 (1973).
120. A.R.Gregory, S.E.Karavelas, et al., J.Amer.Chem. Soc., **97**, 2206 (1975).
121. G.Pass and H.L.Roberts, Inorg.Chem., **2**, 1016 (1963).
122. L.C.Duncan and G.H.Cady, Inorg.Chem., **3**, 850 (1964).
123. L.C.Duncan and G.H.Cady, Inorg.Chem., **3**, 1045 (1964).
124. W.H.Hall and S.M.Williamson, Inorg.Chem., **4**. 1342 (1965).
125. J.Czarnowski and H.J.Schumacher, Z.phys.Chem. (Frankfurt), **78**, 234 (1972).
126. J.M.Shreeve, L.C.Duncan, and G.H.Cady, Inorg. Chem., **4**, 1516 (1965).
127. R.Schmutzler, Angew.Chem., **80**, 466 (1968).
128. W.B.Fox, G.Franz, and L.R.Anderson, Inorg.Chem., **7**, 382 (1968).
129. US P.3 633 588 (1972).
130. M.S.Toy and R.S.Stringham, J.Fluorine Chem., **7**, 315 (1976).
131. M.S.Toy and R.S.Stringham, J.Fluorine Chem., **7**, 229 (1976).
132. US P.3 681 423 (1972).
133. US P.3 654 335 (1972).
134. D.E.Young and W.B.Fox, Inorg.Nuclear Chem.Letters, **7**, 1033 (1971).
135. D.E.Young, L.R.Anderson, and W.B.Fox, Inorg.Chem., **10**, 2810 (1971).
136. K.Seppelt, Angew.Chem., **89**, 325 (1977).
137. F.A.Hohorst and D.D.Desmarteau, Inorg.Chem., **13**, 715 (1974).
138. R.A.DeMarco and W.B.Fox, Inorg.Nuclear Chem. Letters, **10**, 965 (1974).
139. C.J.Schack and K.O.Christe, Inorg.Chem., **13**, 2378 (1974).
140. J.Czarnowski and H.J.Schumacher, Z.phys.Chem. (Frankfurt), **73**, 68 (1970).
141. H.J.Schumacher, Seventh International Symposium on Fluorine Chemistry, Santa Cruz, California, 1973, S.1, S.a., No.P-1.
142. H.L.Roberts, J.Chem.Soc., 4538 (1964).
143. US P.3 230 264 (1966); Chem.Abs., **64**, 12 550 (1966).
144. US P.3 100 083 (1963).
145. R.C.Kennedy and J.B.Levy, J.Phys.Chem., **76**, 3480 (1972).
146. J.B.Levy and R.C.Kennedy, J.Amer.Chem.Soc., **94**, 3302 (1972).
147. B.Descamps and W.Forst, J.Phys.Chem., **80**, 933 (1976).
148. B.Descamps and W.Forst, Canad.J.Chem., **53**, 1442 (1975).
149. US P.3 202 718 (1965).
150. L.R.Anderson and W.B.Fox, Inorg.Chem., **9**, 2182 (1970).
151. D.D.Desmarteau, Inorg.Chem., **9**, 2179 (1970).
152. US P.3 576 837 (1971); Chem.Abs., **75**, 35 130 (1971).
153. P.A.Bernstein et al., J.Amer.Chem.Soc., **93**, 3882 (1971).
154. P.A.Bernstein, F.A.Hohorst, and D.D.Desmarteau, Polymer Prepr., **12**, 378 (1971).
155. G.W.Fraser and J.M.Shreeve, Inorg.Chem., **6**, 1711 (1967).
156. P.J.Aymonino, Photochem.Photobiol., **7**, 761 (1968).
157. M.A.Blesa and P.J.Aymonino, Anales Asoc.quím. argentina, **56**, 101 (1968).
158. M.A.Blesa and P.J.Aymonino, Anales Asoc.quím. argentina, **56**, 113 (1968).
159. P.J.Aymonino, Chem.Comm., 241 (1965).
160. E.L.Varetti and P.J.Aymonino, Chem.Comm., 680 (1967).
161. US P.3 627 799 (1971).
162. D.E.Young and W.B.Fox, Tetrahedron Letters, 723 (1969).
163. US P.3 732 274 (1973).
164. L.Dicelio and H.J.Schumacher, Z.phys.Chem.(Frankfurt), **100**, 55 (1976).
165. R.H.Muller, D.L.Bernitt, and J.C.Hisatsuna, Spectrochim.Acta, **23A**, 233 (1967).
166. A.F.Janzen and R.Pollitt, Canad.J.Chem., **48**, 687 (1970).
167. M.J.Robins and S.R.Naik, J.Amer.Chem.Soc., **93**, 5277 (1971).

168. J.Leroy, F.Dudragne, J.C.Adenis, and C.Michaud, Tetrahedron Letters, 2771 (1973).
169. B.P.1 439 923 (1976).
170. D.H.R.Barton, R.H.Hesse, T.R.Klose, and M.M.Pechet, Chem.Comm., 97 (1975).
171. US P.3 737 533 (1973).
172. D.D.Moldavskii, V.G.Temchenko, and G.L.Antipenko, Zhur.Org.Khim., **7**, 44 (1971).
173. US P.3 541 128 (1970).
174. US P.3 585 218 (1971).
175. R.E.Noftle and J.M.Shreeve, Inorg.Chem., **7**, 687 (1968).
176. US P. 3 689 563 (1972).
177. I.L.Knunyants and V.R.Polishchuk, Uspekhi Khim., **44**, 685 (1975) [Russ.Chem.Rev., No.4 (1975)].
178. J.A.C.Allison and G.H.Cady, J.Amer.Chem.Soc., **81**, 1089 (1969).
179. F.A.Hohorst and J.M.Shreeve, Inorg.Chem., **7**, 624 (1968).
180. P.Tarrant, Polymer Prepr., **12**, 391 (1971).
181. H.-G.Horn, Chem.-Ztg., **95**, 893 (1971).
182. D.D.Desmarteau, F.A.Hohorst, and N.Walker, Seventh International Symposium on Fluorine Chemistry, Santa Cruz, California, 1973, S.1, S.a., No.1–38.
183. W.S.Durrell, E.C.Stump, et al., J.Polymer Sci., **A3**, 4065 (1965).
184. M.S.Toy and R.S.Stringham, J.Fluorine Chem., **5**, 481 (1975).
185. L.R.Anderson, D.E.Young, D.E.Gould, R.Juurik-Hogan, D.Nuechterlein, and W.B.Fox, J.Org.Chem., **35**, 3730 (1970).
186. N.Walker and D.D.Desmarteau, J.Amer.Chem.Soc., **97**, 13 (1975).
187. W.Maya, C.J.Schack, et al., Tetrahedron Letters, 3247 (1969).
188. D.D.Moldavskii, V.G.Temchenko, V.I.Slesareva, and G.L.Antipenko, Zhur.Org.Khim., **9**, 673 (1973).
189. M.S.Toy and R.S.Stringham, J.Fluorine Chem., **5**, 31 (1975).
190. D.H.R.Barton, J.Loughborough Univ.Technol.Chem. Soc., **7**, 37 (1969).
191. T.B.Patrick and E.C.Hayward, J.Org.Chem., **39**, 2120 (1974).
192. H.Gershon, M.W.McNeil, et al., J.Medicin.Chem., **15**, 987 (1972).
193. J.Airey, D.H.R.Barton, A.K.Ganguly, R.H.Hesse, and and M.M.Pechet, Anales quím.real.Soc.españ.Pis.Quím., **70**, 871 (1974).
194. T.B.Patrick, M.H.LeFaivre, and T.E.Koertge, J.Org. Chem., **41**, 3413 (1976).
195. D.H.R.Barton, R.H.Hesse, H.T.Toh, and M.M.Pechet, J.Org.Chem., **37**, 329 (1972).
196. US P.3 804 827 (1974).
197. BRD P.2 149 504 (1972); Chem.Abs., **77**, 126 674 (1972).
198. M.J.Robins, G.Ramani, and M.MacCoss, Canad.J. Chem., **53**, 1302 (1975).
199. M.J.Robins, M.MacCoss, and S.R.Naik, J.Amer.Chem. Soc., **98**, 7381 (1976).
200. R.A.Earl and L.B.Townsend, J.Heterocyclic Chem., **9**, 1141 (1972).
201. D.H.R.Barton, W.A.Bubb, R.H.Hesse, and M.M.Pechet, J.Chem.Soc., Perkin Trans.I, 2095 (1974).
202. C.Chavis and C.M.Mousseron, Bull.Soc.chim.France, **25**, 632 (1971).
203. D.H.R.Barton, Pure Appl.Chem., **21**, 285 (1970).
204. D.H.R.Barton, L.J.Danks, A.K.Ganguly, R.H.Hesse, and G.Tarzia, Chem.Comm., 227 (1969).
205. D.H.R.Barton, R.H.Hesse, L.Ogunkoya, N.D.Westcott, and M.M.Pechet, J.Chem.Soc., Perkin Trans.I, 2889 (1972).
206. D.H.R.Barton, L.J.Danks, A.K.Ganguly, R.H.Hesse, G.Tarzia, and M.M.Pechet, J.Chem.Soc., Perkin Trans. I, 101 (1976).
207. B.P.1 426 500 (1976).
208. US P.3 687 943 (1972).
209. D.H.R.Barton, R.H.Hesse, G.Tarzia, and M.M.Pechet, Chem.Comm., 1497 (1969).
210. D.H.R.Barton, R.H.Hesse, M.M.Pechet, G.Tarzia, H.T.Toh, and N.D.Westcott, Chem.Comm., 122 (1972).
211. D.H.R.Barton, A.K.Ganguly, R.H.Hesse, S.N.Loo, and M.M.Pechet, Chem.Comm., 806 (1968).
212. D.H.R.Barton, L.C.Godinho, R.H.Hesse, and M.M.Pechet, Chem.Comm., 804 (1968).
213. K.Bischofberger et al., J.Chem.Soc., Perkin Trans.I, 2457 (1975).
214. J.Adamson, A.B.Foster, and J.H.Westwood, Carbohydr.Res., 345 (1971).
215. J.Podesva and J.Pacak, Chem.Listy, **67**, 785 (1973).
216. A.B.Foster and J.H.Westwood, Pure Appl.Chem., **35**, 147 (1973).
217. C.J.Butchard and P.W.Kent, Tetrahedron, **27**, 3457 (1971).
218. J.Adamson and D.M.Marcus, Crabohydrate Res., 314 (1970).
219. E.L.Albano, R.L.Tolman, and R.K.Fobins, Carbohydrate Res., 63 (1971).
220. J.Adamson, A.B.Foster, L.D.Hall, et al., Carbohydrate Res., 351 (1970).
221. J.Adamson, A.B.Foster, L.D.Hall, and R.H.Hesse, Chem.Comm., 309 (1969).
222. D.H.R.Barton, R.H.Hesse, R.E.Markwell, M.M.Pechet, and S.Rozen, J.Amer.Chem.Soc., **98**, 3036 (1976).
223. D.H.R.Barton, R.H.Hesse, G.P.Jackman, L.Ogunkoya, and M.M.Pechet, J.Chem.Soc., Perkin Trans.I, 739 (1974).
224. US P.3 775 444 (1973).
225. J.Kollonitsch, L.Barash, and G.A.Doldouras, J.Amer. Chem.Soc., **92**, 7494 (1970).
226. French P.2 126 545 (1972).
227. BRD P.2 136 008 (1970); Chem.Abs., **76**, 154 488 (1972).
228. US P.3 859 276 (1975).
229. Austrian P.322 524 (1975).
230. US P.3 839 170 (1974).
231. French P.2 103 901 (1972).
232. J.Kollonitsch and L.Barash, J.Amer.Chem.Soc., **98**, 5591 (1976).
233. US P.3 956 367 (1976).
234. Swed.P.380 255 (1975).
235. DDR P.94 388 (1972); Ref.Zhur.Khim., 20 013 (1975).
236. US P.3 917 688 (1975).
237. B.P.1 437 074 (1974).
238. D.H.R.Barton, R.H.Hesse, M.M.Pechet, and H.T.Toh, J.Chem.Soc., Perkin Trans.I, 732 (1974).
239. D.H.R.Barton, R.H.Hesse, D.E.Markwell, M.M.Pechet, and H.T.Toh, J.Amer.Chem.Soc., **98**, 3034 (1976).
240. C.T.Ratcliffe and J.M.Shreeve, J.Amer.Chem.Soc., 90, 5403 (1968).
241. J.Kollonitsch, S.Marburg, and L.M.Perkins, J.Org. Chem., **41**, 3107 (1975).
242. D.B.Denney and D.Z.Denney, J.Amer.Chem.Soc., 95, 4064 (1973).
243. D.B.Denney and D.Z.Denney, J.Amer.Chem.Soc., **95**, 8191 (1973).
244. C.Wakselman and J.Leroy, Chem.Comm., 611 (1976).

245. US P.3 539 690 (1970).
246. US P.3 684 786 (1972); Chem.Abs., **77**, 140 762 (1972).
247. K.O.Christe, C.J.Schack, and R.D.Wilson, J.Fluorine Chem., **11**, 183 (1978).